Journal of Organometallic Chemistry 751 (2014) 201–212

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Review

Recent advances in the synthesis of stannanes and the scope of their posterior chemical transformations

Roberto A. Rossi*

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, X5000HUA Córdoba, Argentina

ARTICLE INFO

Article history:
Received 24 June 2013
Received in revised form
15 July 2013
Accepted 17 July 2013

Keywords:
$S_{RN}1$
Stannanes
Stille
Triarylphosphines
Triarylarsines
Vinylstannanes

ABSTRACT

The $S_{RN}1$ reactions of trimethylstannyl and triphenylstannyl anions, and other tin nucleophiles with haloarenes are quite versatile. Thus, the $S_{RN}1$ mechanism can afford triorganylstannyl aromatic compounds which otherwise would be synthesized by routes employing harsher reaction conditions.

The sequence $S_{RN}1$-Pd-catalysis is a powerful synthetic tool, and the scope of the reaction is unlimited owing to the nature of the sequence, i.e. $ArX \rightarrow ArSnR_3 \rightarrow ArAr$, which can be iteratively repeated when appropriate substituted substrates are chosen.

From stannanes obtained by the $S_{RN}1$ reaction, it is possible to obtain by electrophilic reactions aromatic ketones, or through transmetalation reactions to produce boronic acids that can be used in Suzuki reactions. Using the novel dianion Me_2Sn^{-2}, it is possible to synthesize Me_2SnAr_2, which by Cu catalysis reaction affords Ar–Ar through homocoupling reactions.

By a new methodology, organotin compounds with a Sn- heteroatom bond can be obtained and by Stille reactions aryl phosphines, arsines, stibines and selenides can be synthetized, all in one-pot reaction. The triarylarsines can be used as ligands in cross-coupling reactions.

From vinyl chlorides, it is possible to obtain vinylic stannanes, which by cross-coupling reactions afford aryl substituted alkenes.

Contents

---

* Tel.: +54 351 5353867.
E-mail address: rossi@fcq.unc.edu.ar.

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.07.049

1. Introduction

The reaction of triorganostannyl ions as nucleophiles with haloarenes has long been known, with the products obtained depending on the nucleophile, solvent, and on the reaction conditions. Thus, the reactions of sodium trimethyltin ($NaSnMe_3$) with halobenzenes (chloro-, bromo- and iodo-) in tetraglyme as the solvent afford phenyltrimethyltin (Me_3SnPh) and variable amounts of the reduction product benzene, along with diphenyldimethyltin (Ph_2SnMe_2) and tetramethyltin ($SnMe_4$). From trapping experiments, it has been proposed that this reaction occurs by a halogen metal exchange (HME) mechanism in a solvent cage [1]. The reaction of *o*-dibromobenzene with $NaSnMe_3$ affords the disubstitution product *o*-bis(trimethylstannyl) benzene in 42% yield. In this reaction, the intermediate *o*-bromophenyl anion can decompose into benzyne, which can then be trapped with furan to render the corresponding DielsAlder adduct [2].

The reaction of *o*-, *m*- and *p*-bromotoluenes with $LiSnBu_3$ in THF as solvent affords the expected substitution product, but when *p*-chloro and *p*-fluorotoluenes are used as substrates, *cine* substitution products are obtained, indicating that a benzyne mechanism operates. When radical traps are added, *cine* substitution products increase their yields. According to these results, the reaction should proceed, at least in part, by a radical mechanism [3]. Similar results were found in hexamethylphosphoric acid triamide (HMPT) as solvent [4].

There are several methods of synthesis for trialkylarylstannanes, typically by the reaction of aryllithium or organomagnesium derivatives with trialkyltin halides. However, these reactions have the drawback that many substituents on the aromatic ring are incompatible with the formation of aryllithium or organo-magnesium derivatives [5].

Another approach is the palladium catalysis (Stille reaction) of aryl halides or aryl triflates with hexamethyl- and hexabutyl-distannanes [6]. Bis(trimethylstannyl) arenes can also be synthesized by Pd catalysis with the yields of the disubstitution products ranging from 40 to 60% [7]. However, there are only a few examples involving reactions of bis(trimethylstannyl) arenes with aryl halides, which afford a double arylation by the palladium cross-coupling reaction. The examples known afford modest to good yields (6–85% yield) of double arylation [8].

We have described the photostimulated reactions of haloarenes with triorganylstannyl ions by the $S_{RN}1$ mechanism. These reactions afford good to excellent yields of the nucleophilic substitution products with many substituents being compatible with the $S_{RN}1$ mechanism, such as $-CO_2^-$, $-CO_2R$, $-CONR_2$, $-OR$, $-CN$, $-R$, $-$aryl, $-NH_2$, NR_2 and $-SO_2R$ [9].

The $S_{RN}1$ mechanism is a chain process, whose main steps are presented in Scheme 1.

Initiation

$$RX \xrightarrow{ET} (RX)^{\bullet -} \qquad (1)$$

Propagation

$$(RX)^{\bullet -} \longrightarrow R^{\bullet} + X^{-} \qquad (2)$$

$$R^{\bullet} + Nu^{-} \longrightarrow (RNu)^{\bullet -} \qquad (3)$$

$$(RNu)^{\bullet -} + RX \longrightarrow RNu + (RX)^{\bullet -} \qquad (4)$$

$$RX + Nu^{-} \longrightarrow RNu + X^{-} \qquad (5)$$

Scheme 1.

Overall, Eqs. (2)–(4) depict a nucleophilic substitution (Eq. (5)) in which radicals and radical anions are intermediates. In addition to halides, other leaving groups are known, and the most important are $(EtO)_2P(O)O-$ with phenols as initial substrates, and R_3NI, with anilines as precursors.

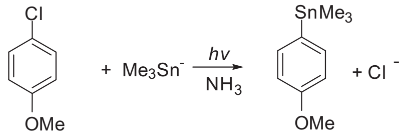
This chain process requires an initiation step (Eq. (1)). In a few systems, the spontaneous electron transfer (ET) from the nucleophile to the substrate has been observed. However, when the ET does not occur spontaneously, it can often be induced by light stimulation.

In this review the results of the reactions of organotin nucleophiles to form stannanes and their synthetic applications are presented.

2. Reactions of $S_{RN}1$

2.1. With Me_3Sn^- ions as nucleophile

Trimethylstannyl ion (Me_3Sn^-) is prepared in liquid ammonia through the reaction of Me_3SnCl with Na metal. Although *p*-chloroanisole (**1**) does not react with Me_3Sn^- ions in the dark after 1 h, upon irradiation the substitution product **2** has been obtained in high yield (Eq. (6)) [10]. The photostimulated reaction is inhibited by *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of $S_{RN}1$ processes [9].

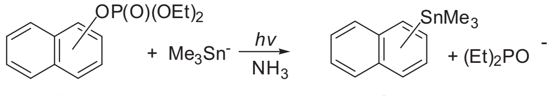


1 **2** (100%) (6)

Several ArCl with different substituents, polycyclic and heterocycles react with Me_3Sn^- ions in liquid ammonia under irradiation to give the substitution product in high yields (88–100%) [10]. 1-Chloro-3,5-dimethoxybenzene reacted with Me_3Sn^- ions to afford the substitution product in 80% yield, which is higher yield than the obtained by the Grignard reaction [11].

Bromides and iodides react by the HME reaction faster than by the $S_{RN}1$ mechanism having a very fast protonation by liquid ammonia, and with only the reduction product being obtained. When 2-chloroquinoline was allowed to react in the dark with Me_3Sn^- ions, low yields of the substituted product was obtained, a reaction which is inhibited by *p*-DNB but accelerated by light (96% yield) [10].

Aryldiethylphosphates have the $(EtO)_2P(O)O$- moiety as leaving group, which is as good as chlorines, and the synthesis of aryltrimethylstannanes from phenols through aryldiethylphosphates has been reported to proceed with high yields in liquid ammonia. For instance, the photostimulated reaction of **3a**–**b** with Me_3Sn^- ions afforded the substitution product **4a**–**b** in high yields (Eq. (7)) [12,13]. However, these reactions do not occur in the dark.



3a: 1-
3b: 2-

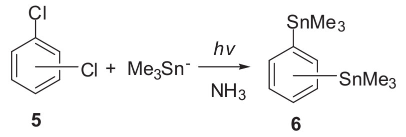
4a: 1- (93%)
4b: 2- (98%)

(7)

Phenyltrimethyl ammonium salts also reacted with Me_3Sn^- ions in liquid ammonia to give the substitution product in 98% yields [14]. Other examples are known with NMe_3I as the leaving group [15,16].

When an aromatic substrate bearing two leaving groups reacts by the $S_{RN}1$ mechanism, either monosubstitution or disubstitution products can be formed, depending on the structure of the substrate, the nature of the nucleofugal group, the nucleophile, and the reaction conditions [9]. The reaction of *o*-, *m*-, and *p*-$C_6H_4Cl_2$ **5** with Me_3Sn^- ions gives disubstitution products **6** in 50%, 90%, and 88%

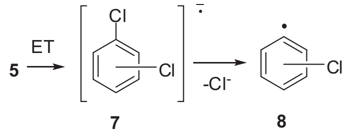
respectively. However, the monosubstitution products are not intermediates of these reactions (Eq. (8)) [17].



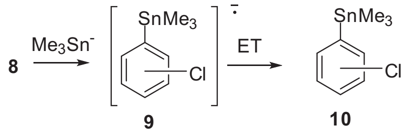
(8)

When **5** accepts an electron, the radical anion **7** is formed, and fragmentation of one C–Cl bond gives the first reactive intermediate in these reactions, namely the haloaryl radical **8** (Eq. (9)).

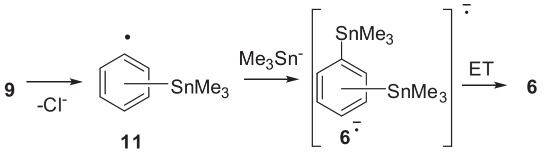
The coupling reaction of the radical **8** with the nucleophile forms a new radical anion **9**, which can undergo two competing reactions. Either ET to the substrate to give the monosubstitution product **10** with retention of the second leaving group (Eq. (10)), or another C–Cl bond fragmentation occurs to afford a new radical **11**, which then reacts with the nucleophile to yield the disubstituted product radical anion $\mathbf{6}^{-\cdot}$ that by an ET reaction renders the disubstitution product **6** (Eq. (11)). In this latter case, **10** is not an intermediate to form **6**.



(9)

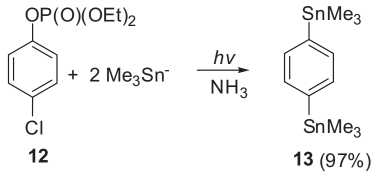


(10)



(11)

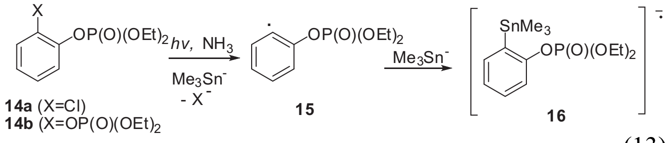
With two different leaving groups, such as in **12**, compound **13** was obtained in high yields (Eq. (12)) [13].



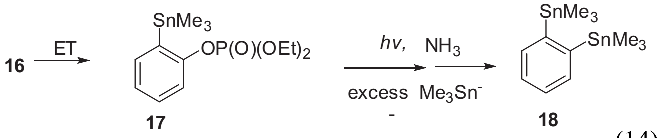
(12)

The photostimulated reaction with *m*-, and *p*-$C_6H_4[OP(O)(OEt)_2]_2$ afforded the disubstitution product in 79% and 95% yields, respectively [13].

For the 1,2-disubstituted compounds **14**, the monosubstitution products are intermediates of the reactions. Thus, with a relation of **14**:Me_3Sn^- ions of 1:1, the monosubstitution product **17** was formed in 45% yield with a 6% yield of the disubstitution product **18**. With a relation of **14**:Me_3Sn^- ions of 1:5, the disubstitution product **18** was formed in 65% yield (Eqs. (13) and (14)) [18]. In contrast, the *m*- and *p*-isomers gave the disubstitution products in good yields, with the monosubstitution products not being intermediates of these reactions. With **14a** as the substrate, the monosubstitution product **17** is formed, which indicates that Cl is a better nucleofugal group than $OP(O)(OEt)_2$.

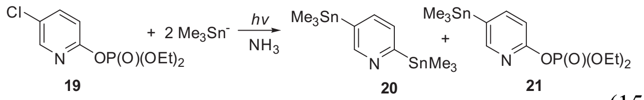


(13)



(14)

Photostimulated reaction (30 min) of **19** with Me_3Sn^- ions afforded 2,5-bis(trimethylstannyl)pyridine **20** in 96% yield with no monosubstituted product **21** being formed (Eq. (15)) [19].



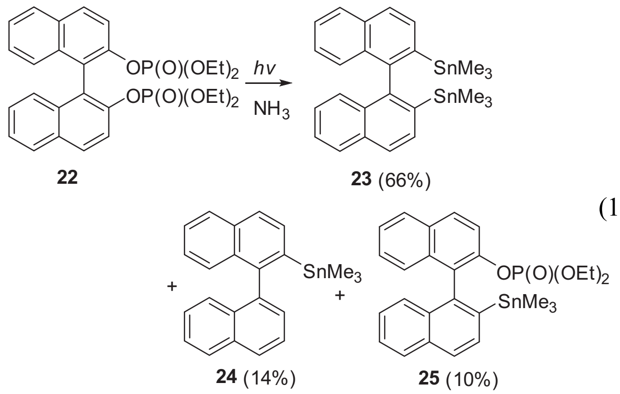
(15)

When this reaction was carried out in the dark (60 min), it was found that there was a spontaneous reaction between the substrate **19** and Me_3Sn^- ions, giving as the only product the monostannylated compound diethyl 5-(trimethylstannyl)pyridin-2-yl phosphate **21** in a 98% yield of pure compound. No starting material was detected and this reaction was totally inhibited by the addition of *p*-DNB. This dark reaction also supported a spontaneous ET from Me_3Sn^- ions to the substrate **19**.

The fact that the reaction is stimulated by irradiation, and that the reaction in the dark is suppressed by *p*-DNB, shows the radical-chain character of the substitution process. The reaction between **19** and Me_3Sn^- ions, quenched at shorter times, showed that the yield of **20** progressively increased with time at the expense of **21**. From these results, it was concluded that **21** is an intermediate in the formation of **20**, with chlorine being the first nucleofuge replaced in the reaction.

Similar results were obtained with the isomeric 2,3, 3,5 and 2,6 chloro-pyridinyl diethyl phosphates. In addition under irradiation, high yields of the disubstitution product were obtained, and the monosubstitution product with retention of the OP(O)(OEt) nucleofugal group was obtained in dark conditions [19].

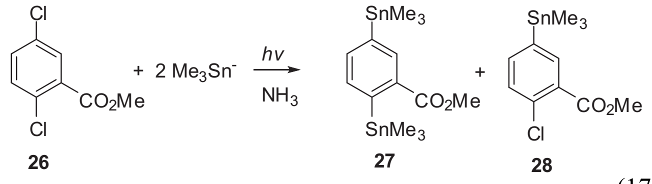
Binaphthol was converted into the corresponding aryl diethyl phosphate ester **22**. Although there is no reaction between **22** and Me_3Sn^- ions in the dark, under irradiation the disubstitution product 2,2′-bis(trimethylstannyl)-1,1′-binaphthyl **23** has been obtained together with 2-(trimethylstannyl)-1,1′-binaphthyl **24** and 2-(trimethylstannyl)-2′-(diethylphosphoxy**)**-1,1′-binaphthyl (**25**). These results suggest **25** is a intermediate of these reactions [18]. It should be noted that Kuivila could not prepare **23** from the more readily accessible binaphthol by applying the Pd-catalyzed coupling of aryl triflates with hexamethyldistannane, even after prolonged heating [20].



(16)

When a substrate has a two $OP(O)(OEt)_2$ and also a chlorine as leaving groups, the reaction with Me_3Sn^- ions in liquid ammonia afforded entirely different distribution of stannylated products. These differences are explained through theoretical DFT studies. Experimental evidence for the involvement of an $S_{RN}1$ mechanism was obtained [21].

The reaction of methyl 2,5-dichlorobenzoate **26** with Me_3Sn^- ions under irradiation afforded the disubstitution product **27** in 99% yield, with only a trace of the monosubstitution product **28** [22]. However, in the dark, **26** reacted with Me_3Sn^- ions to give the mono-substitution product **28** in 81% yield (Eq. (17)) [22,23].



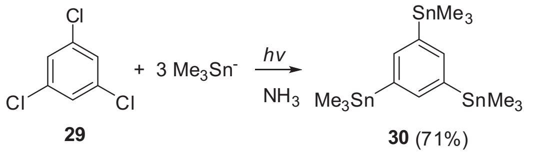
(17)

The fact that the monosubstitution product **28** was formed indicates that the intermolecular ET of the radical anion intermediate to the substrate is faster than intramolecular ET to the C–Cl bond. The intermediate stannane **28** reacted further by the $S_{RN}1$ mechanism under irradiation with Me_3Sn^- ions and finally afforded the disubstitution product **27**.

The reactivity and theoretical calculations of methyl chlorobenzoates (*para*, *ortho* and *meta*) and methyl 2,5-dichloro benzoate with Me_3Sn^- ions under irradiation have been reported. The relative reactivity of chlorine as the leaving group with respect to the ester group in methyl chlorobenzoates being *para* >= *ortho* >> *meta*. Based on calculations including solvent effects, the activation energies obtained for the fragmentation process reproduced the observed experimental reactivity trend [23].

Substrates such as 2,5-, 2,6- and 3,5- dichloropyridines afford the respective disubstitution products in 80–86% yields [17]. Several chloro, bromo, dichloro and dibromo pyridines and quinolines were reported to react with Me_3Sn^- ions in dimethoxyethane to render the mono and disubstitution products in 60–88% yields. However, there was not photostimulation in these reactions, and no information was provided about the mechanism [24]. Nevertheless, it was demonstrated that haloarenes reacted in diglyme with Me_3Sn^- ions under irradiation by the $S_{RN}1$ mechanism [25].

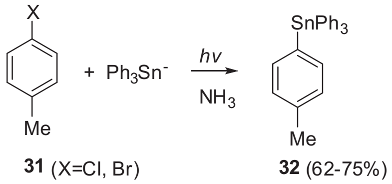
It was found that the photostimulated reaction of 1,3,5-trichlorobenzene **29** in the presence of an excess of Me_3Sn^- ions afforded the trisubstitution product **30** (Eq. (18)) [17].



(18)

2.2. With Ph_3Sn^- ion as nucleophile

The triphenylstannyl ion (Ph_3Sn^-) can be prepared either from the reaction of Ph_3SnCl or $Ph_3SnSnPh_3$, with Na metal in liquid ammonia. Although neither *p*-chloro nor *p*-bromotoluenes **31** reacted with Ph_3Sn^- ions in the dark in liquid ammonia, upon irradiation the substitution product **32** was obtained (Eq. (19)) [10].

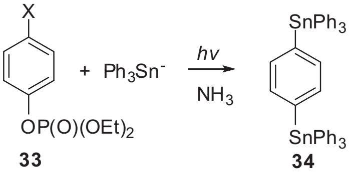


(19)

However, when *p*-iodotoluene and *p*-iodoanisole are utilized as substrates, a fast HME reaction takes place, affording only the reduced products.

The 1-chloro and 1-bromo naphthalenes afforded 80% and 73% yields respectively of the substitution product when irradiated in liquid ammonia in the presence of Ph_3Sn^- ions. With DMSO as solvent, 1-chloronaphthalene afforded 72% yield of substitution, i.e.: 1-(triphenylstannyl)-naphthalene. However, the bromo derivative gave only the HME reaction [26]. The 1- and 2-naphthyl diethyl-phosphates gave excellent yields (ca. 100%) of substitution products when irradiated in liquid ammonia in the presence of Ph_3Sn^- ions [12].

When *p*-dichlorobenzene was allowed to react with Ph_3Sn^- ions under photostimulation in liquid ammonia or DMSO, good yields of the disubstitution product were obtained (69% or 90% respectively) [26]. In addition, *p*-dibromobenzene reacted with Ph_3Sn^- ions in the absence of photostimulation to afford a 96% yield of PhBr by the HME reaction followed by protonation. In the case of ArI as substrates and Ph_3Sn^- ions as nucleophiles, the predominant reaction is the HME in liquid ammonia. However, substrates **33**, have been shown to afford excellent yields of the disubstitution product **34** (**33**, X = Cl, Br, 100% yield [13], **33**, X = $OP(O)(OEt)_2$ 70% yield [12]) (Eq. (20)).



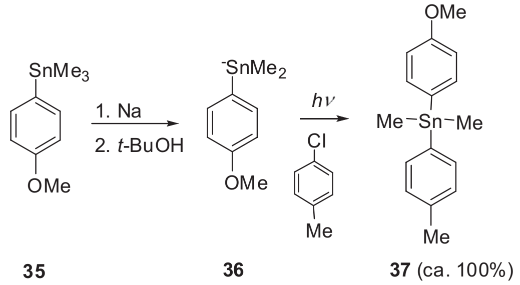
(20)

Heterocycles afford high yields of substitution products when irradiations are conducted in the presence of Ph_3Sn^- ions in liquid ammonia or DMSO. Thus, in DMSO, the 2- and 3-chloropyridines afforded the substitution products in 82% and 93% yields, respectively [26], and in liquid ammonia, 2-

chloroquinoline furnished 2-(triphenylstannyl)quinoline in 80% yield [10].

2.3. With other tin-derived nucleophiles

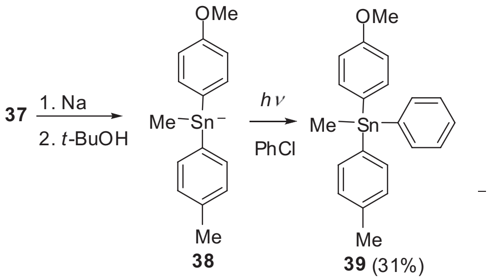
When *p*-anisyltrimethyltin **35** reacts with Na metal in liquid ammonia, the Sn–Me bond is cleaved to render nucleophile **36**, after neutralization of the generated amide ions with *t*-butyl alcohol (Eq. (21)) [27]. This result is consistent with the bond dissociation energy difference between the tin-phenyl bond (347 kJ mol^{-1}) [28] and the tin-methyl bond (259–272 kJ mol^{-1}) [28,29]. When nucleophile **36** was then allowed to react with *p*-chlorotoluene under irradiation, it afforded substitution product **37** in almost quantitative yields (Eq. (21)).



(21)

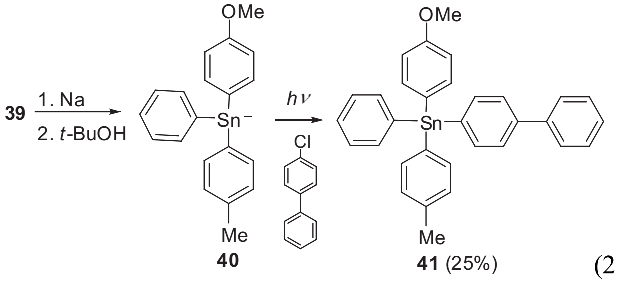
Product **37** can also be obtained in a one-pot fashion starting from Me_3Sn^- ion and *p*-chloroanisole under photostimulation. When intermediate product **35** was not isolated, but treated in situ with Na metal to afford nucleophile **36**, then by a subsequent photostimulated reaction in the presence of *p*-chlorotoluene product **37** was rendered in 89% overall yield.

When **37** are treated with Na metal in liquid ammonia under the same reaction conditions as those employed above, forms nucleophile **38**, and addition of PhCl followed by irradiation generated product **39** (Eq. (22)). The overall yield was significantly reduced in this case owing to the presence of products arising from some tin-aryl bond fragmentation.



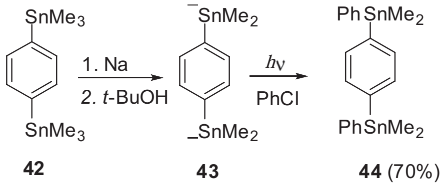
(22)

When **39** is further treated with Na metal in liquid ammonia following the same procedures, nucleophile **40** is obtained. Upon photostimulation of **40** in the presence of 4-chlorobiphenyl, product **41**, an asymmetrical organostannyl compound was obtained (Eq. (23)) [27].



(23)

When **42**, the product formed by reaction of Me_3Sn^- ion with *p*-$C_6H_4Cl_2$ without isolation, was first treated with Na metal to produce the Sn–Me bond fragmentation and then with *t*-BuOH to neutralize the amide ions formed, the dinucleophile **43** was produced. After addition of PhCl and irradiation (90 min), the disubstitution product **44** was obtained in a one-pot reaction (Eq. (24)) [17].

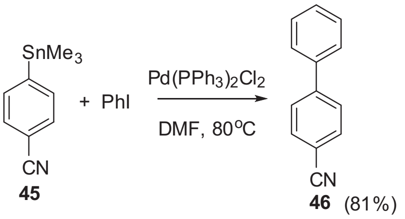


(24)

3. $S_{RN}1$ reactions followed by a Stille reaction

The photostimulated reaction of aryl chlorides with Me_3Sn^- ions in liquid ammonia to synthesize the trimethylarylstannanes, followed by the Pd(0) cross coupling reaction with haloarenes, is an important approach for the synthesis of arylated or polyarylated compounds.

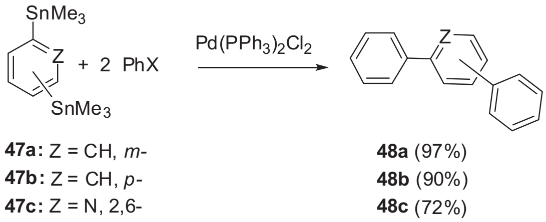
The reaction of 4-(trimethylstannyl)benzonitrile **45** (prepared by the photostimulated reaction of *p*-chlorobenzonitrile and Me_3Sn^- ions in liquid ammonia in 85% yield [17]), with PhI as electrophile and $Pd(PPh_3)_2Cl_2$ (6 mol%) as catalyst in DMF (80 °C, 3 h), afforded the coupled product biphenyl-4-carbonitrile **46** in good yield (Eq. (25)) [14].



(25)

When the distannane **47a** was heated at 80 °C for 24 h in the presence of PhBr and $Pd(PPh_3)_2Cl_2$(3 mol%) in DMF as solvent, the *m*-terphenyl **48a** was obtained in good yield.

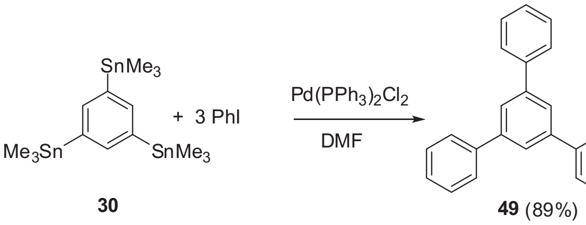
Under the same reaction conditions, the distannane **47b** reacted with PhBr and $Pd(PPh_3)_2Cl_2$ to yield **48b**. The reaction of 2,6-di(trimethylstannyl)pyridine **47c** with PhI (xylene, 140 °C, 24 h) and $Pd(PPh_3)_2Cl_2$, afforded the diphenylated pyridine **48c** (Eq. (26)) [14].



(26)

The synthesis of the distannane and the Stille reaction has also been studied in a one-pot procedure. A solution of *m*-, *p*- dichlorobenzenes and 2,6-dichloropyridine substrates in liquid ammonia and Me_3SnNa were irradiated. Then, the ammonia was allowed to evaporate, and the residue was redissolved in DMF. To this solution, PhX and the catalyst $Pd(PPh_3)_2Cl_2$ were added and heated at 80 °C and the products **48a**–**c** were obtained in 76%, 71%, and 60% yields, respectively [14].

The reaction of the tristannane **30** (see Eq. (18)) with PhI and $Pd(PPh_3)_2Cl_2$ (5 mol%) gave the triphenylated product **49** in good yield (Eq. (27)).



(27)

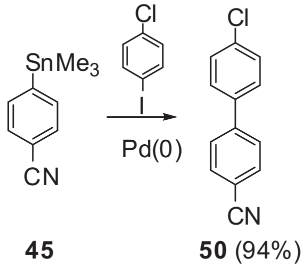
Following the procedure of the one pot reaction as described above, **49** was obtained in 61% isolated yield from $1,3,5\text{-}C_6H_3Cl_3$ [14].

The fact that chloroarenes react with Me_3Sn^- ions under irradiation to form aryltrimethylstannanes, and that in the palladium-catalyzed reaction with stannanes the reactivity of iodoarenes is much greater than that of chloroarenes, a substrate bearing both the leaving groups chlorine and iodine, will react faster by the C–I bond via a chemoselective cross-coupling reaction with a stannane catalyzed by palladium (product $Ar–Ar^1–Cl$, Eq. (28)). This will allow the remaining leaving group, chlorine, to react later in another $S_{RN}1$-type reaction to form an organotin intermediate (product $Ar–Ar^1–SnMe_3$), which can subsequently furnish product $Ar–Ar^1–Ar^2$ by a cross-coupling palladium-catalyzed reaction (Eq. (29)) [25].

$$\text{Ar-Cl} \xrightarrow[S_{RN}1]{Me_3Sn^-} \text{Ar-SnMe}_3 \xrightarrow[\text{Pd(0)}]{\text{I-Ar}^1\text{-Cl}} \text{Ar-Ar}^1\text{-Cl} \qquad (28)$$

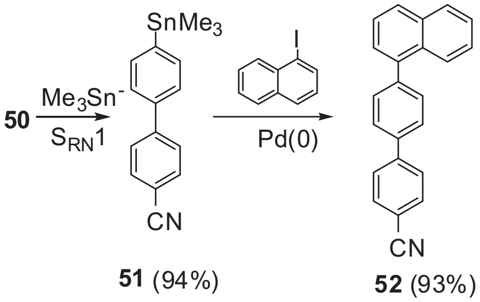
$$\text{Ar-Ar}^1\text{-Cl} \xrightarrow[S_{RN}1]{Me_3Sn^-} \text{Ar-Ar}^1\text{-SnMe}_3 \xrightarrow[\text{Pd(0)}]{\text{I-Ar}^2} \text{Ar-Ar}^1\text{-Ar}^2 \qquad (29)$$

The above iterative sequence, the $S_{RN}1$ reaction-Pd catalyzed process, was investigated in order to foster a methodology to build large molecules [25]. The photostimulated reaction of *p*-chlorobenzonitrile with Me_3Sn^- ions afforded the stannane **45** (85% yield), which by a Pd(0)-catalyzed reaction with *p*-chloroiodobenzene furnished substitution product **50** in high yield (Eq. (30)).



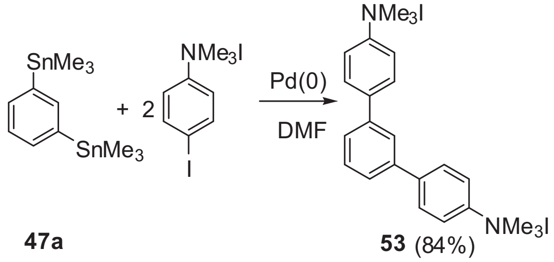
(30)

By a photostimulated reaction of Me_3Sn^- ions with the chloroarene **50**, stannanes **51** was obtained. A second Pd(0)-catalyzed reaction with 1-iodonaphthalene as electrophile renders product **52** in high overall yield (Eq. (31)).



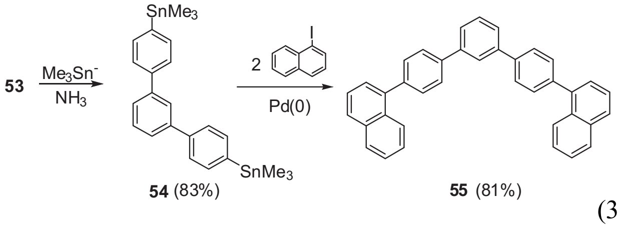
(31)

Through sequential schemes of combined transformations, it has been reported that high yields of polyaromatic compounds are obtained [25]. When 1,3-bis(trimethylstannanyl)benzene **47a**, obtained through a $S_{RN}1$ reaction (such as that depicted in Eq. (26)), was allowed to react under Pd catalysis with 4-iodophenyltrimethylammonium iodide, product **53** was obtained (Eq. (32)) [25].



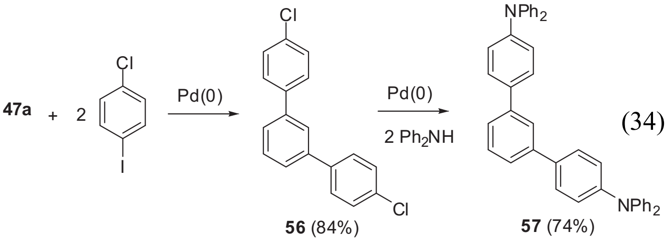
(32)

Compound **53** reacted with Me_3Sn^- ions by the $S_{RN}1$ mechanism to afford compound **54** in a fairly good yield as shown in Eq. (33). In turn, **54** can react under Pd catalysis with 1-iodo naphthalene to afford by double cross coupling reaction the polyaromatic compound **55** in high yield, according to Eq. (33) [25].



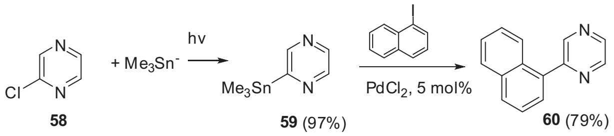
(33)

It is known that aryl chlorides can react with amines with different palladium catalysts and ligands [30], such as $Pd_2(dba)_3$ and the ligand (*o*-biphenyl)-P(*t*-Bu)$_2$ [31]. From the reaction of **47a** with *p*-chloroiodobenzene and the catalyst $Pd(PPh_3)_2Cl_2$ in DMF, the disubstitution product **56** was obtained. When **56** was treated with this catalytic system, and diphenylamine as substrate, product **57** was obtained (Eq. (34)) [25].



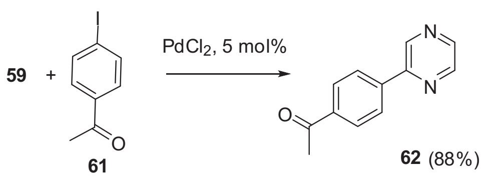
(34)

Some other examples are also known. For instances from a fast reaction (15 min) of Me_3Sn^- ions and 2-chloropyrazine **58** the stannane **59** is obtained in excellent yield. Then, using stannane **59**, the cross coupling reaction with 1-iodonaphthalene afforded 2-(1-naphthyl)pyrazine **60** in good yields (Eq. (35)) [32].



(35)

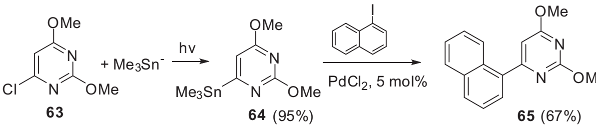
The 4-iodoacetophenone **61** was another electrophile studied, and by the cross-coupling reaction with **59**, good yields of the product **62** was obtained (Eq. (36)).



(36)

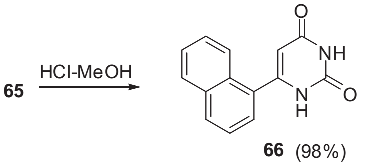
A new methodology for the synthesis of 6-substituted uracils by $S_{RN}1$ reactions from the commercial 6-chloro-2,4-dimethoxy pyrimidine **63**, has also been studied. The photostimulated reaction of **63** with Me_3Sn^- ions, followed by cross-coupling reactions of the stannane thus obtained, with electrophiles, and then followed by the hydrolysis of these products gives 6-substituted uracils [32].

The photostimulated reaction of **63** with Me_3Sn^- ions, 2,4-di methoxy-6-(trimethylstannyl)pyrimidine **64** was obtained in high yield. In addition, after the reaction of stannane **64** and 1-iodonaph thalene in the presence of $PdCl_2$ as catalyst (5 mol %), the 2,4-dimethoxy-6-(1-naphthyl) pyrimidine **65** was obtained (Eq. (37)) [32].



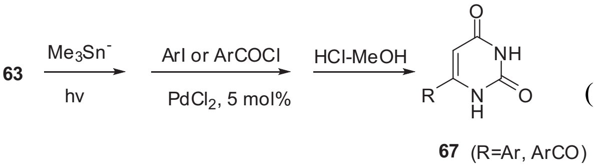
(37)

To end the reaction sequence to yield 6-substituted uracil, product **65** was hydrolyzed with HCl–MeOH, and 6-(1-naphthyl)pyrimidine-2,4(1*H*,3*H*)-dione **66** was obtained quantitatively (Eq. (38)).



(38)

The sequences of these three-steps, in one-pot reactions were studied: $S_{RN}1$-Stille-hydrolysis from the commercial pyrimidine **63** with ArI or ArCOCl as electrophile to obtain 6-aryl and 6-acyl substituted uracils **67**, respectively, without the need to isolate the intermediate products (Eq. (39)) [32].

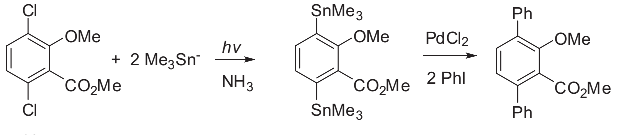


(39)

When this novel three-step approach was applied to a one-pot reaction, 6-aryl uracils (1-naphthyl, 4-chlorophenyl, 3-chlorophenyl, 2,3,4,5,6-pentafluorophenyl) were formed and isolated (43–57%) as pure products. When acid chlorides were the electrophiles, 6-benzoyl and 6-(3-chlorobenzoyl) uracils were obtained in 54%, and 49% isolated yields, respectively [32].

3,6-Dichloro-2-methoxy benzoic acid (known as Dicamba) is among the most widely used chlorinated herbicide in many countries, but contributes and has become prominent contaminants to the soil and hydrologic systems. Thus, the synthesis and testing of new derivatives that present advantages over known herbicides, is a current challenge for organic chemists.

Methyl 3,6-dichloro-2-methoxybenzoate **68** (methyl ester of Dicamba) reacted under photostimulation with Me_3Sn^- ions in liquid ammonia to give disubstitution product **69** (Eq. (40)) [22]. When **69** was treated with $PdCl_2$, and CsF/CuI in DMSO at 80 °C with PhI as the electrophile, the diphenylate product **70** was formed. There are other examples of compounds synthetized with moderate yields, with the phytotoxicity evaluated by bioassays [33].



(40)

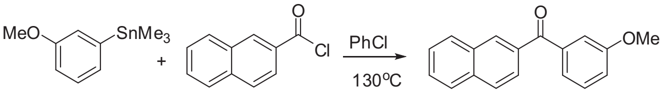
A series of arylstannanes have been synthesized, through the $S_{RN}1$ mechanism, with good to excellent yields (74–99%), by the photostimulated reaction of Me_3Sn^- ions with substrates supporting different nucleofugal groups. The arylstannanes thus obtained were suitable intermediates for Stille cross-coupling reactions, and lead to asymmetric bi- and triaryl compounds in acceptable global yields. An attractive feature of this route is that simple commercially available benzenediols, and chloro- and methoxy phenols might be useful starting substrates, giving good yields of products in fewer steps [34].

All these results indicate that the $S_{RN}1$ mechanism is an excellent method to obtain stannanes by the photostimulated reactions of mono-, di- and trichloroarenes with Me_3Sn^- ions in liquid ammonia. The stannanes thus obtained can be arylated by further reaction with bromo or iodoarenes through palladium-catalyzed reactions. If the Pd(0)-catalyzed reaction is performed with a chloroiodoarene substrate, the product obtained can be further arylated by a consecutive $S_{RN}1$-Stille reaction.

4. $S_{RN}1$ reactions followed by other chemical transformations

4.1. Synthesis of diarylketones

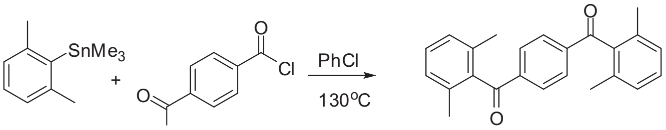
Based on the exceptional leaving group ability of the trimethylstannyl group in electrophilic aromatic substitutions, the synthesis of different stannanes has been reported by the $S_{RN}1$ mechanism, from substituted anilines or phenols through the ArNMe$_3$I and ArO-P(O)(OEt)$_2$ substrates. Then, by reaction with ArCOCl in PhCl as solvent at 130 °C, the aromatic ketones are afforded in good yields [35]. For instance, the reaction of the stannanes **71** with 2-naphthoyl chloride **72** gave the aromatic ketone **73** (Eq. (41)).



71 **72** **73** (65%)

(41)

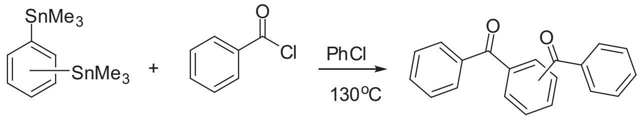
Even when using (2,6-dimethylphenyl)trimethylstannane **74**, the reaction with terephthaloyl chloride**75** led to diketone **76** (Eq. (42)).



74 **75** **76** (64%)

(42)

With distannanes, the diketone products are obtained in good yields. Thus, using *m*- and *p*-bis(trimethylstannyl)benzene **77** with PhCl as solvent at 130 °C, the 1,3- and 1,4-phenylenebis(phenylmethanones) **78** were obtained (Eq. (43)) [36].



77 (1,3 - 1,4) **78** (82-88%)

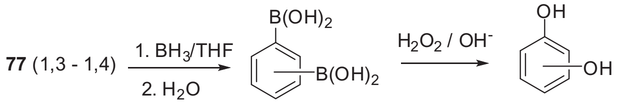
(43)

The reaction time was reduced using *o*-dichlorobenzene as solvent at 180 °C. Even with 1,3,5-tris(trimethylstannyl)benzene, a triketone was obtained although in moderate yield (25%) [36].

Recently, highly hindered benzophenones were regiospecifically synthesized by the reaction of stannanes and ArCOCl using *o*-dichlorobenzene as solvent at 180 °C in good yields (53–85%). These reactions also take place using AlCl$_3$ as catalyst in dichloromethane. Also it was established that also In(0) acts as a promoter in these reactions, with even as little as 0.2 equiv % of In(0) being enough to promote them. The ketones were synthesized in good to excellent yields (49–91%) at relatively low temperatures in the absence of solvent, and it has been suggested that the reactions promoted by In(0) occur with radicals as intermediates [37].

4.2. Synthesis of aryldiboronic acids

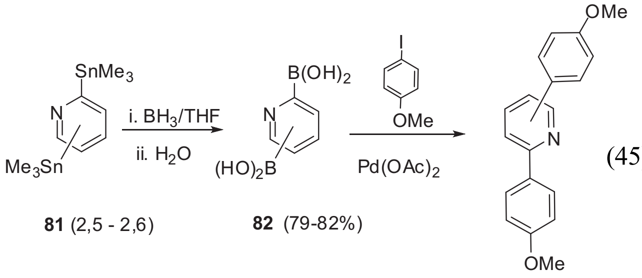
A very convenient synthesis of arylboronic acids has been reported via transmetalations between aryltrialkylstannanes and borane in THF [38]. The areneboronic and arenediboronic acids are very useful intermediates in organic synthesis [39]. The stannanes 1,4- and 1,3-bis(trimethylstannyl) benzenes **77** prepared by the S$_{RN}$1 mechanism reacted with borane in THF to give intermediates which on hydrolysis lead to benzenediboronic acids **79** in high yields, and oxidation of the benzenediboronic acids **79** with alkaline hydrogen peroxide gives the corresponding 1,3- and 1,4-dihydroxybenzenes **80** [40].



79 (82-83%) **80** (70-72%)

(44)

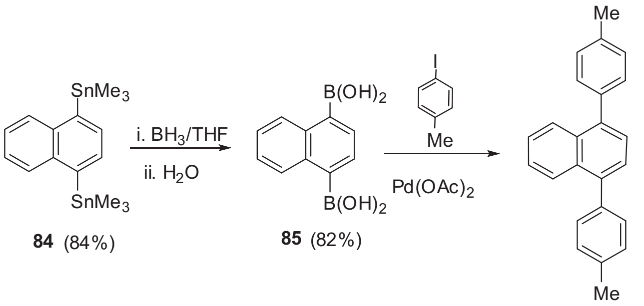
Using the same methodology, the stannanes 2,5- and 2,6-bis(trimethylstannyl)pyridines **81** reacted with borane, which on hydrolysis afforded pyridinediboronic acids **82** in high yields. The pyridinediboronic acids, via a double Suzuki reaction with 4-iodoanisole catalyzed by Pd(OAc)$_2$, gave the 2,5- and 2,6-bis(4-methoxyphenyl)pyridines **83** (Eq. (45)) [40].



81 (2,5 - 2,6) **82** (79-82%) **83** (75-77%)

(45)

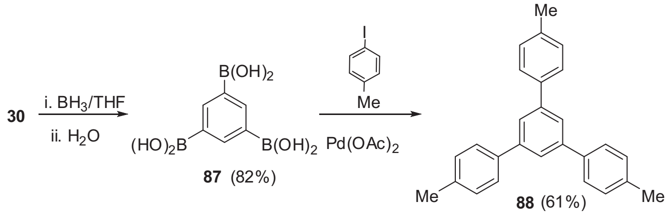
Several bis(trimethylstannyl)arenes were prepared from chlorophenols of dihydroxy arenes by the S$_{RN}$1 mechanism and by reaction with borane, which on hydrolysis leads to benzenediboronic acids. For instance, the synthesis of **84** afforded **85**, and by a Suzuki reaction gave **86**, with all three steps having good yields (Eq. (46)) [41].



84 (84%) **85** (82%) **86** (78%)

(46)

Several other polycyclic compounds have been prepared. Even using 1,3,5-tris(trimethylstannyl)benzene **30** gave the benzene-1,3,5-triyltriboronic acid **87**, and a triple Suzuki reaction leads to product **88** (Eq. (47)) [41].



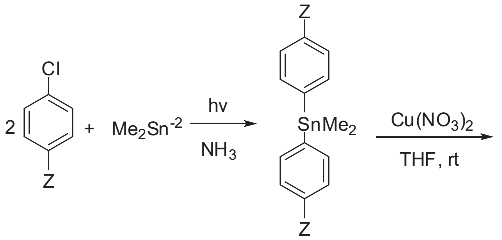
87 (82%) **88** (61%)

(47)

The homocoupling of Ar_2SnMe_2 was described, to afford Ar—Ar catalyzed by $Cu(NO_3)_2$, the stannanes used were prepared by the reaction of aryllithiums with Me_2SnCl_2 [42].

To avoid the use of aryllithium, a method was developed to synthesize the stannanes by the $S_{RN}1$ mechanism. When Me_2SnX_2 (X = Br or Cl) was treated with Na metal in excess in liquid ammonia, and the reaction was quenched with benzyl chloride to trap the dianion formed, the double substitution product $Me_2Sn(CH_2Ph)_2$ was obtained in 93% yield, which indicates that the dianion Me_2Sn^{-2} was formed almost quantitatively [43].

To evaluate the reactivity of the dianion Me_2Sn^{-2}, it was allowed to react with ArCl in liquid ammonia under photostimulation and afforded the double $S_{RN}1$ product. Although there was no reaction of *p*-chloroanisole **89a** with the dianion Me_2Sn^{-2} in dark conditions, under irradiation it gave the double substitution product **90a** in good yields (Eq. (48)). Similar results were obtained with substrates **89b**—**c**. In addition, good yields (68%) of the disubstitution product di(1-naphthyl)dimethylstannane was obtained from the reaction of 1-chloronaphthalene with the dianion Me_2Sn^{-2} under irradiation.



89a: Z=OMe
89b: Z=CN
89c: Z=Me

90a (85%)
90b (68%)
90c (81%)

91a (99%)
91b (86%)

(48)

In a synthetic application of theAr_2SnMe_2 thus obtained, the homocoupling reaction mediated by $Cu(NO_3)_2$ was carried out in THF, and gave good yields of the biphenyls **91a**—**b** (Eq. (48)) [43].

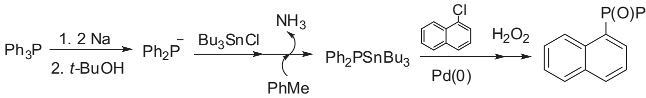
5. Synthesis of stannanes bonded to heteroatoms followed with other chemical transformations

5.1. Synthesis of triarylphosphines

Triarylphosphines are important types of compounds, both as intermediates in organic synthesis and as ligands in transition metal catalyzed reactions. In fact, the palladium-catalyzed coupling reactions are an extremely useful synthetic tool in organic chemistry, which has been used for forming C—C or C-heteroatom bonds. However, only a few reports of C—P bond are related with the synthesis of triarylphosphines by this reaction. Palladium-catalyzed coupling of aryl halides with the stannane Me_3SnPPh_2 was reported by Stille and Tunney [44], but this method has remained largely unexplored.

Although the stannanes R_3SnPPh_2 are known, and methods for their preparation having been reported, their chemistry has not been explored due to inherent difficulties in their preparation and manipulation [45].

Pd catalyzed cross-coupling phosphination with Bu_3SnPPh_2, using Ph_3P as the initial phosphination agent in a one-pot reaction has been reported. In a typical procedure, after formation of the anion Ph_2P^- from PPh_3 and Na metal in liquid ammonia, and after adding *t*-BuOH to neutralize the amide ions formed, the stannane Bu_3SnCl was added. Next, the ammonia was allowed to evaporate and toluene was added. The Pd catalyzed cross-coupling reaction was carried out in the solution of Bu_3SnPPh_2 thus obtained and 1-chloronaphthalene as electrophile in the presence of $(PPh_3)_2PdCl_2$ at 80 °C. Then, after 24 h, the phosphine obtained was oxidized with H_2O_2 and afforded diphenyl-1-naphthylphosphine oxide **92** in one pot reaction (Eq. (49)) [46,47].



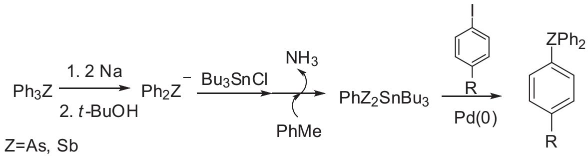
92 (93%)

(49)

With the same methodology, different phosphines oxides *p*-$RC_6H_4P(O)Ph_2$ were synthesized with excellent yields [R = Cl (97%), Br (93%), CF_3 (90%) and NH_2 (88%)]. Using *o*-iodophenol as electrophile, *o*-$HOC_6H_4P(O)Ph_2$ was obtained with 69% yield [46].

5.2. Synthesis of triarylarsines and triarylstibines

To extend the applications of the Pd-catalyzed cross-coupling, using the same synthetic strategy, triaryl-arsines and stibines were obtained. The reaction of Ph_2Z^- anion, generated from Ph_3Z and Na metal in liquid ammonia, with Z = As, Sb, and then adding Bu_3SnCl afforded the stannanes Bu_3SnZPh_2 (Z = As, Sb). Next, the ammonia was allowed to evaporate and toluene was added. The Pd-catalyzed cross-coupling reaction was carried out with the solution of stannanes in toluene and ArI in the presence of $Pd(PPh_3)_2Cl_2$. All these steps were performed in a one-pot reaction in very good yields, regardless of the electronic nature of the substituent (Eq. (50)) [48].

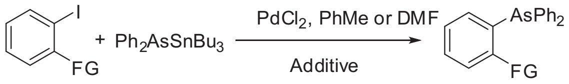


(Z=As, R=OMe, 98%)
(Z=As, R=Cl, 90%)
(Z=Sb, R=OMe, 99%)
(Z=Sb, R=Cl, 98%)

(50)

Although tertiary phosphines constitute the group of ligands most widely used in transition metal chemistry, mainly due to their versatile tuning abilities via steric and electronic properties [49], arsines are attracting particular attention as ligands in transition metal-catalyzed reactions. The efficiency of such reactions largely depends on the fine electronic and structural properties of the ligands, but as unsatisfactory results may be observed, novel types of ligands are still generally required.

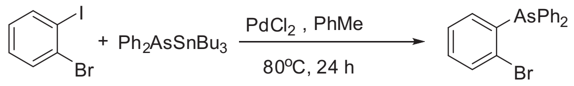
Arsines have been reported to be ligands more suitable than phosphines in several transition metal-catalyzed organic reactions, such as in the Stille [50] or Suzuki—Miyaura reactions [51]. Using the "one pot" methodology described above, several triarylarsines **93** have been prepared [FG = CO_2Me, (75%), Br (83%), Cl (88%), NH_2 (75%), Ph (71%)] (Eq. (51)), and their properties as ligand were evaluated [52].



93

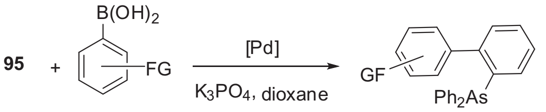
(51)

Another synthetic approach has been recently developed concerning to the synthesis of arsine ligands, taking into account that iodine is more reactive than bromine in the Pd catalyzed reaction. Using a chemoselective reaction, the (2-bromophenyl)diphenylarsine **95** was synthesized and then employed as a synthetic intermediate for the synthesis of biarylarsine ligands, with the one-pot, two-step reaction of stannane $Bu_3SnAsPh_2$ with1-bromo-2-iodobenzene **94** catalyzed by $Pd(PPh_3)_2Cl_2$ in toluene afforded **95** (Eq. (52)) [53].



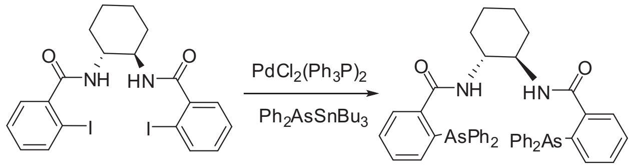
94 **95** (83%) (52)

Due to the particular usefulness of the Suzuki–Miyaura coupling reaction as a method for the formation of C–C bonds [39], it was chosen to build the biaryl structure. In this way, the reaction of arsine **95** with different arylboronic acids **96** (FG = H, 2-Me, 2,6-diMe, 1,4,6-triMe, 2-OMe, 2,6-diOMe, 1-naphthyl) was tested with different Pd catalysts giving the arsine ligands **97** in excellent yields (Eq. (53)) [53].



96 **97** (80-98%) (53)

Chiral diphosphine ligands have been one of the largest classes of ligands used in asymmetric substitutions. Trost and co-workers have reported the development and application of the diphosphine ligand *N*,*N*′-bis[2′-9-(diphenylarsino)benzoyl]-(1*R*,2*R*)-cyclohexanediamine, normally referred to as the "Trost ligand" [54]. A new chiral bis(arsine) ligand **99**, based on the structure of the Trost ligand, but changing the two diphenylphosphino moieties by diphenylarsino moieties, was synthesized recently by the reaction of the diiodide **98** with $Bu_3SnAsPh_2$ by the Pd-catalyzed arsination in one-pot reaction [55].



98 **99** (48%) (54)

In the asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate, very high conversion was achieved, but with a modest enantioselectivity [55].

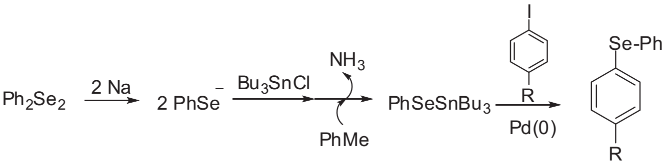
5.3. Other related syntheses

The arsine ligands **93** and **97** were evaluated using the same methodology described above, but with perfluoroalkyl iodides (R_fI) as electrophiles in the Pd catalyzed reactions. For example, with $C_{10}F_{21}I$ as electrophile in the reaction with $Bu_3SnAsPh_2$ catalyzed by Pd, the perfluoroarsine **100** was obtained. With Ph_3P as the ligand, **100** was obtained in 48% yield, whereas with the arsine ligand **93** (GF = Ph), **100** was obtained with 78% yield (Eq. (55)). For other R_fI, ligand **93** (GF = Ph) always gives better yields than with Ph_3P [52]. In the case of arsine **97** (FG = 2-OMe), the yield of **100** was 92% yield [53].

$$C_{10}F_{21}I + Ph_2AsSnBu_3 \xrightarrow[\text{Ligand}]{PdCl_2,\ PhMe} \underset{\mathbf{100}}{C_{10}F_{21}\text{-}AsPh_2} \qquad (55)$$

The Pd-catalyzed cross-coupling reaction of organoheteroatom stannanes Bu_3SnZPh_2 (Z = P, As) with R_fI catalyzed by Pd was studied with a one-pot two-step reaction forming R_fPPh_2 (15–51%) and R_fAsPh_2 (43–65% yield) being reported [56].

Using the same approach, but with Ph_2Se_2 as the starting substrate and following the same methodology described above, phenylarylselenides were obtained with good yields (Eq. (56)) (R = Cl, 96%; MeCO, 98%; MeO, 83%; NH_2, 78%; NO_2 38%) [57].

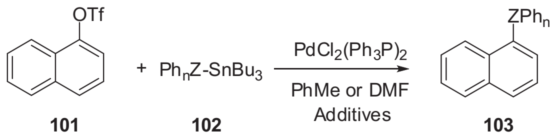


(56)

With *p*-iodophenol as electrophile, the yield of the selenide was only 50%. However, with the phenolic group protected as 4-iodophenyl acetate, the product obtained was the unprotected phenol 4-(phenylselanyl)phenol in 95% yield. In addition, using 1-iodonaphthalene, the 1-naphthylphenyl selenide was obtained in 94% yield [57].

The palladium-catalyzed cross-coupling reaction of organic electrophiles with organostannanes is a widely used methodology, with the aryl halides being one of the most thoroughly studied groups [6]. However, as organic triflates are readily available, they have become important coupling partners used in synthesis. Stille and co-workers have studied the scope and limitation of the cross-coupling reactions of triflates with organostannanes [58], and a number of effective palladium-catalyzed coupling reactions have been developed for vinyl and aryl triflates as electrophiles [59].

The reaction of 1-naphthyltriflate **101**, as a model triflate, with different stannanes **102** were studied to obtain the cross coupling products **103** in a two step one-pot reaction (Eq. (57)). The **103** products were: *n* = 2, Z = P (51%); *n* = 2, Z = As (90%); *n* = 2, Z = Sb (18%); *n* = 1, Z = Se (70%) [60].

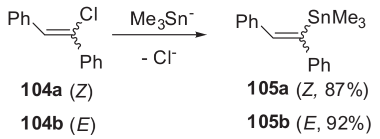


101 **102** **103** (57)

6. Vinylic $S_{RN}1$ reaction followed by a Stille reaction

The reaction of organostannyl anions with vinyl halides is known, but no mechanistic studies have been carried out to determine if these reactions occur by the $S_{RN}1$ mechanism [61]. This mechanism was recently proposed for the photostimulated reaction of vinyldiethyl phosphate esters with Me_3Sn^- ions affording vinyltrimethylstannanes in liquid ammonia [62]. Some of the vinyldiethyl phosphate esters do not react. Thus, structurally similar compounds do not behave in the same way. This behavior is mainly due to differences in spin density of their radical anions intermediates, which affect their fragmentation rates. These results are supported by computational calculations [63].

Vinylstannanes can also be obtained in very good yields through the reactions of vinyl chlorides with Me_3Sn^- ions in liquid ammonia by the $S_{RN}1$ mechanism (Eq. (58)) [64]. The substrate **104b** reacts in the dark, while substrate **104a** needs photostimulation.

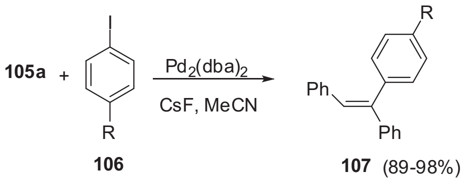


(58)

These reactions are inhibited by *p*-DNB and radical traps, indicating that they react by the $S_{RN}1$ mechanism. The fact that the reaction affords only one isomer with the same configuration as the starting vinyl chlorides is noteworthy, as this indicates that the inversion of the vinyl radical intermediate is slower than that of the coupling reaction with the nucleophile.

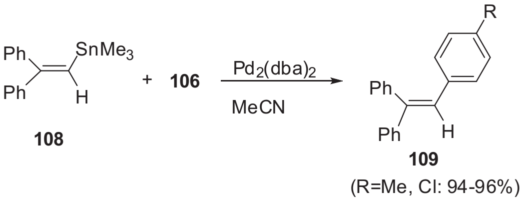
When this reaction takes place with 1,1-dichloro-1-alkenes and Me_3Sn^- ions, monosubstitution reduced products are formed in an *E*/*Z* mixture [64].

The reaction of **105a** with iodoarenes **106** (R = H, OMe, Me, Cl) catalyzed by $Pd_2(dba)_3$ gave in all cases the corresponding triarylolefin in good yields (Eq. (59)). With 1-iodonaphthalene, the product (*Z*)-1-(1,2-diphenylvinyl)naphthalene was obtained in 89% yield [64].



(59)

The reaction of trimethyl(2,2-diphenylvinyl)stannane **108**, also synthesized by the $S_{RN}1$ mechanism, with **106** (R = Me, Cl)) giving the cross-coupling products **109** in high yields (Eq. (60)) [64].



(60)

7. Conclusions

The $S_{RN}1$ reaction of R_3Sn^- ions with ArX, $ArOP(O)(OEt_2)_2$, and $ArNMe_3I$ are quite versatile and afford triorganylstannyl aromatic compounds. Using more than one leaving group, bis- and even tris(triorganylstannyl) aromatic compounds are obtained.

The sequence $S_{RN}1$ reaction to synthesize stannanes followed by Pd-catalysis with electrophiles is a powerful synthetic tool to obtain polycyclic aromatic compounds. When appropriate substituted substrates are chosen, this sequence can be iteratively repeated to synthesize complex molecules.

From the stannanes obtained, it is possible to prepare aromatic ketones or boronic acids by transmetalation, which can be used in Suzuki reactions. The stannane Me_2SnAr_2 prepared with the novel dianion Me_2Sn^{-2}, followed by Cu catalyzed reactions afforded the homocoupling products Ar–Ar.

From a simple precursor, such as Ph_3Z (Z = P, As, Sb) and by three steps (formation of Ph_2Z^-, reaction with Bu_3SnCl, and Pd catalyzed cross-coupling reaction with electrophiles), it is possible to obtain $ArPh_2Z$ in one pot reactions, and using this methodology triarylarsines can be synthesized as ligands for Pd catalyzed reactions. With Ph_2Se_2 as precursor, ArSePh is produced with good yields,

From vinyl chlorides it is possible to obtain vinylic stannanes, which by cross-coupling reactions, afford aryl substituted alkenes.

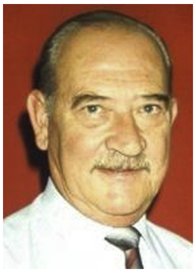
Acknowledgments

This work was supported by Agencia Córdoba Ciencia, Consejo Nacional de Investigaciones Científicas y Técnicas, FONCYT and SECYT, Universidad Nacional de Córdoba.

References

[1] K.R. Wursthorn, H.G. Kuivila, G.F. Smith, J. Am. Chem. Soc. 100 (1978) 2779–2789.
[2] K.R. Wursthorn, H.G. Kuivila, J. Organomet. Chem. 140 (1977) 29–39.
[3] J.P. Quintard, S. Hauvette-Frey, M. Pereyre, Metallation des halogenures d'aryle par le tributylstannyllithium dans le tetrahydrofuranne, J. Organomet. Chem. 159 (1978) 147–164.
[4] J.P. Quintard, S. Hauvette-Frey, M. Pereyre, Mettallation de ArX per Bu_3SnLi in HMPT, Bull. Soc. Chim. Belg. 87 (1976) 505–515.
[5] F.A. Carey, R.J. Sundberg, Advanced Organic Chemistry, Part B, third ed., 1990, pp. 575–581 (and references cited therein).
[6] V. Farina, V. Krishnamurthy, W.J. Scott, in: L.A. Paquette (Ed.), The Stille Reaction, Organic Reactions, vol. 50, Wiley, Chichester, 1997.
[7] T.R. Kelly, G.J. Bridger, C. Zhao, J. Am. Chem. Soc. 112 (1990) 8024–8034.
[8] (a) S. Gronowitz, D. Peters, Heterocycles 30 (1990) 645–658;
(b) T. Otsubo, Y. Kono, N. Hozo, H. Miyamoto, Y. Aso, F. Ogura, T. Tanaka, M. Sawada, Bull. Soc. Chem. Jpn. 66 (1993) 2033–2041;
(c) J.J.S. Lamba, J.M. Tour, J. Am. Chem. Soc. 116 (1994) 11723–11736;
(d) Y. Yang, H.N.C. Wong, Regiospecific synthesis of 3,4-disubstituted furans and 3-substituted furans using 3,4-Bis(tri-*n*-butylstannyl)furan and 3-(tri-*n*-butylstannyl), Tetrahedron 50 (1994) 9583–9608.
[9] (a) R.A. Rossi, A.B. Pierini, A.B. Peñéñory, Chem. Rev. 103 (2003) 71–167;
(b) J.I. Bardagí, V.A. Vaillard, R.A. Rossi, in: C. Chatgilialoglu, A. Studer (Eds.), Encyclopedia of Radicals in Chemistry, Biology & Materials, vol. 1, John Wiley & Sons Ltd, Chichester, UK, 2012, pp. 333–364;
(c) R.A. Rossi, A.B. Pierini, A.N. Santiago, in: L.A. Paquette, R. Bittman (Eds.), Organic Reactions, vol. 54, 1999, pp. 1–271.
[10] C.C. Yammal, J.C. Podestá, R.A. Rossi, J. Org. Chem. 57 (1992) 5720–5725.
[11] C. Dol, P.C.J. Kamer, M. van Leeuwen, Eur. J. Org. Chem. (1998) 359–364.
[12] A.B. Chopa, M.T. Lockhart, G.A. Silbestri, Organometallics 19 (2000) 2249–2250.
[13] A.B. Chopa, M.T. Lockhart, V.B. Dorn, Organometallics 21 (2002) 1425–1429.
[14] E.F. Córsico, R.A. Rossi, Synlett (2000) 230–232.
[15] A.B. Chopa, M.T. Lockhart, G. Silbestri, Organometallics 20 (2001) 3358–3360.
[16] G.F. Silbestri, M.T. Lockhart, A.B. Chopa, Arkivoc vii (2011) 210–220.
[17] E.F. Córsico, R.A. Rossi, Synlett (2000) 227–229.
[18] A.B. Chopa, M.T. Lockhart, G.F. Silbestri, Organometallics 21 (2002) 5874–5878.
[19] G.F. Silbestri, M.L. Lo Fiego, M.T. Lockhart, A.B. Chopa, J. Organomet. Chem. 695 (2010) 2578–2585.
[20] R. Krishnamurti, H.G. Kuivila, N.S. Shaik, J. Zubieta, Organometallics 10 (1991) 423–431.
[21] V.B. Dorn, G.F. Silbestri, M.T. Lockhart, A.B. Chopa, A.B. Pierini, New J. Chem. 37 (2013) 1150–1156.
[22] A.N. Santiago, S.M. Basso, J.P. Montanez, R.A. Rossi, Trimethylstannylation of mono- and dichloroarenes by the S(RN)1 mechanism in liquid ammonia, J. Phys. Org. Chem. 19 (2006) 829–835.
[23] J.P. Montanez, J.G. Uranga, A.N. Santiago, New J. Chem. 34 (2010) 1170–1175.
[24] Y. Yamamoto, A. Yanagi, Chem. Pharm. Bull. 30 (1982) 1731–1737.
[25] E.F. Córsico, R.A. Rossi, J. Org. Chem. 67 (2002) 3311–3316.
[26] M.T. Lockhart, A.B. Chopa, R.A. Rossi, J. Organomet. Chem. 582 (1999) 229–234.
[27] C.C. Yammal, J.C. Podestá, R.A. Rossi, J. Organomet. Chem. 509 (1996) 1–8.
[28] P.G. Harrison, Chemistry of Tin, Blackie, London, 1989, pp. 13–15.
[29] R.A. Jackson, J. Organomet. Chem. 166 (1979) 17–19.
[30] (a) M. Beller, T.H. Riermeier, C.P. Reisinger, W.A. Herrmann, Tetrahedron Lett. 38 (1997) 2073–2074;
(b) R. Sturmer, Angew. Chem. Int. Ed. Engl. 38 (1999) 3307–3308;
(c) I.P. Beletskaya, A.D. Averin, A.G. Bessmertnykh, R. Guilard, Tetrahedron Lett. 42 (2001) 4983–4986.
[31] J.P. Wolfe, H. Tomori, J.P. Sadighi, J.J. Yin, S.L. Buchwald, J. Org. Chem. 65 (2000) 1158–1174.

[32] J.I. Bardagi, R.A. Rossi, J. Org. Chem. 73 (2008) 4491–4495.
[33] S.M. Basso, J.P. Montanez, A.N. Santiago, Lett. Org. Chem. 5 (2008) 633–639.
[34] A.B. Chopa, G.F. Silbestri, M.T. Lockhart, J. Organomet. Chem. 690 (2005) 3865–3877.
[35] G.F. Silbestri, R.B. Masson, M.T. Lockhart, A.B. Chopa, J. Organomet. Chem. 691 (2006) 1520–1524.
[36] M.J. Lo Fiego, M.A. Badajoz, G.F. Silbestri, M.T. Lockhart, A.B. Chopa, J. Org. Chem. 73 (2008) 9184–9187.
[37] M.J. Lo Fiego, G.F. Silbestri, A.B. Chopa, M.T. Lockhart, J. Org. Chem. 76 (2011) 1707–1714.
[38] M.B. Faraoni, L.C. Koll, S.D. Mandolesi, A.E. Zúñiga, J.C. Podestá, Transmetallations between aryltrialkyltins and borane: synthesis of arylboronic acids and organotin hydrides, J. Organomet. Chem. 613 (2000) 236–238.
[39] For reviews, see: (a) N. Miyaura, in: A. de Meijere, F. Diederich (Eds.), Metal-Catalyzed Cross-Coupling Reactions, Wiley-VCH, Weinheim, Germany, 2004, pp. 41–124 (Chapter 2);
(b) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483;
(c) A. Suzuki, J. Organomet. Chem. 576 (1999) 146–168;
(d) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359–1470.
[40] S.D. Mandolesi, S.E. Vaillard, J.C. Podestá, R.A. Rossi, Organometallics 21 (2002) 4886–4888.
[41] P.M. Fidelibus, G.F. Silbestri, M.T. Lockhart, S.D. Mandolesi, A.B. Chopa, J.C. Podestá, Appl. Organomet. Chem. 21 (2007) 682–687.
[42] G. Harada, M. Yoshida, M. Iyoda, Chem. Lett. (2000) 160–161.
[43] P.M. Uberman, S.E. Martin, R.A. Rossi, J. Org. Chem. 70 (2005) 9063–9066.
[44] S.E. Tunney, J.K. Stille, J. Org. Chem. 52 (1987) 748–753.
[45] H. Schumann, H. Köpf, M. Schmidt, J. Organomet. Chem. 2 (1964) 159–165;
(b) C.W. Lai, F.Y. Kwong, Y. Wang, K.S. Chan, Tetrahedron Lett. 42 (2001) 4883–4885.
[46] S.E. Martin, M. Bonaterra, R.A. Rossi, J. Organomet. Chem. 664 (2002) 223–227.
[47] R.A. Rossi, S.E. Martin, Coord. Chem. Rev. 250 (2006) 575–601.
[48] M. Bonaterra, S.E. Martin, R.A. Rossi, Org. Lett. 5 (2003) 2731–2734.
[49] J.H. Downing, M.B. Smith, in: A.B.P. Lever (Ed.), Comprehensive Coordination Chemistry II, vol. 1, Elsevier, Oxford, 2004, pp. 253–296.
[50] (a) V. Farina, B. Krishnan, J. Am. Chem. Soc. 113 (1991) 9585–9595;
(b) Y. Obora, Y. Tsuji, M. Kobayashi, T. Kawamura, J. Org. Chem. 60 (1995) 4647–4649;
(c) K.C.Y. Lau, P. Chiu, Tetrahedron Lett. 48 (2007) 1813–1816.
[51] (a) C.R. Johnson, P. Braun, J. Am. Chem. Soc. 115 (1993) 11014–11015;
(b) F.S. Ruel, M.P. Braun, C.R. Johnson, Org. Synth. 75 (1998) 69–77;
(d) F. Bellina, C. Anselmi, R. Rossi, Tetrahedron Lett. 42 (2001) 3851–3854.
[52] P.M. Uberman, M.N. Lanteri, S.E. Martin, Organometallics 28 (2009) 6927–6934.
[53] P.M. Uberman, M.N. Lanteri, S.C. Parajón Puenzo, S.E. Martin, Dalton Trans. 40 (2011) 9229–9237.
[54] B.M. Trost, M.L. Crawley, Chem. Rev. 103 (2003) 2921–2944.
[55] P.M. Uberman, M.R. Caira, S.E. Martín, Organometallics 32 (2013) 3220–3226.
[56] M.N. Lanteri, R.A. Rossi, S.E. Martin, J. Organomet. Chem. 694 (2009) 3425–3430.
[57] M. Bonaterra, S.E. Martin, R.A. Rossi, Tetrahedron Lett. 47 (2006) 3511–3515.
[58] (a) W.J. Scott, G.T. Crisp, J.K. Stille, J. Am. Chem. Soc. 106 (1984) 4630–4632;
(b) W.J. Scott, J.K. Stille, J. Am. Chem. Soc. 108 (1986) 3033–3040;
(c) J.K. Stille, A.M. Echavarren, R.M. Williams, J.A. Hendrix, Org. Synth. 71 (1993) 97–106 (and references cited therein).
[59] (a) V. Farina, B. Krishnan, D.R. Marshall, G.P. Roth, J. Org. Chem. 58 (1993) 5434–5444;
(b) B. Domínguez, Y. Pazos, A.R. de Lera, J. Org. Chem. 65 (2000) 5917–5925.
[60] M. Bonaterra, R.A. Rossi, S.E. Martin, Organometallics 28 (2009) 933–936.
[61] (a) T.N. Mitchell, W. Reimann, Organometallics 5 (1986) 1991–1997;
(b) T.N. Mitchell, K. Böttcher, P. Bleckmann, B. Costisella, C. Schwittek, C. Nettelbeck, Eur. J. Org. Chem. (1999) 2413–2417.
[62] A.B. Chopa, V.B. Dorn, M.A. Badajoz, M.T. Lockhart, J. Org. Chem. 69 (2004) 3801–3805.
[63] V.B. Dorn, M.A. Badajoz, M.T. Lockhart, A.B. Chopa, A.B. Pierini, J. Organomet. Chem. 693 (2008) 2458–2462.
[64] E.F. Córsico, R.A. Rossi, J. Org. Chem. 69 (2004) 6427–6432.



Roberto A. Rossi was born in the province of Córdoba, Argentine. He is Professor in the Department of Organic Chemistry, National University of Córdoba, from which he received his Ph.D. degree. He did postdoctoral work with Professor Joseph F. Bunnett at the University of California at Santa Cruz. He is a Scientist Researcher of National Research Council of Argentina and Secretary of the National Academy of Science of Argentine. His current research interests include the reaction of radicals with nucleophiles, the chemistry of radical anions, organometallic chemistry, and transition metal catalyzed reactions.