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Review

Syntheses and applications of organostannanes bonded to elements of groups XIV, XV, and XVI

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Contents

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Abstract

This review highlights the synthesis and applications of bimetallic and heteroatoms stannanes R_3Sn–M (M = Si, Sn, Ge, P, As, Sb, S, Se, and Te) derived from elements of the groups XIV, XV, and XVI. Different types of reactions are described: transition metal-catalyzed addition of hetero-bimetallic (R_3Sn–SiR^1_3 or R_3Sn–SnR^1_3) compounds to multiple bonds, transition metal-catalyzed cross-coupling reactions of the organostannanes with a variety of electrophiles and other general reactions, such as substitution or complex formation.

Keywords: Organostannanes; Silylstannanes; Distannanes; Stannylphosphanes; Stannylsulfides; Stannylselenides

1. Introduction

Organotin compounds with elements of the groups XIV, XV and XVI are useful reagents in organic synthesis. Different types of reactions have been described. Transition metal-catalyzed reactions of ArX with organoheteroatom compounds are widely used for the synthesis of different heteroatom-containing compounds. Organotin compounds are extensively utilized as nucleophiles in cross-coupling reactions with the formation of C–C, C–N, C–P, C–S, and C–Sn bonds [1]. The Pd-catalyzed coupling of organo halides or triflates with organostannanes (the Stille reaction) is a powerful tool in organic synthesis.

Transition metal-catalyzed addition of hetero-bimetallic ($R_3SnSiR^1_3$ or $R_3SnSnR^1_3$) compounds to multiple bonds is of interest because new metal-carbon bonds are formed in the product, and these bonds can be utilized in further transformations as an active bimetal functional group. The selective reactions of bis(metalated)alkenyl compounds with various electrophiles allow for the synthesis of complex products in a sequential fashion. Primarily, this process results in the formation of a bifunctional organic dianion equivalent, and each metal moiety can be substituted separately with different electrophiles to furnish polysubstituted alkenes in a regio- and stereoselective manner. Indeed, they may also act as precursors to more reactive nucleophilic species through the action of a transition metal catalyst and may serve as organic group transfer reagents. Often, the metallic groups in a non-symmetric bis(metalated) species will exhibit significant changes in reactivity as a result of their proximity to other functional groups, allowing discrimination and selective modification.

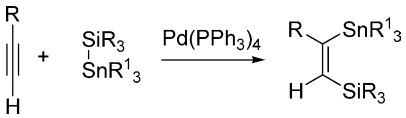
Metal-catalyzed element–element addition to alkynes represents a unique route to bis-functionalized alkenes. Several combinations of elements, such as B–B, Si–Si, Sn–Sn, Ge–Ge, B–Si, Sn–B, Ge–Sn, and Si–Sn may be added to the triple bond via metal-catalysis, where the Group 10 metals Pd, Ni, and Pt, typically in combination with a phosphane ligand, has been primary choices of catalysts. The reaction products are valuable intermediates in the synthesis of tri- and tetrasubstituted alkenes, e.g. via subsequent metal-catalyzed cross-coupling reactions, such as the Stille [1] or Suzuki reactions [1d,2].

This review highlights the synthesis and applications of bimetallic and heteroatoms stannanes R_3Sn–M (M = Si, Sn, Ge, P, As, Sb, S, Se, and Te). Considering the large number of papers published on bimetallic and heteroatoms stannanes, a complete coverage of all reported reactions were outside the scope of this review. A number of transition metal-catalyzed transformations are now standard reactions and recent reviews have been published [3,4]. Thus, some of the most common applications have not been included. Reactions of unusual substrates, new reaction conditions, and new catalyst systems have been included.

It is important to mention that although organotin compounds are generally air and moisture stable, and can be conveniently purified and stored, many are toxic, especially the lower alkyl derivatives. Trimethyltin derivatives are expected to be highly toxic, and the toxicity decreases dramatically with increasing alkyl group length. As a precaution, the preparation and use of all stannanes should be carried out with care.

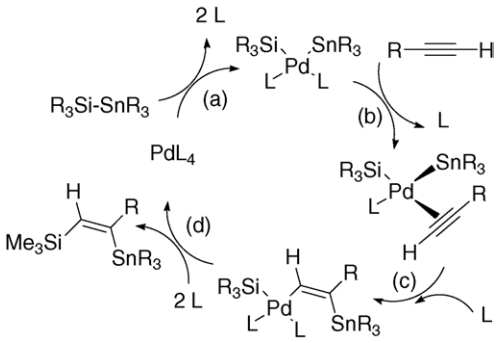
2. Silylstannanes

Much work has been done for the addition reactions of silylstannanes to alkynes [3,4]. Compounds having both C–Si and C–Sn bonds in the molecule would allow stepwise transformations of the two carbon–metal bonds based on the difference in their intrinsic reactivities. Reactions of silylstannanes with a variety of terminal alkynes cleanly proceeded in the presence of $Pd(PPh_3)_4$ to give addition products in moderate to good isolated yields (Eq. (1)).



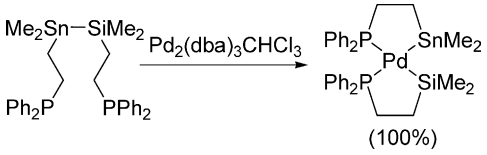
(1)

Ito et al. have performed a theoretical study using ab initio Hartree–Fock calculations concerning the reaction mechanism including the regioselectivity of these reactions [5], which gives support to the generally accepted catalytic cycle. The catalytic cycle involves the following steps: (a) oxidative addition of R_3SnSiR_3 to a coordinately unsaturated $Pd(L_4)$ species to afford organopalladium adduct, this step is exothermic; (b) coordination of the alkyne; (c) insertion of the alkyne into the Pd–Sn bond, which is the rate limiting step; (d) reductive elimination to afford the silylstannane product and complete the catalytic cycle (Scheme 1).



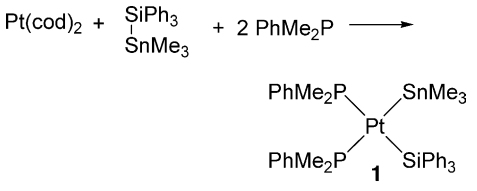
Scheme 1.

The first isolation of a complex between an silylstannane-Pd(L)$_2$ was achieved by use of a silylstannane having two 2-(diphenylphosphino)ethyl groups on both silicon and tin atoms (Eq. (2)). The complex was characterized by X-ray structural analysis [6].



(100%) (2)

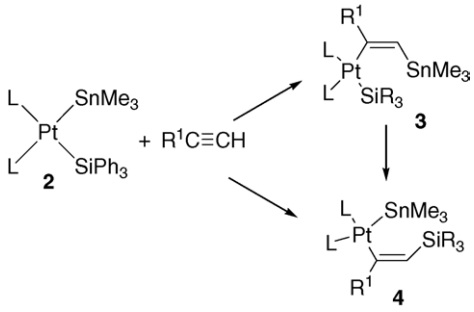
Recently, the synthesis and characterization of *cis*-silyl(stannyl)platinum(II) complexes has been published. These complexes were prepared by the reactions of Pt(cod)$_2$ with silylstannanes and phosphanes. For example, Pt(cod)$_2$ was dissolved in PhMe and successively treated with $Me_3SnSiPh_3$ (1 equivalent) and $PhMe_2P$ (2 equivalent) at 0 °C to yield the complex **1** (Eq. (3)) [7].



(3)

$^{31}P\{^1H\}$ NMR analysis of the resulting solution revealed a selective formation of **1**, which was isolated as a yellow crystalline solid in 38% yield. The structure of **1** was also determined by X-ray crystallography. Several *cis*-silyl(stannyl)platinum(II) complexes **2** have been prepared with this methodology. Complexes **2** reacted with alkynes in solution to give two types of products, **3** and **4**, which are formed by the insertion into Pt–Sn and Pt–Si bonds, respectively (Scheme 2). The ratio of **3** to **4** varied significantly with the types of silyl and phosphane ligands, alkynes employed, and reaction conditions; two types of processes are operative. One is competitive formation of **3** and **4** (kinetics products), and the other is subsequent conversion of **3** to **4** (thermodynamic product).

Complex **2** (L = PMe_2Ph) rapidly reacted with PhC≡CH in $CDCl_3$ to give the insertion complex into the Pt–Si bond (**3**, R^1 = Ph). By kinetics, it has been shown that the



Scheme 2.

insertion reactions into the Pt–Sn and Pt–Si bonds compete with each other under kinetic conditions, giving a 93/7 ratio of **3** and **4** at 50 °C, but complex **3** is entirely converted to **4** under thermodynamic conditions. Conversion of **1** obeyed good pseudo-first order kinetics up to 80% conversion ($k_{obs} = 1.02 \times 10^{-4}\ s^{-1}$) [7].

The reaction of the silylstannane with $Pd_2(dba)_3{\cdot}CHCl_3$ proceeded rapidly at room temperature to give *cis*(silyl) (stannyl) palladium complex in quantitative yield.

2.1. Addition to alkynes and diynes

The Pd-catalyzed silastannation of alkynes was first reported by the groups of Mitchell [8] and Chenard [9]. When performed on terminal alkynes, the reaction proceeds in a *syn*-fashion with excellent regio- and stereoselectivity, attaching the trialkyltin moiety to the internal carbon of the triple bond.

In general, the addition reactions were carried out without solvent or in THF at 60–70 °C. Although several R and R^1 have been used in $R_3SnSiR^1{}_3$, the most common reagent used was $Bu_3SnSiMe_3$. Some representative results are shown in Table 1.

It is remarked that complete regio- and stereoselectivity was observed: *cis*-adducts with the silyl group at the terminal carbon were selectively obtained. A terminal alkyne with sterically bulky group underwent the silastannation sluggishly: a long reaction time at lower temperature was found to be

Table 1
Reaction of R–C≡C–H with $Bu_3SnSiMe_3$[a]

Entry	R	Yield (%)	Ref.
1	Ph	91	[10]
2	Bu	52	[11]
3	*t*-Bu	45[b]	[11]
4	$Ph(CH_2)_3$	92	[12]
5	$NC(CH_2)_3$	90	[10]
6	Me_3Si	85	[10]
7	$HO(CH_2)_3$	87	[10]
8	Me_2NCH_2	57	[11]
9	$Ph(Me)NCH_2$	64	[12]
10	$(EtO)_2CH$	65	[13]
11	$AcO(CH_3)_2C$	0	[10]
12	$BrCH_2$	0	[10]

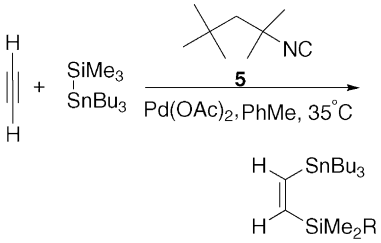
[a] At 60–70 °C.
[b] At 20 °C, 240 h.

better to attain reasonable yield (Table 1, entry 3). Many functionalities were tolerated in the reaction conditions. Alkynes bearing acetoxy as well as bromine groups at the propargylic position completely failed to give the corresponding adducts (entries 11 and 12).

Silastannation of unreactive alkynes with $Me_3SnSiMe_3$ led to a disproportionation reaction to form $Me_3SnSnMe_3$ and $Me_3SiSiMe_3$. The former products may react with alkynes to give by-products arising from distannylation. This disproportionation could be avoided by using the higher alkyl homologues of silylstannanes.

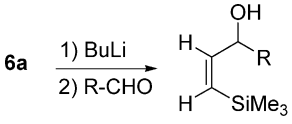
(*Z*)-1-Silyl-2-stannylethenes were stereoselectively synthesized by silastannation of ethyne, catalyzed by a Pd-*tert*-alkyl isocyanide catalyst, and the synthetic utilities were demonstrated by subsequent transformations.

When $Bu_3SnSiMe_3$ was stirred for 1 day under a balloon pressure of ethyne in the presence of $Pd(OAc)_2$ and 1,1,3,3-tetramethylbutyl isocyanide (**5**) in PhMe, the addition reaction proceeded to completion to yield **6** (Eq. (4)) [14].



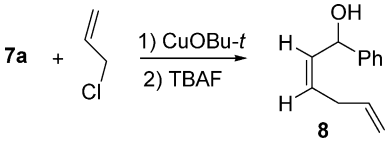
6a: R=Me (86%, *Z*/*E*=96/4)
6b: Ph (81%, *Z*/*E*=94/6) (4)

Lithiation of **6a** with *n*-BuLi followed by the reaction with aldehydes gave γ-trimethylsilyl allylic alcohols **7** with retention of the *Z* stereochemistry (Eq. (5)).



7a: R=Ph (73%, *Z*/*E*:95/5)
7b: R=$BzCH_2$ (85%, *Z*/*E*:97/3) (5)

The allylic alcohols **7** were subjected to the Cu(I)-promoted cross-coupling reaction. For instance, the cross-coupling of **7a** with allyl chloride successfully took place to afford only (*Z*)-allylic alcohol **8** (Eq. (6)).



67% (100% *Z*) (6)

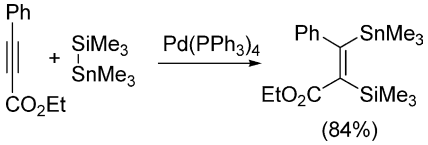
Recently, it has been reported that Pd(0)-catalyzed addition of silylstannanes to terminal alkynes has been shown to proceed in ionic liquids like 1-*n*-butyl-3-methylimidazolium hexafluorophosphate and 1-*n*-butyl-3-methylimidazolium tetrafluoroborate [15]. These reactions generally proceed in excellent yields to give 1-trialkylsilyl-2-tributylstannyl-1-*Z*-alkenes regio- and stereoselectively as a single product with reaction times comparable to those reported for reactions performed in THF (Table 2). Each of the ionic liquids containing the immobilized Pd catalyst has been recycled up to 10 times without loss of activity, allowing extensive reuse of the expensive solvent/catalyst system [15].

Table 2
$Bu_3SnSiMe_3$ addition to terminal alkynes R—C≡CH in ionic liquid [bmim]PF_6/Et_2O (**A**) and bmim]BF_4/Et_2O (**B**) in the presence of $Pd(PPh_3)_4$ [15]

Entry	R-group of alkyne	Ionic liquid	Pd (mol%)	Reaction time (h)	Isolated yield (%)
1	Ph	**A**	5	36	100
2	Ph	**A**	1	17	99
3	Ph	**B**	5	36	100
4	$(CH_2)_7CH_3$	**A**	5	15	97
5	$(CH_2)_7CH_3$	**A**	1	72	100
6	$(CH_2)_7CH_3$	**B**	5	120	82
7	$(CH_2)_4OH$	**A**	5	18	89
8	$(CH_2)_4OH$	**A**	1	24	87
9	$(CH_2)_4OH$	**B**	5	24	61
10	$(CH_2)_4OTHP$	**A**	5	84	99
11	$(CH_2)_4Cl$	**A**	5	120	68
12	$(CH_2)_4Cl$	**A**	1	144	22

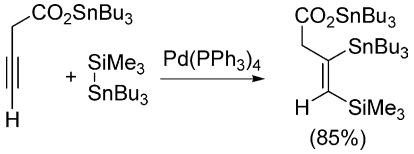
Reaction conditions: 1 mmol alkyne, 1.2 mmol $Bu_3SnSiMe_3$, 1.0 mL ionic liquid, 5.0 mL Et_2O, 70 °C oil. THP, tetrahydropyranyl.

In the reaction of phenyl-propynoic acid ethyl ester with $Me_3SnSiMe_3$ only the *Z* isomer was formed in high yield (Eq. (7)) [8].



(84%) (7)

The reaction of $Bu_3SnSiMe_3$ with a propynoate derivative gave a 1:1 mixture of inseparable acrylate derivatives (the addition of the Bu_3Sn-group on the triple bond occurred at both sites) [16]. However, the stereospecific addition of $Bu_3SnSiMe_3$ on the tributylstannyl ester of but-3-ynoic acid gave good yields of product (Eq. (8)) (with no protection, no reaction was obtained) [17].

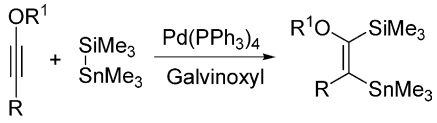


(85%) (8)

The reactivity of this compound was then studied using Stille coupling reactions with various organic halides under catalysis with Pd(II) complexes [17,18].

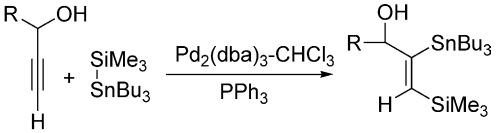
A variety of 1-alkoxy-1-alkynes underwent the regioselective silastannation with $Me_3SnSiMe_3$ in the presence of $Pd(PPh_3)_4$ with galvinoxyl at rt. In these reactions, the stannyl group was attached to the vinylic carbon with the R-group,

and the silyl group to the carbon with the alkoxy substituent (Eq. (9)). The high regioselectivity was found to be insensitive to the steric demand of the alkoxy moieties [19].



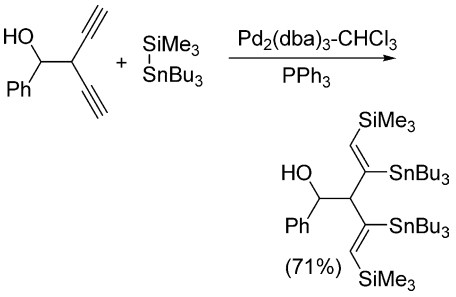
R = H, Me, Bu, Hex (32-91%) (9)

Recently, it has been reported the reaction of silastannation of several secondary propargylic alcohols (protected and unprotected) with $Pd_2(dba)_3$-$CHCl_3$ as the catalysts in combination with 1–2 equivalents of Ph_3P per Pd. Good to excellent yields were obtained with the expected regio- and stereoselectivity (Eq. (10)) [20].



R = alkyl, aryl, styryl (67-95%) (10)

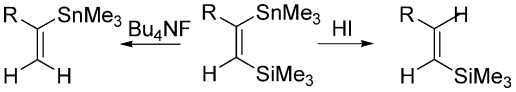
A sterically congested diyne was efficiently silastannated, providing the first example of a bis-silastannation (Eq. (11)). The monosilastannated product was not observed [20].



(11)

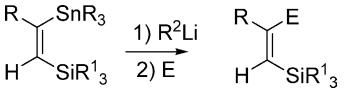
Silastannation of 1-phenylthioalkynes catalyzed by $Pd(PPh_3)_4$ proceeded with high regioselectivity, which is similar to that observed in the silastannation of the alkoxyalkynes [19].

Selective protodesilylation of the products, thus obtained was achieved by treatment with Bu_4NF leading to the formation of 2-stannylalkenes. Protodestannylation was performed with hydriodic acid to afford the corresponding (*E*)-1-silylalkenes in high yields through cleavage of the Sn–C bond (Eq. (12)) [12,21].



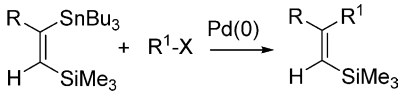
(12)

By treatment the silylstannanes with R^2Li at low temperature β-silylvinyllithiums were obtained and trapped with electrophiles (E = H, Me, RCHO, $SiMe_3$, $GeMe_3$, etc.) to afford a variety of vinylsilanes. Although the vinyllithium reagents (R^2 = Ph) were configurationally unstable, they resulted in the formation of *trans*-vinylsilanes, but with R^2 = alkyl groups they were successfully converted to vinylsilanes with complete retention of the geometry of the double bonds (Eq. (13)) [10,11].



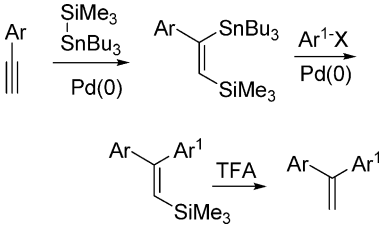
(13)

Alkenylsilanes have been synthesized from the silylstannanes products by cross-coupling reactions catalyzed by Pd (Eq. (14)) [1c]. Several electrophiles, such as allyl bromide, BzBr, PhBr, and some acyl chlorides were successfully coupled [11].



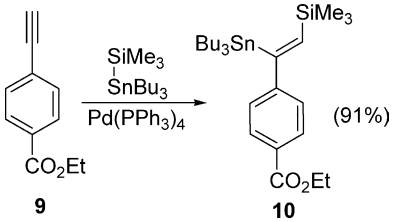
R = alkyl, aryl, CO_2Et (14)

Recently, a protocol has been developed to obtain 1,1-diarylethenes by a sequence of silylstannation of alkynes, Stille reaction and protodesilylation of vinylsilane (Eq. (15)) [22].

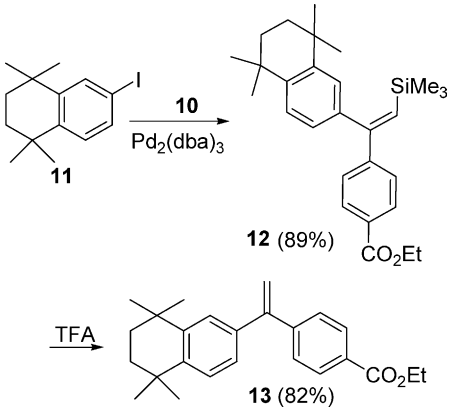


(15)

The addition of the $Bu_3SnSiMe_3$ to the alkyne **9** afforded the silylstannane **10** in high yield (Eq. (16)). The regio- and stereochemical assignments have been confirmed by chemical and spectroscopic means. Silylstannane **10** was coupled with iodide **11** under palladium catalysis to afford vinylsilane **12**. By treatment of compound **12** with 10% TFA/CH_2Cl_2 afforded the desired product **13** in good overall yield (Eq. (17)).



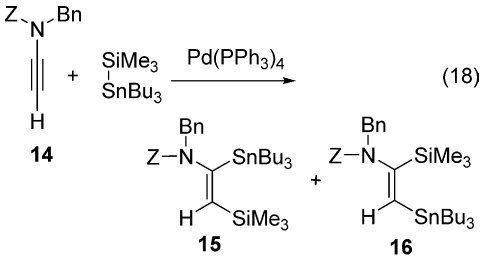
9 **10** (16)



(17)

Several aryl and heteroaryl bromides or iodides were studied with vinylstannane **10** to afford 1,1-diarylethene with a 56–89% yield of the combines Stille and protodesilylation reactions.

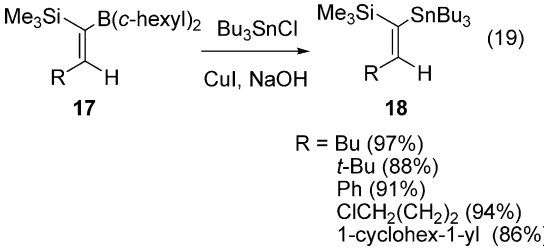
The silylstannation of the ynamine **14** (Z = Tos) by $Bu_3SnSiMe_3$ gave the pure compound (*Z*)-**15** as the sole regio- and stereoisomer, as established from the NMR spectrum [23]. However, when Z = COPh, the introduction of $Bu_3SnSiMe_3$ was also achieved in good yield although almost no regioselectivity was observed (Eq. (18)) [24].



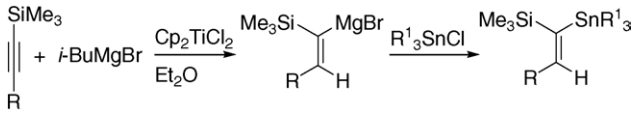
(18)

The enamide **15a** prepared by a modified Stille coupling procedure [$Pd_2(dba)_3$, $AsPh_3$, CuCl in THF, rt] was allowed to react with aromatic and heteroaromatic halides, acyl chloride, as well as benzyl and allyl halides [25].

Although 1-boryl-1-silylalkene is readily available via hydroboration of 1-silyl-1-alkyne, 1-silyl-1-stannylalkene cannot be obtained regioselectively by hydrostannation of 1-silyl-1-alkyne [26]. However, it was reported a regio- and stereoselective route to (*E*)-1-(Bu_3Sn)-1-(Me_3Si)-1-alkenes (**18**) by the CuI-catalyzed reaction of (*Z*)-1-(Me_3Si)-1-alkenyldialkylboranes (**17**) with Bu_3SnCl in the presence of aq. NaOH (Eq. (19)) [27].

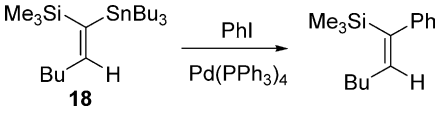


(19)



Scheme 3.

The reaction of **18** (R = Bu) with Bu_3SnCl followed by iodinolysis, where the conversion of C–Sn bond to C–I bond proceeds with retention of configuration [28], and gave (*E*)-1-iodo-1-(Me_3Si)-1-hexene in 63% overall yield in a "one-pot" manner from the dicyclohexylborane, and corroborates the stereochemistry of this reaction. Furthermore, the reaction of **18** (R = Bu) with PhI catalyzed by $Pd(PPh_3)_4$ afforded the coupling product as the sole isomer in 93% yield (Eq. (20)).

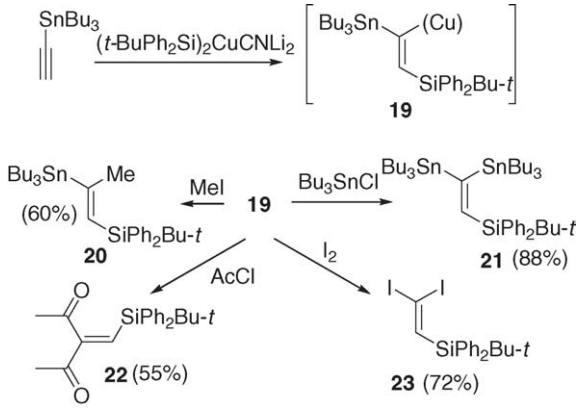


(20)

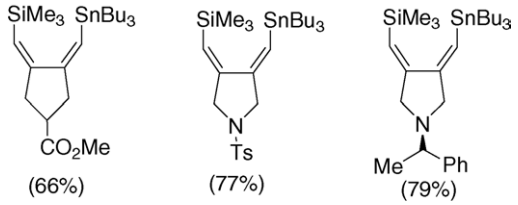
Recently, a new approach to the synthesis of (*E*)-1-($R^1{}_3Sn$)-1-(Me_3Si)-1-alkenes has been developed by the hydromagnesiation reaction of alkynylsilanes, followed by the reaction with $R^1{}_3SnCl$. The hydromagnesiation of alkynylsilanes catalyzed by Cp_2TiCl_2 in ether is almost 100% regio- and stereoselective. The Mg/Sn metathesis reaction on the silylvinyl Grignard reagent intermediates occurs with total retention of the configuration. For instance, when R^1 = Bu, R = Bu, *i*-C_5H_{11}, *n*-C_6H_{13}, and Bz, the yields are 81–90% (Scheme 3) [29].

(*E*)-1-(Bu_3Sn)-1-(Me_3Si)-1-alkenes can undergo the cross-coupling reaction with ArI in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI to afford (*Z*)-1,2-disubstituted vinylsilanes in good yields.

The *syn-tert*-butyldiphenylsilylcupration of $Bu_3SnC{\equiv}CH$ affords the trimetalated intermediate **19**, which reacted with different electrophiles, such as MeI, affording **20** and Bu_3SnCl giving silylstannylalkenes **21** with good yields. By treatment with AcCl and I_2 furnishes the products **22** and **23**, respectively (Scheme 4) [30].

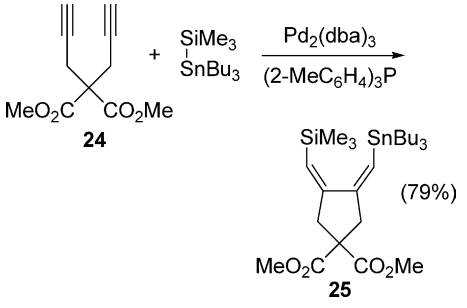


Scheme 4.



Scheme 5.

The Pd-catalyzed reaction of 1,6-diynes such as **24** with $Bu_3SnSiMe_3$ afforded the cyclized product **25** in good yields with high regio- and stereoselectivity. The structure, stereochemistry, and the fluxional nature of the compound **25** were unambiguously established (Eq. (21)). Sterically demanding Me_3Si and $SnBu_3$ substituents impose a non-planar, therefore, helically chiral structure for such a diene [31].

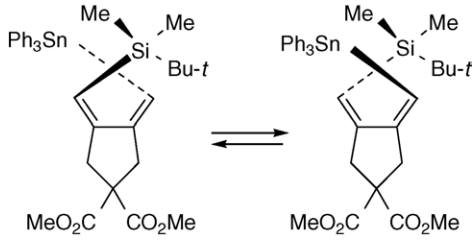


(21)

Cyclizations of a number of other 1,6-diynes were carried out and some of the results are shown in Scheme 5.

The (*ZZ*)-geometry of these *S-cis*-1,3-dienes, resulting, forces the silicon and tin groups to be non-planar, thus making the molecules axially chiral. There is rapid equilibration between the two helical forms at rt irrespective of the size of the Si and Sn substituents. The rates of enantiomerization (Scheme 6), which depend on the Si and Sn substituents, and the substitution pattern of the cylopentane ring have been studied by dynamic NMR spectroscopy [32].

When one of the acetylenes was non-terminal, the reaction of silylstannation occurred only in the terminal acetylene. The reactions were remarkably regio- and stereoselective for monosubstituted acetylenes (Scheme 7). Such chemoselectivity results in the formation of a (*Z*)-1,2-silylstannyl olefins leading to the olefin with a terminal SiR_3 group and an internal SnR_3 group as the only product [33].

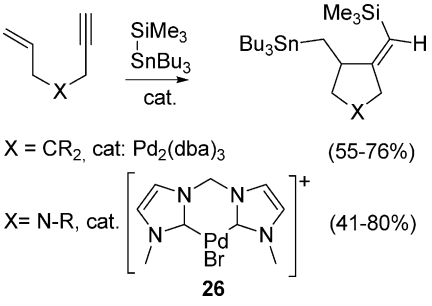


Scheme 6.

The (*Z*)-1,2-silylstannyl olefins are useful intermediates for further synthesis. For example, the acetylenes upon treatment with iodine in CH_2Cl_2 give very high yields of vinyl iodides with complete retention of stereochemistry at the double bond. Several examples of Stille and Heck reaction were performed with these vinyl iodides.

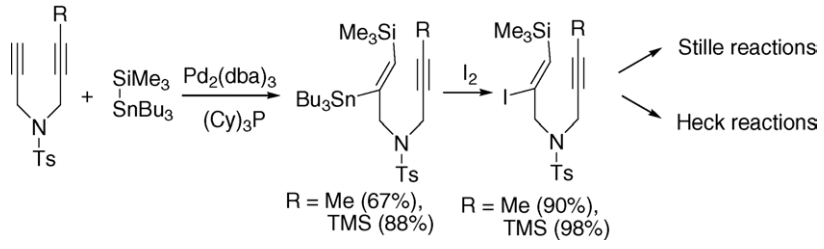
2.2. Reactions with enynes

The palladium-catalyzed silylstannation of 1,6-enynes to afford cyclized products was studied. Among several catalytic systems tested, it was concluded that Pd(0)/Cy_2P(*o*-biphenyl) complex was optimal for carbocyclic formation of cyclopentanes, and a cationic *N*-heterocyclic carbene-based Pd(II) system **26** with a non-coordinating counterion using $NaB[3,5\text{-}(CF_3)_2C_6H_4]_4$ was optimal for pyrrolidine formation (Eq. (22)) [34].

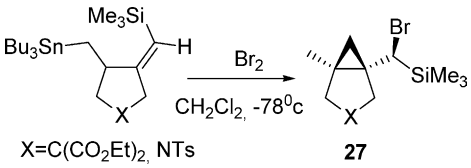


(22)

These cyclic silylstannanes react with bromine to give cyclopropanes **27** quantitatively (Eq. (23)). HPLC data indicated that a single diastereomer was formed and X-ray crystal diffraction data proved the relative configuration of the enantiomeric pair [34].

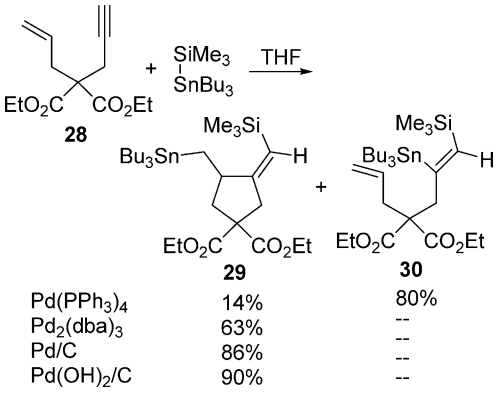


Scheme 7.



(23)

The reaction of the enyne **28** with $Bu_3SnSiMe_3$ catalyzed by Pd(0) complexes gave two products depending on the experimental conditions (Eq. (24)).



(24)

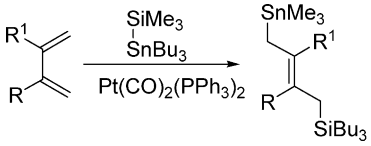
When a THF solution containing equimolar quantities of enyne **28** and $Bu_3SnSiMe_3$ in the presence of a catalytic amount of $Pd(PPh_3)_4$, a small amount of the cyclized product **29** containing both a silyl group and a stannane group was obtained in 14% yield. In this reaction, a bismetallated product of the alkyne **30** was obtained as a main product in 80% yield [35].

The formation of the alkyne bismetallation product **30** could be suppressed by using a Pd catalyst in the absence of a phosphane ligand. The $Pd_2(dba)_3{\cdot}CHCl_3$ seemed to be the most effective catalyst. It is noteworthy that heterogeneous Pd catalysts, Pd/C or $Pd(OH)_2/C$, also afforded the desired product **29** in high yield. Several examples of this novel Pd-catalyzed bismetallative cyclization of enynes in the presence of $Bu_3SnSiMe_3$ have been reported [35,36].

The possible mechanism suggested for this cyclization is shown in Scheme 8. Initially, oxidative addition of $Bu_3SnSiMe_3$ to Pd(0) complex occurs to give $Bu_3Sn{-}Pd{-}SiMe_3$ complex **A** (the ligands are not shown by clarity). Insertion of the alkyne moiety in the model substrate **B** into the Pd–Si bond of **A** produces intermediate **C**. The alkyne bismetallation product **D** and Pd(0) should be directly formed from the intermediate **C** through reductive elimination. For the formation of the cyclized product **F** from the intermediate **C**, two possibilities can be considered. Intramolecular insertion of the bond into the C–Pd bond of **C** then occurs to give complex **E**, and reductive elimination finally affords cyclized product **F**, and Pd(0). On the other hand, the possibility of the formation of **G** cannot be excluded in this mechanism [37]. Reductive elimination from **G** should afford the same cyclized product **F**.

2.3. Addition to alkenes and butadienes

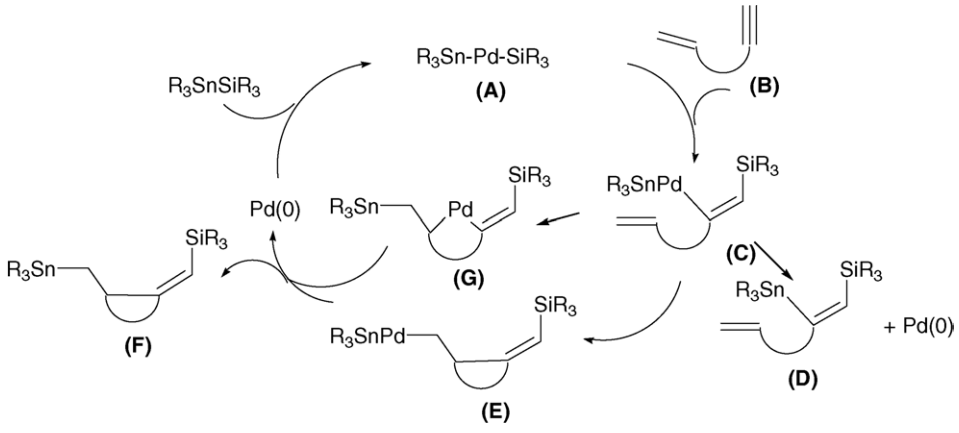
The reaction of $Bu_3SnSiMe_3$ with 1,3-butadiene in the presence of $Pt(CO)_2(PPh_3)_2$ afforded *trans*-1-stannyl-4-silyl-2-butene as a single isomer in high yield (Eq. (25)) [38]. It is noted that 2-substituted 1,3-dienes afforded the corresponding *trans*-1,4-silastannation adducts with excellent regioselectivity, in which the stannyl group was attached to the 1-position.



R = R^1 = H (93%)
R = Me, R^1 = H (84%)
R = Ph, R^1= H (85%)
R = Me, R^1 = Me (70%)

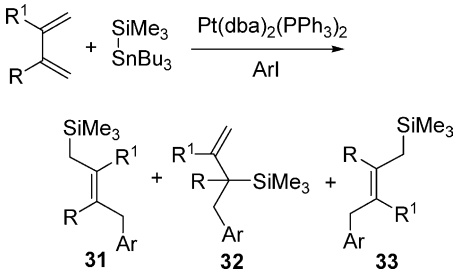
(25)

Three-component coupling reaction of acid chlorides, organodisilanes, and 1,3-dienes achieves 1,4-carbosilylation of the 1,3-dienes to afford allylic silanes as the product with high yields regio- and stereoselectively [39]. A similar three-component coupling reaction using ArI, organosilylstannanes and dienes also proceeded in the same way.



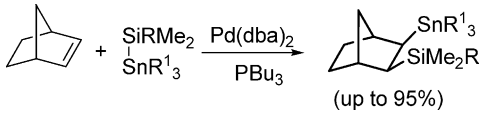
Scheme 8.

However, the selectivity and the yield decreased considerably. Thus, the reaction of symmetric dienes (R = R^1 = H, Me) with PhI, 4-MeC_6H_4I, 4-ClC_6H_4I, and 1-$IC_{10}H_8$ affords the products **31** and **32** in 40–67% with variable amounts of each (Eq. (26)). With asymmetrical dienes (R = H, R^1 = Me, Ph) the yields are similar, with ca. 6–16% of relative yields of product **33** [39].



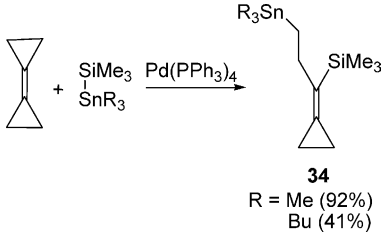
(26)

Silylstannanes added to the carbon–carbon double bond of alkenes in the presence of a Pd catalyst. The reaction was limited to ethylene (97%), norbornene (95%), and benzonorbornadiene (59%), and the catalysts were $Pd(dba)_2$ with the ligands PEt_3 or PBu_3. Other ligands were not effective for the addition reaction to norbornene. In the reactions with bicyclic alkenes, such as norbornene and benzonorbornene, only (*exo*,*exo*) stereoisomers were formed, indicating that the addition took place with stereospecific *cis*-addition. For instance, the reaction with norbornene is shown in Eq. (27). No reaction occurred with other alkenes such as 1-hexene, styrene, cyclohexane, or cyclopentene [40].



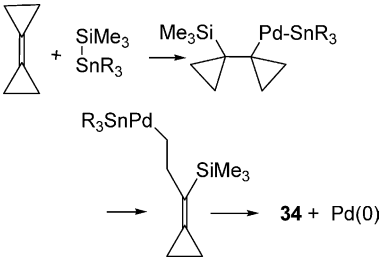
(27)

The Pd-catalyzed ($Pd(PPh_3)_4$) addition of $R_3SnSiMe_3$ (R = Me, Bu) to bicyclopropylidene afforded the product **34** (Eq. (28)) [41].



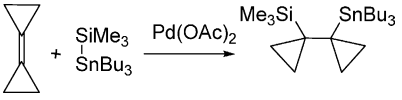
(28)

The mechanism proposed was the silylpalladiation of the double bond to afford the intermediate with a concomitant cyclopropylmethyl to homoallyl rearrangement, with remarkable regioselectivity to yield only the observed products (Eq. (29)).



(29)

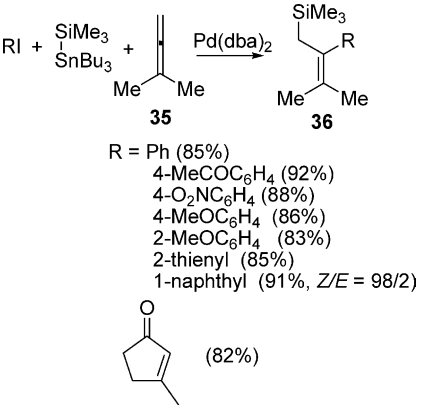
However, in the presence of the Pd(OAc)-1,1,3,3-tetramethylbutylisocyanide complex as a catalyst, the addition of $Bu_3SnSiMe_3$ to bicyclopropylidene occurred without ring opening to yield 45% of 1-(Bu_3Sn)-1′-(Me_3Si) bicyclopropyl (Eq. (30)).



(30)

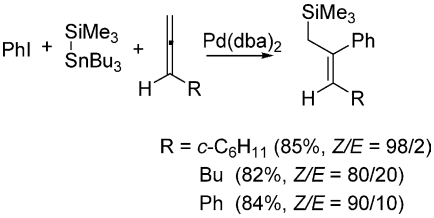
2.4. Addition to allenes and bis-allenes

The Pd-catalyzed three-component coupling reaction between aryl or vinyl iodides, $Bu_3SnSiMe_3$, and 1,1-dimethylallene (**35**) in the presence of $Pd(dba)_2$ give an allylic silane **36** in good to excellent yields. This carbosilylation reaction is highly regioselective, with the R-group adding to the middle carbon and the silyl group to the unsubstituted terminal carbon. Bromides gave lower yields and chlorides are unreactives. Some examples are depicted in Eq. (31) [42,43].

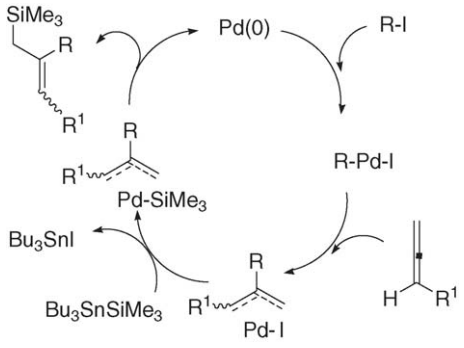


(31)

Monosubstituted allenes also undergo carbosilylation with PhI and $Bu_3SnSiMe_3$, producing the carbosilylation adducts stereoselectively with *Z*/*E* between 98/2 and 80/20. Bulkier organic halides and allenes give products with higher *Z*/*E* ratios (Eq. (32)).



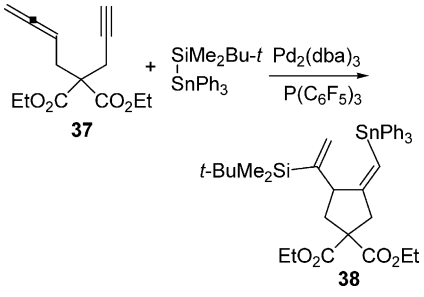
(32)



Scheme 9.

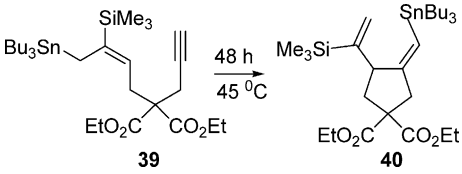
The mechanism proposed (Scheme 9) involves oxidative addition of RI to a Pd(0) to give an R–Pd–I intermediate (the ligands are not shown by clarity). Coordination of allene to the Pd(II) center followed by migration of R to the central carbon of allene gives a π-allyl Pd(II) species. Transmetalation with the silylstannane followed by reductive elimination yields the final allylic silane, Bu_3SnI and Pd(0) species. The proposed formation of Bu_3SnI was evidenced by its observation in the ^1H NMR spectra of the product mixtures from reactions of ArI.

The allenyne **37**, in the presence of $Ph_3SnSiMe_2Bu$-*t*, $Pd_2(dba)_3$, $CHCl_3$, and $P(C_6F_5)_3$ underwent a clean reaction at rt to give the cyclic product **38** in 80% isolated yield (Eq. (33)). The structure and configuration of **38** were established by NMR spectroscopy and elemental analysis [44].



(33)

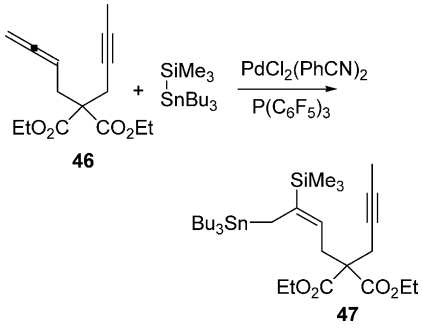
In the reaction with a less reactive $Bu_3SnSiMe_3$, the uncyclized adduct **39** was isolated in excellent yield (81% isolated yield). On heating the intermediate allylstannane **39**, it was quantitatively converted into the cyclic product **40** (Eq. (34)).



(34)

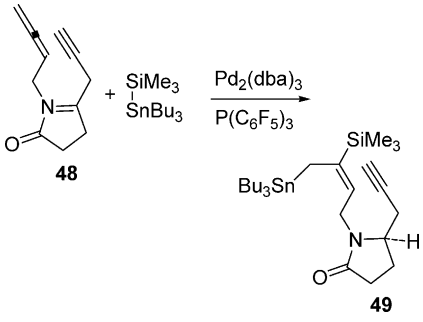
Recently, RajanBabu and co-workers [45] have published the silylstannylation-cyclization of allenynes. Some representative examples are indicated in Scheme 10. The yields indicated are isolated products. By NMR spectroscopy, the yields were >90%.

The cyclization appears to be limited to allenynes with terminal acetylenes. For example, substrate **46**, internal acetylene, failed to undergo the cyclization reaction even under forcing conditions (Eq. (35)). While $Ph_3SnSiMe_2Bu$-*t* failed to react, $Bu_3SnSiMe_3$ gave only an acyclic adduct **47** under the standard conditions.

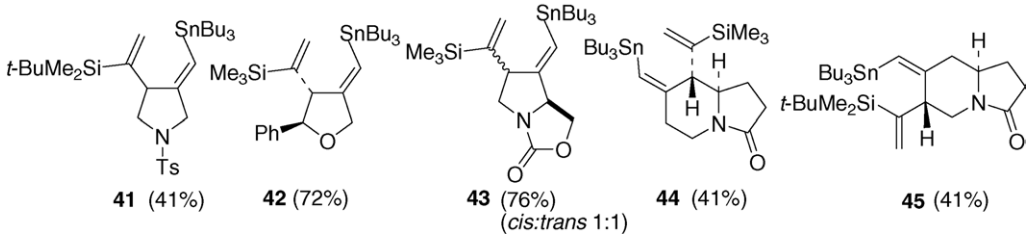


(35)

For some substrates, the success of the reaction also depends on the choice of the silylstannane reagent. For example, substrate **48**, which underwent smooth cyclization with $Ph_3SnSiMe_2Bu$-*t* to afford product **45**, gave only acyclic product **49** (88% yield) with $Bu_3SnSiMe_3$ (Eq. (36)).



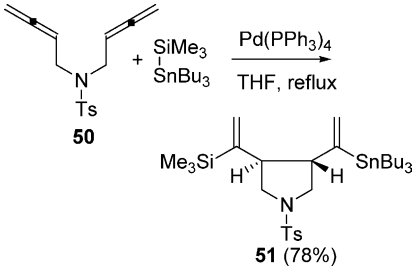
(36)



Scheme 10.

The allenynes that have been discussed previously in connection with the silylstannylation-cyclization reaction to give the products **41**–**45**, gave addition to the allene without cyclization under mild conditions. By careful monitoring of the reaction by NMR spectroscopy, the reaction can be optimized to get maximum yields of the expected allylstannanes, which are formed with excellent regio- and stereoselectivity [45].

It has been reported the carbocyclization via silastannylation of bis(allenes) to form five-membered ring systems. When bis(allene) **50** reacted with $Bu_3SnSiMe_3$ in the presence of $Pd(PPh_3)_4$ in refluxing THF, the cyclization proceeded to afford the *trans*-fused cyclized product **51** (Eq. (37)). The *trans*-stereochemistry of the cyclized product **51** was confirmed by NMR spectroscopy [46].

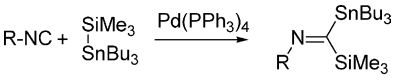


(37)

Several systems were tested, and the products **52**–**54** were obtained in good yields (Scheme 11).

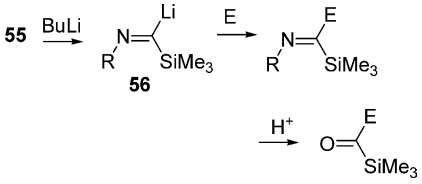
2.5. Others reactions

Alkyl- and aryl-isocyanides react with silylstannanes to afford (silyl)(stannyl)-iminomethanes **55** by Pd-catalyzed 1,1-silastannation (Eq. (38)). The sterically bulky *tert*-alkyl isonitrile was not reactive [47].



(38)

The imines **55,** thus obtained were useful precursors for the generation of *N*-substituted-imino(organosilyl) methyllithiums **56** by reaction with BuLi, which served as a synthetic equivalent of organosilylcarbonyl anion or carbonyl dianion by reaction with electrophiles and acidic hydrolysis (Eq. (39)) [48].

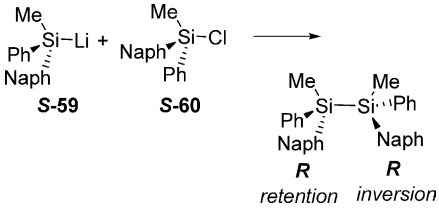


(39)

In an attempt to prepare optically active triorgannylsilyllithium from optically active triorgannylchlorosilane by reaction with Li metal, the triorgannylsilyl lithium obtained was completely racemized. By reaction of an optically active triorgannylchlorosilane with Me_3SnLi, the silylstannane **57** obtained was optically active. By reaction of **57** with MeLi, afforded the silyllithium **58** in 46–63%, being this reaction 94–99% stereospecific (Eq. (40)) [49].

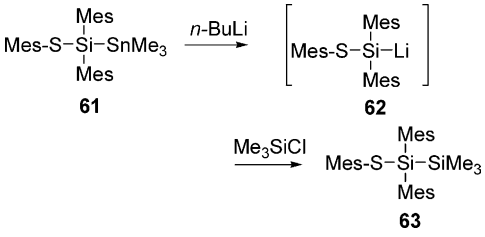
(40)

The reaction between (*S*)-methyl(1-naphthyl)phenylsilyllithium (***S*-59**, 82% ee) and (*S*)-methyl(1-naphthyl) phenylchlorosilane (***S*-60**) gave the optically pure substitution compound. It was elucidated as (*R*,*R*) by X-ray diffraction, which confirmed retention and inversion for silicon stereocenters of silyllithium and chlorosilane in the nucleophilic substitution reaction (Eq. (41)) [50].

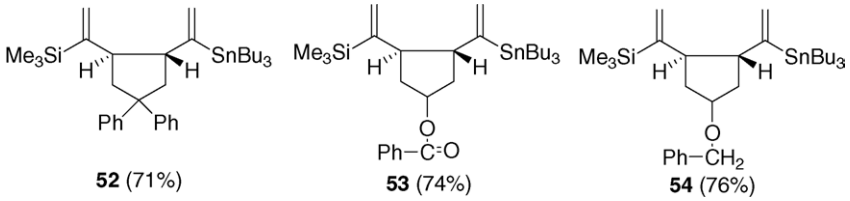


(41)

By a tin–lithium exchange reaction of the silylstannane **61** with BuLi, the [(mesitylthio)silyl]lithium intermediates **62** was prepared and trapped quantitatively with Me_3SiCl to give the disilane **63** (Eq. (42)) [51].

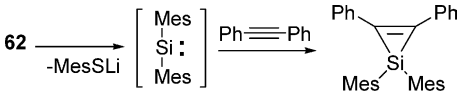


(42)



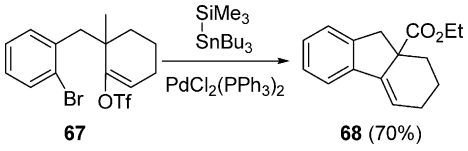
Scheme 11.

The intermediate **62** underwent α-elimination at 0 °C to release MesSLi (**64**) and dimesitylsilylene (**65**). The silylene **65** was trapped with several reagents. For instance, it was trapped with PhC≡CPh to give the adduct **66** (Eq. (43)) [51].



(43)

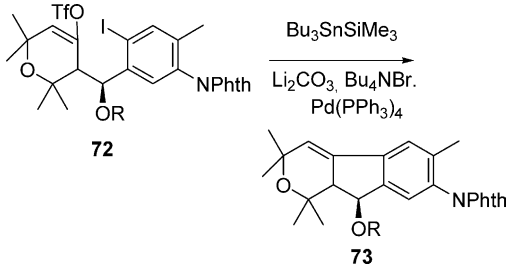
Mori et al. [52] have developed a protocol in a Pd-catalyzed tandem transmetalation-intramolecular cyclization involving the use of $Bu_3SnSiMe_3$ with vinyl triflates. The vinyl triflate **67** cyclized in the presence of $PdCl_2(PPh_3)_2$, Bu_4NBr, and Li_2CO_3 to afford the cyclic product **68** (Eq. (44)). Several examples of this reaction have been reported [52].



(44)

It has been proposed that the mechanism of this reaction was that the initial step is the formation of vinylpalladium triflate **69a** by intermolecular oxidative addition of the vinyl triflate **67** to the Pd(0) species (Scheme 12). The product of this reaction was then converted into vinylpalladium bromide **69b** by reaction with Bu_4NBr. Transmetalation of vinylpalladium bromide **69b** by $Bu_3SnSiMe_3$ afforded vinylpalladium stannane **69c**. The reductive elimination of a vinylstannane from **69c** was followed by intramolecular oxidative addition of an ArBr to form arylpalladium complex **70**. The intramolecular transmetalation of a vinyl group from the vinylstannane to the arylpalladium bromide afforded palladametalacycle **71** which provided **68** upon reductive elimination.

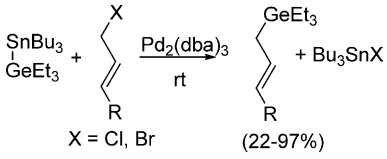
The synthesis of nodulisporic acid A subunit **73** was achieved using this methodology. The intermolecular formation of a stannane from **72** with $Bu_3SnSiMe_3$, followed by an intramolecular coupling with a tethered electrophile afforded **73** (Eq. (45)) [53].



(45)

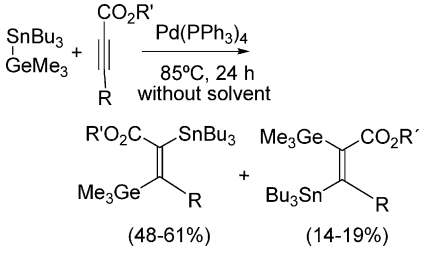
3. Germylstannanes

The synthesis of 2-alkenylgermanes under mild conditions is of great importance because of the applications of allylic germanes in organic synthesis. In contrast to silylstannylation, germylstannylation has not been developed and few examples have been reported. A novel reaction was reported for the regioselective synthesis of allylic germanes from allylic halides with $Bu_3SnGeEt_3$ catalyzed by Pd complex [54]. $Bu_3SnGeEt_3$ reacted with allylic bromides or chlorides in the presence of a catalytic amount of $Pd_2(dba)_3$ to give 2-alkenyltriethylgermanes (Eq. (46)). The reaction regioselectively gave the products in moderate to good yields.

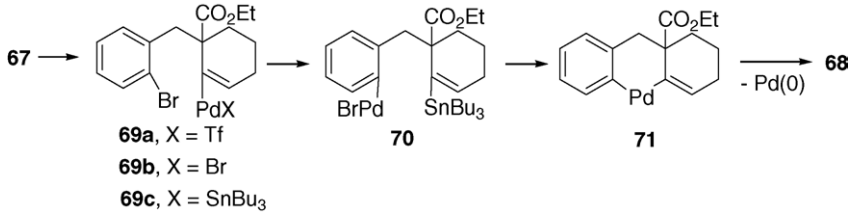


(46)

Pd-catalyzed addition of $Bu_3SnGeMe_3$ to α,β-unsaturated esters was reported [55]. Treatment of α,β-acetylenic esters with $Bu_3SnGeMe_3$ in the presence of $Pd(PPh_3)_4$ afforded two isomers (Eq. (47)). The reaction was not regioselective, but the two products were readily separated by column.

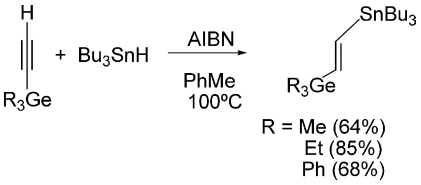


(47)



Scheme 12.

The vinylgermanyl stannanes were transformed into a variety of germyl-containing 1,4-dienes using Sn–Li transmetalation and reactions with allyl moieties [55]. On the other hand, vinyltin compounds bearing a germyl group at the β-position were easily obtained by hydrostannation of alkynylgermanes (Eq. (48)) [56].

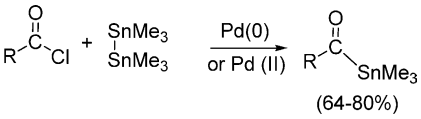


(48)

4. Distannanes

4.1. Cross-coupling reactions

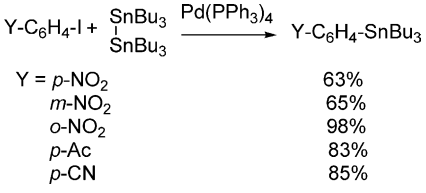
Distannanes derivatives are useful reagents in conjunction with a variety of electrophiles. The reaction of aroyl chlorides with $Et_3SnSnEt_3$ gave symmetrical ketones or α-diketones, depending on the nature of the Pd catalyst and the reaction conditions. The synthesis of α-diketones from RCOCl and ArCOCl has been performed [57]. However, under suitable conditions, the acylstannanes could be obtained [58]. By reaction of acyl chloride with $Me_3SnSnMe_3$ in the presence of Pd catalyst, trimethylacyltins were prepared in THF at reflux (Eq. (49)).



(49)

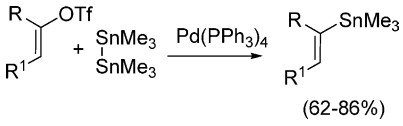
The cross-coupling reaction of diorganostannanes has received little attention. A problem with this reaction was the disproportionation of the distannane, and an excess of the reagent had to be used. However, ArBr and ArI have been shown to react with $(R_3Sn)_2$ (R = Bu or Me) in the presence of $Pd(PPh_3)_4$ or $PdBr_2(PPh_3)_2$ to give the cross-coupling products in high yield [59]. Also, benzylic bromides were high yielding; however, allyl and alkenyl halides gave the stannanes in low yields.

The coupling reaction of distannanes with ArX has also been investigated by Kosugi et al. [60]. Nitro-, acyl-, and cyanophenyltributyltin were prepared in good yields by the reaction of $(Bu_3Sn)_2$ with the ArI in the presence of catalytic amount of $Pd(PPh_3)_4$ (Eq. (50)).



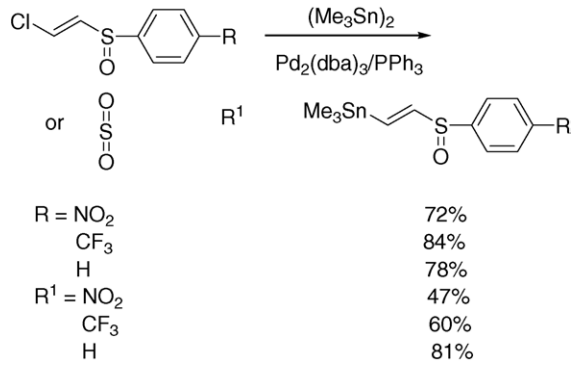
(50)

The reaction of distannanes with vinyl triflates is an important route to obtain vinylstannanes regiochemically. The Pd-catalyzed coupling of enol triflates with $(Me_3Sn)_2$ afforded the vinyltrimethylstannanes in good yields (Eq. (51)) [61].



(51)

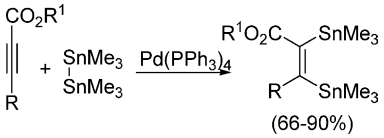
The synthesis of vinylstannanes of unsymmetrical ketones was limited to obtain the vinyl triflate selectively. The cleavage of vinylstannanes with RLi provided the regioselective formation of vinyllithium. In addition, some activated vinylic chlorides derived from sulfoxides or sulfones coupled with $(Me_3Sn)_2$ in the presence of catalytic amount of $Pd_2(dba)_3/PPh_3$ (Scheme 13) [62].



Scheme 13.

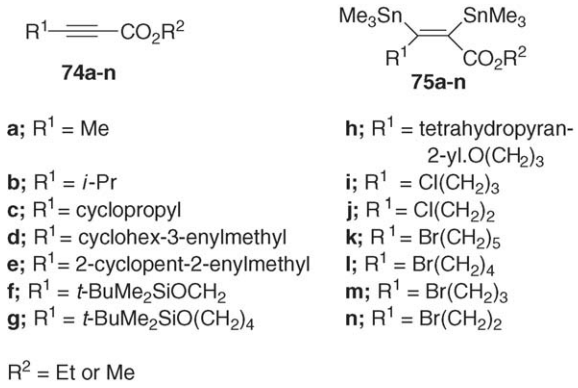
4.2. Addition reactions

Bis-stannylation of alkynes is one of the most widely used metalometalation reactions [3]. Like silylstannylation, bis-stannylation is usually a Pd-catalyzed *syn*-selective process and it also proceeds best on terminal alkynes or activated internal alkynes. The distannation of terminal alkynes, as catalyzed by $Pd(PPh_3)_4$, has been known since 1983 [63] and has showed that terminal acetylenes reacted with $(R_3Sn)_2$ (R = Me, Et, Bu) in a *syn* addition, giving products with *Z* configuration (Eq. (52)) [64].



(52)

The reaction is not quantitative. With very few exceptions, there is no reaction in the case of non-terminal alkynes. Moreover, Pd-catalyzed addition of $(Me_3Sn)_2$ to α,β-acetylenic esters **74** afforded the addition products **75** (yields 66–90%) (Scheme 14) which were upon warming (75–95 °C) rearrange to the corresponding (*E*)-isomers [65,66]. Similar results were obtained with *N*,*N*-dimethyl (*E*)-2,3-bis(trimethylstannyl)alk-2-enamides, although these reactions were slower and less efficient. Furthermore, the (*Z*)-addition products were rearranged to the (*E*)-isomers

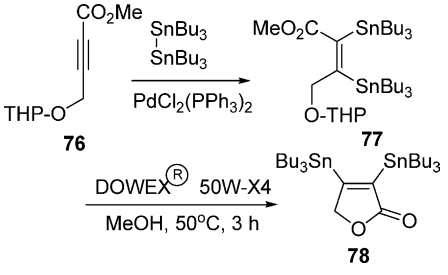


Scheme 14.

under the reaction conditions. The transmetalation of certain addition products containing ω-halogen substituent afforded cyclic products.

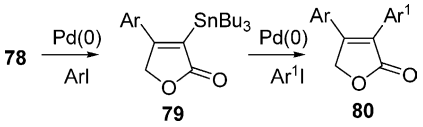
A possible pathway for the Pd-catalyzed addition of $(R_3Sn)_2$ to the α,β-acetylenic esters was described as the oxidative addition of the Pd catalyst to the Sn–Sn bond of the distannane, coordination of the substrate followed by the insertion of the triple bond to the Pd–Sn bond, and finally the reductive elimination would provide the bis(stannane) products [66]. 1-Alkoxy-1-alkynes and 1-phenylthio-1-alkynes react with $(R_3Sn)_2$ in a Pd-catalyzed reaction in benzene, giving the product of distannylation in modest to high yields [19]. Quintard has reported one successful example using $(Bu_3Sn)_2$ in the bis(stannylation) of 3,3-diethoxypropyne whereby the distannylated product was obtained in 52% yield [13].

Distannylation of internal alkynes is generally a difficult process and can be facilitated by conjugation to an EWG, as Sweeny et al. has demonstrated in the distannylation of two non-terminal alkynoate substrates with $(Bu_3Sn)_2$ [16]. The distannylation of butynoate THP-protected **76** with $(Me_3Sn)_2$ in the presence of $PdCl_2(PPh_3)_2$ gave the product **77** in 75% yield. Upon reaction with acidic ion-exchange resin in methanolic solution, the hydroxyl group of **77** was unmasked and cyclization occurred to furnish lactone **78** in 74% yield (Eq. (53)).



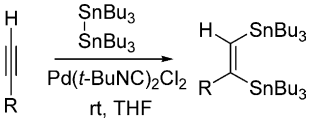
(53)

The distannane **78** reacted regioselectivity with 1 equivalent of ArI in THF in the presence of Pd catalyst to give **79** (22–49% yield). The monostannanes, thus obtained reacted with other Ar^1I to afford the disubstituted products **80** (69–73% yield) (Eq. (54)).



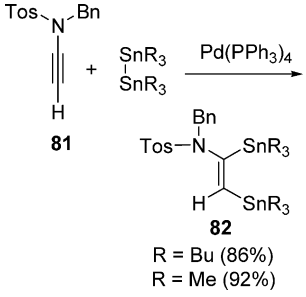
(54)

Recently, the distannylation of alkynes with $(Bu_3Sn)_2$ has been reported as stannyl group transfer in mild conditions using $Pd(t\text{-}BuNC)_2Cl_2$ as catalyst (Eq. (55)) [67]. Only activated internal alkyne, such as dimethylacetylene dicarboxylate underwent distannylation in moderate yield, allowing access to symmetrical bis(alkenyl)stannanes.



(55)

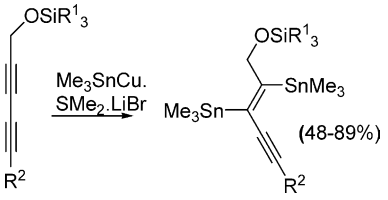
In terminal alkynes, various functional groups were tolerated (R = CH_2NBoc, CH_2NMe_2, CH_2NHTs, CH_2OR, CO_2Me). The distannylated products were obtained in 67–83% yield [67]. Regio- and stereocontrolled synthesis of stannylated enamines has been achieved. The stannation of the ynamine **81** by $(R_3Sn)_2$ (R = Me, Bu) exclusively gave the product **82** via *cis* addition (Eq. (56)) [23].



(56)

An alternative Cu mediation methodology to obtain unsymmetrically substituted butadiynes has been reported by Zweifel and Leong [68]. Butadiynes reacted with the stannyl-copper species, $Me_3SnCu{\cdot}SMe_2$-LiBr, in a highly regio- and stereoselective fashion to afford (*E*)-distannane products directly.

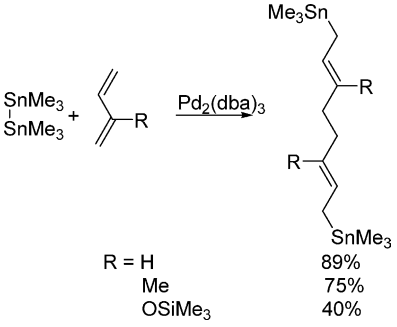
With this approach, propargylic silyloxy substituted butadiyne was region- and stereoselective distannylated [69]. Thus, the reaction of the stannylcopper reagent, prepared from equimolar quantities of Me_3SnLi and $CuBr{\cdot}Me_2S$ with butadiynes provided the desired distannanes as a single stereo- and regioisomer in good yield (Eq. (57)).



(57)

This (*E*)-stereoselective distannylation reaction was the key step in the synthesis of a novel diethynylethene containing an internal *trans*-substituted β-(chloro) vinylsilane. This

transformation allowed the sequential installation of the silyl and chloro groups in a selective and predictable fashion [69]. On the other hand, $(Me_3Sn)_2$ reacted with 1,3-dienes in the presence of Pd catalyst to afford dimerization-distannation products in good yields (Eq. (58)) [70]. The reaction proceeded with high regio- and stereoselectivities (head to head; *E,E*-1,4-adduct) and no other isomers were detected. The reaction was almost instantaneous even at −30 °C.

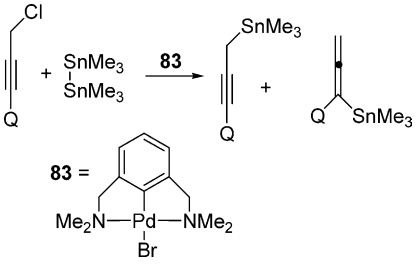


(58)

Under polar conditions, asymmetric $R_3SnSnR^1{}_3$ disproportionated rapidly at rt to give the symmetrical ditins $(R_3Sn)_2$ and $(R^1{}_3Sn)_2$. The equilibrium constants observed for a series of such reactions (R = Me; R^1 = Et, Pr, Bu, *i*-Bu) suggested a predominance of steric rather than inductive effects [71]. Also, under polar conditions, hexaalkylditins were found to react with alkynes in HMPT solutions, and in the presence of a catalytic amount of a base (MeONa, MeLi, Li) to give the corresponding *trans*-adducts exclusively [71a]. Thus, hexamethyl-, hexaethyl-, and hexabutylditin added to a variety of allenes in the presence of $Pd(PPh_3)_4$ in a reversible reaction [72].

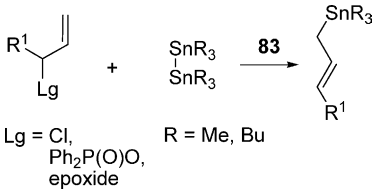
4.3. Other reactions

Instead of distannane addition, the pincer complex of Pd **83** catalyzed the reaction of $(Me_3Sn)_2$ with propargylic substrates to afford the substitution product propargyl stannanes and allenyl stannanes (Eq. (59)) [73].



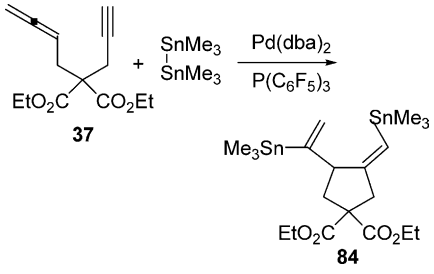
(59)

The catalytic reactions were conducted under mild conditions and the functional group tolerance of the reaction was remarkably high. Reaction of propargylic substrates with electron-donating groups gave propargyl stannanes, while substitution of propargyl chlorides with EWG gave allenyl stannanes. The pincer complex **83** also catalyzed allylic substitution reactions in the presence of $(R_3Sn)_2$ [74]. Thus, when allylic chloride, phosphonate, and epoxide substrates were reacted with $(R_3Sn)_2$ in the presence of catalytic amounts of pincer complex **83**, allylstannane products were obtained under mild neutral reaction conditions (Eq. (60)).



(60)

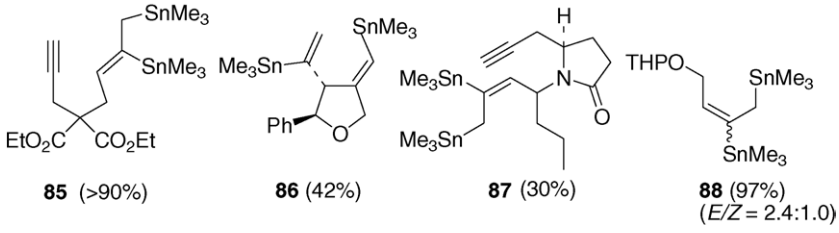
This catalytic reaction proceeds via Pd(II) intermediates without involvement of allyl-Pd complexes, and therefore the allylstannane product does not interfere with the Pd catalyst. Recently, the cyclization of allenynes mediated by hexamethyldistannane catalyzed by Pd has been described [45]. The distannylation of **37** proceeded to give a good yield of the cyclization product **84** by in situ NMR analysis (>90%) at 45 °C (Eq. (61)). Isolation of Sn–Sn compounds presented significant problems, and upon chromatography only a 46% of isolated product **84** was obtained (Eq. (61)).



(61)

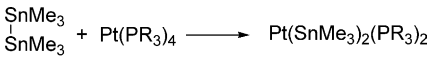
Other typical products, similar to the silylstannylation reactions, were obtained and are shown in Scheme 15 [45]. The conclusion of the author was that the silyltin reagents were generally superior to ditin reagents or other bis-functionalization reagents.

A series of bis(stannyl)bis(phosphane)platinum complexes (**90a–c**) were obtained by oxidative addition of $(Me_3Sn)_2$ to Pt(0) phosphane complexes such as **89a–c** (Eq.



Scheme 15.

(62)). The solution ^{31}P NMR spectra indicated that the complex showed reversible fluxional behavior [75]. Related complexes were also described [75].

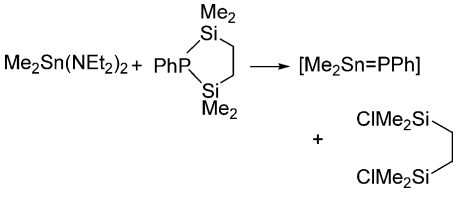


89a R = Ph **90a** (91%)
89b 4-MeC$_6$H$_4$ **90b** (83%)
89c Ph$_2$Me **90c** (70%) (62)

Tetrakis(trimethylstannyl) compounds $(Me_3Sn)_4Sn$ and bis(trimethylstannyl) dimethyl compounds $(Me_3Sn)_2SnMe_2$ were prepared and studied by ^{1}H, ^{13}C, ^{29}Si, ^{73}Ge, and ^{119}Sn NMR spectroscopy [76].

5. Stannylphosphanes

Ar_3P are important types of compound, both as intermediates in organic synthesis and as ligands in transition metal-catalyzed reactions. Some stannylphosphane have been described. The primary stannylphosphanes Bu_3SnPH_2 and $Bu_2Sn(PH)_2$ were synthesized by Hänssgen and Aldenhoven [77]. The reactions of P–Li salts of these stannylphosphanes with organochlorosilanes and stannanes were investigated [78]. The secondary stannylphosphanes $(Bu_3SnPH)_2ER_2$ (E = Si; Sn) and $(Bu_3SnPHSnBu_2)_2PH$, and cyclic tertiary stannylphosphanes were obtained. Some properties of the new compounds have been described. Also, the formation of a series of organoyltin(IV)phosphane and phosphido complexes of the type $R_2SnX_2(HPR^1{}_2)$, $R_2SnX(PR^1{}_2)$, and $R_2Sn(PR^1{}_2)_2$ (where R = Ph, Me, Bu; R^1 = *c*-C_6H_{11}, Ph; X = Cl, Br) in solution have been reported [79]. In addition, the first example of a species with sp^2 tin and dicoordinated phosphorus has been obtained [80]. The dimethylstanna(phenyl)-phosphimine, [Me$_2$Sn = PPh], has been synthesized in an exchange reaction between organotin-diamines $Me_2Sn(NEt_2)_2$ and 2,5-disilaphospholanes (Eq. (63)).

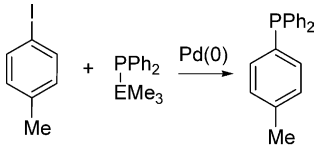


(63)

5.1. Cross-coupling reactions

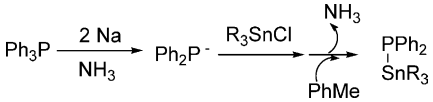
The most extensively used stannylphosphanes for C–P bond formation are the $R_3SnPR^1{}_2$, which were employed in cross-coupling reactions, addition reactions and nucleophilic substitution. As already mentioned, the Pd-catalyzed coupling reactions are an extremely useful synthetic tool in organic chemistry, which have been used for C-heteroatom bond formation. However, only a few reports of C–P bond formation are known on the synthesis of triarylphosphanes by this reaction. Although the $R_3SnPR^1{}_2$ has been known for a long time, and a number of methods for their preparation have been reported [81], their chemistry has not been explored due to inherent difficulties in their preparation and manipulation. All these methods of preparation include the use of a secondary phosphane as starting material.

The Pd-catalyzed coupling of ArX with Me_3SiPPh_2 and Me_3SnPPh_2 has been reported by Tunney and Stille [82]. The stannylphosphane reacted about twice as fast as the silylphosphane, to give similar yields (Eq. (64)). Even though the stannylphosphane reacted faster, the silylphosphane was favored as PPh_2 source, since the starting Me_3SiCl is cheaper and non-toxic, and most of the studies were carried out with Me_3SiPPh_2.

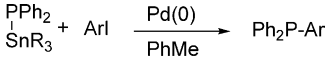


E = Si (83%)
Sn (75%) (64)

The Pd-catalyzed cross-coupling phosphination with R_3SnPPh_2 in a "one-pot" reaction has been recently reported [83]. The R_3SnPPh_2 was synthesized using Ph_3P as the initial phosphination agent. After formation of the anion Ph_2P^- with Na metal in dry liquid ammonia, R_3SnCl (R = Me, Bu) was added; the ammonia was allowed to evaporate and PhMe was added (Eq. (65)). The Pd-catalyzed cross-coupling reaction was carried out with the solution of R_3SnPPh_2 in PhMe and the ArI in the presence of a Pd catalyst in a "one-pot" type procedure (Eq. (66)). This method was found to be compatible with many functional groups and a variety of tertiary functionalized phosphanes could be obtained in very good yields (Eq. (66)) [83].



(65)

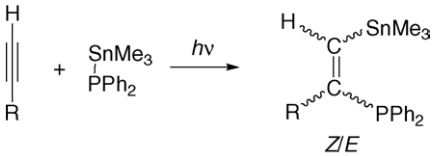


Ar = 1-Naph 93%
p-ClC$_6$H$_4$ 97%
p-BrC$_6$H$_4$ 93%
p-F$_3$CC$_6$H$_4$ 90%
p-H$_2$NC$_6$H$_4$ 88%
o-HO$_2$CC$_6$H$_4$ 69% (66)

5.2. Addition reactions

On the other hand, Schumann et al. have presented preliminary reports without structural proof of the addition of $R_3SnPR^1{}_2$ to alkenes and alkynes [84]. The addition of Me_3SnPPh_2 to alkynes and allenes under free-radical conditions has been reported [85]. The alkynes reacted with Me_3SnPPh_2 under photolytic conditions to give two stereoisomers (Eq. (67)). The major product was the *E*-

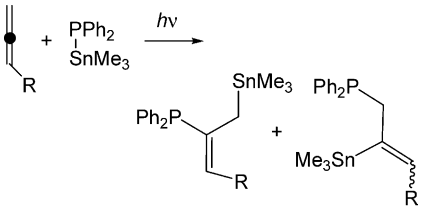
isomer, which is the kinetic product. The addition to non-terminal alkynes has been also described [85].



R = Ph	59% (10/90)
$MeOCH_2CH_2$	30% (40/60)
Et_2NCH_2	59% (20/80)
Bu	82% (38/62)
$PhCH_2$	16% (50/50)

(67)

Under the same photolytic conditions, Me_3SnPPh_2 added to allene and monosubstituted allenes to give a mixture of mainly two regioisomeric products (Eq. (68)), in which the predominate products were with the phosphane attached to the central carbon atom [84].



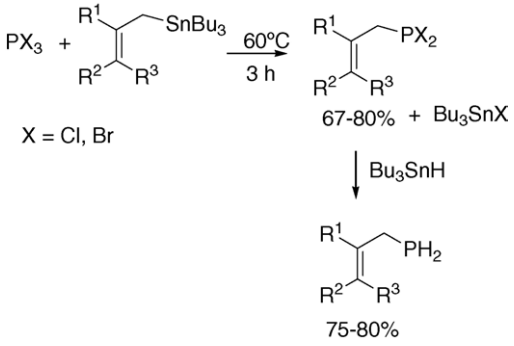
R = H	78% (94/6)
Me	68% (78/28)
Bu	58% (88/12)
Ph	83% (99/1)

(68)

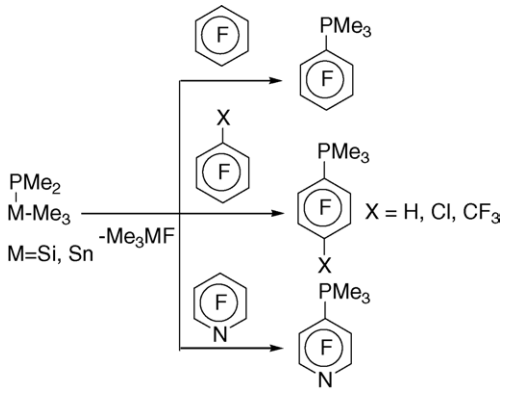
5.3. Other reactions

Allylic dihalophosphanes were obtained by the reaction between an allylic tributylstannane and PCl_3 or PBr_3 (Scheme 16) [86]. A reduction using Bu_3SnH led to the corresponding vinylphosphanes in good yields.

Me_3SiPMe_2 and the corresponding tin compound Me_3SnPMe_2 were used as reagents for the substitution of fluorine by the Me_2P-group in a variety of C_6F_5X (X = F, H, Cl, CF_3) and C_5NF_5 (Scheme 17) [87]. The reaction occurred under mild conditions (T = 0–20 °C), either in benzene or without a solvent to give the *p*-$XC_6F_4PMe_2$ and 4-$Me_2PC_5NF_4$ in yields between 75 and 95%.



Scheme 16.



Scheme 17.

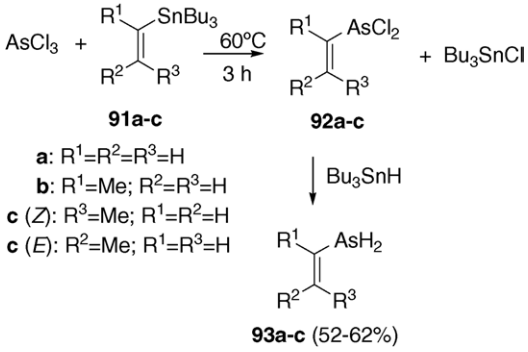
6. Stannylarsanes and stannylstibanes

The chemistry of organoarsanes and organostibanes, the analogous compounds of organophosphanes, has been extensively developed and the uses of these compounds to organic synthesis are of current interest [88]. Organoarsanes and organostibanes are an important class of compounds, both as intermediates in organic synthesis and as ligands in transition metal-catalyzed reactions. Arsanes have been reported to be superior ligands to phosphanes in a number of transition metal-catalyzed organic reactions [89].

6.1. Reactions of organostannanes with trihaloarasanes and stibanes

The reaction of stannanes with AsX_3 has been established by Seyferth and Stone. They have reported the formation of vinyl- and divinylhaloarsanes from divinyldibutylstannane and $AsCl_3$ or $AsBr_3$ [90]. Primary and secondary vinylarsanes have been obtained [91]. Vinylarsanes dichlorides **92a–c** were prepared in very good yield (≈85%) starting from $AsCl_3$ and vinyltributylstannnes **91a–c** (Scheme 18). A chemoselective reduction using Bu_3SnH led to the corresponding vinylarsanes **93a–c** in moderate yields.

Also, allenyl- and alkynylarsanes were synthesized by addition of allenyltributylstannanes and alkynyltributylstannanes to $AsCl_3$ by a similar procedure at rt [92].

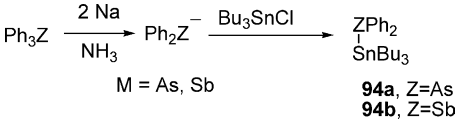


Scheme 18.

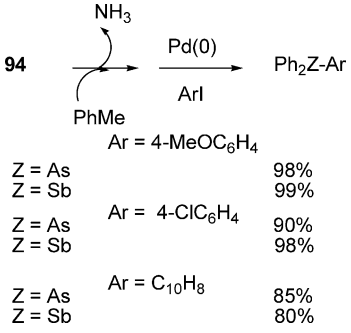
Allylic dihaloarsanes and stibanes were obtained by the reaction between an allylic tributylstannane and arsenic or antimony trihalide, in the same way as described by dihalophosphanes [86].

6.2. Cross-coupling reactions

Recently, the use of organotin-arsanes and organotin-stibanes to form C–As and C–Sb bonds has been reported for the first time [93]. To extend the applications of the already powerful Pd-catalyzed cross-coupling, the stannanes Bu_3SnMPh_2 (**94**), M = As (**94a**), Sb (**94b**) were allowed to react with ArI in a reaction catalyzed by Pd(0). Reagent **94** was formed in almost quantitative yield, by the reaction of Ph_2Z^- anion (generated from Ph_3Z and Na metal in liquid ammonia, with Z = As, Sb) with Bu_3SnCl (Eq. (69)). The Pd-catalyzed cross-coupling reaction was carried out with the solution of **94** in toluene and the ArI in the presence of $Pd(PPh_3)_2Cl_2$ (Eq. (70)). All steps were carried out in "a one-pot reaction". Substituted ArI afforded triaryl-arsanes and -stibanes in very good yields, regardless of the electronic nature of the substituent. ArBr and ArCl did not react by these coupling reactions. On the other hand, the Pd-catalyzed coupling reaction could also be successfully performed with **94a** and 1-naphthyl-trifluoromethanesulfonate to obtain the corresponding triaryl arsane (68%) [93].



(69)

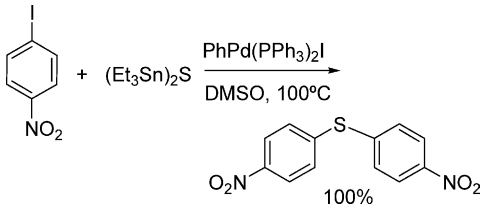


(70)

7. Stannylsulfides

7.1. Bis(trialkylstannyl)sulfide as sulfur transfer reagent

The formation of C–S bonds via organotin sulfides was described [94]. $(R_3Sn)_2S$ derivatives are useful reagents in conjugation with a variety of electrophiles. A cross-coupling Pd-catalyzed reaction with ArI has been reported by Beletskaya and coworkers (Eq. (71)) [95].

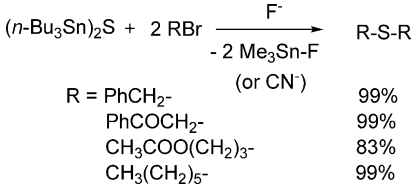


(71)

$(Bu_3Sn)_2S$ is an effective and general sulfur transfer reagent. It is commercially available and easy to prepare [96,97]. With $(Bu_3Sn)_2S$, the reaction occurs at rt with a variety of organic halides to afford the corresponding R_2S in good overall yields (69–100%) (Eq. (72)) [97], and some examples are presented in Table 3. The rate of the reaction increased as the polarity and ability of the solvent to coordinate $(Bu_3Sn)_2S$ increase, suggesting an ionic mechanism.

$$(Bu_3Sn)_2S + 2RX \xrightarrow[-2Bu_3SnX]{} R-S-R \quad (72)$$

Diacyl sulfides, bis(alkoxycarbonyl) sulfides, sulfides in the α-position of a carbonyl group and bis(dialkylaminocarbonyl) sulfides were synthesized by this method [97]. On the other hand, F^- and CN^- ions produced destannylation of $(R_3Sn)_2S$ and R_3SnSR^1 that allowed the preparation of organosulfides in the presence of a variety of alkyl halides under mild conditions [98,99].



(73)

Table 3
Organic sulfides from organic halides and $(Bu_3Sn)_2S$ [72]

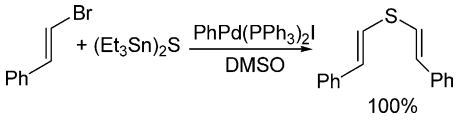
Entry	Halide	Solvent	Products	Yields[a] (%)
1	CH_3COCl	$CHCl_3$	$(CH_3CO)_2S$	(99)
2	CH_3COCl	CH_2Cl_2	$(CH_3CO)_2S$	86
3	C_6H_5COCl	$CHCl_3$	$(C_6H_5CO)_2S$	(98)
4	C_2H_5OCOCl	$CHCl_3$	$(C_6H_5CO)_2S$	(98)
5	$(CH_3)_2NCOCl$	$CHCl_3$	$[(CH_3)_2NCOCl]_2S$	(92)
6	$C_6H_5CH_2Br$	CH_2Cl_2	$(C_6H_5CH_2)_2S$	25
7		$CHCl_3$		93
8	$C_6H_5COCH_2Br$	CH_2Cl_2	$(C_6H_5COCH_2)_2S$	Trace
9		$CHCl_3$		(98)
10	$C_2H_5COCH_2Br$	DMF/EtOAc (5:1)	$(C_2H_5COCH_2)_2S$	69
11	CH_3COCH_2Cl	DMF/EtOAc (5:1)	$(CH_3COCH_2)_2S$	Trace

[a] Yields of isolated products (GC yields in parentheses).

In the presence of alkyl halides, $(R_3Sn)_2S$ were smoothly destannylated using CsF, CsF with crown ether, $(Bu)_4NF$ or cyanide ions under neutral solvent conditions to afford the corresponding RSR in excellent yields (averaging over 90%) (Eq. (73)) [98]. Additionally, the formation of unsymmetrical sulfides from R_3SnSR^1 and alkyl halides were reported (Eq. (74)) [98].

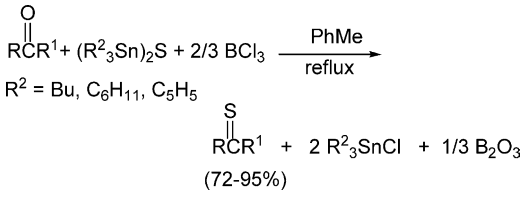
$$Bu_3SnSCH_2Ph + CH_3(CH_2)_5Br \xrightarrow{F^-} \underset{(84\%)}{PhCH_2S(CH_2)_5CH_3} + Me_3Sn\text{-}F \quad (74)$$

Divinyl sulfides may be obtained from vinyl bromides, as shown in the case of *E*-β-bromostyrene reaction with $(Et_3Sn)_2S$. The reaction was fully stereospecific (Eq. (75)) [100].



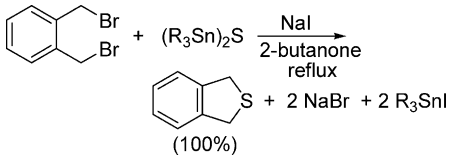
(75)

Tin assisted sulfuration with $(R_3Sn)_2S$ and BCl_3 in the presence of carbonyl compound has been reported [101]. The carbonyl compounds were converted to the corresponding thiocarbonyl analogue in good yield, and thioaldehydes, thioketenes, thiolactones, and thiolactams were prepared (Eq. (76)). In this reaction, the organotin sulfide acted only as a transporter of sulfur to the reaction medium where potent sulfurating agent B_2S_3 was formed.



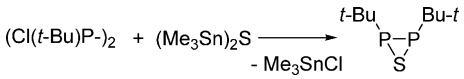
(76)

These readily available reagents $(R_3Sn)_2S$ can also be used for efficient synthesis of cyclic organosulfides. Thus, when bis-benzylic bromides were treated with alkyl- or aryltin sulfides in boiling 2-butanone with stoichiometric amount of NaI, a quantitative yield of the cyclic benzylic sulfide was obtained (Eq. (77)) [102].



(77)

The approach was used for the [2 + 1]-cyclocondensation of 1,2-di-*tert*-butyl-1,2-dichlorodiphosphane with $(Me_3Sn)_2S$ in THF (Eq. (78)) [103]. The di-*tert*-butylthiadiphosphirane was obtained in about 60% yield.



(78)

The reaction of methylthiostannanes with MeI gave iodostannane and trimethylsulfonium iodide (Eqs. (79) and (80)) [104].

$$R_2Sn(SMe)_2 \xrightarrow{MeI} R_2SnI_2 + 2Me_3S^+I^- \quad (79)$$

$$R_3SnSMe \xrightarrow{MeI} R_3SnI + Me_3S^+I^- \quad (80)$$

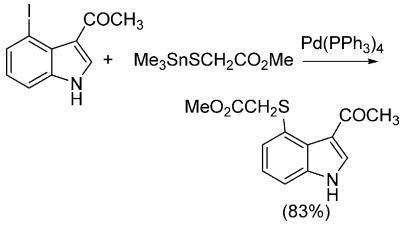
where R = Me, Et, Bu.

7.2. Nucleophilic substitution reactions

Otherwise, when R_3SnSAr were allowed to react with RX at higher temperature, RSAr were obtained in nearly quantitative yields [105]. A nucleophilic attack of the stannyl sulfur atom on the RX was suggested, and the different reactivity of arylthio and methylthiostannanes was explained in terms of the lower nucleophilicity of the arylthio group. A kinetic study of the reaction of Me_3SnSAr with haloalkanes was studied [106]. A mechanism involving a nucleophilic attack of the sulfur atom on the haloalkane was proposed. The kinetics of the reaction of Me_3SnSAr with 1-bromo-1-phenylethane was carried out. The reaction was found to proceed mainly by a bimolecular nucleophilic attack, with a minor contribution of a S_N1 process [107].

7.3. Cross-coupling reactions

An approach to aromatic thiation by Pd-catalyzed cross-coupling of ArI with R_3SnSR^1 has been studied (Eq. (81)) [108]. In general, these Pd-catalyzed reactions are higher yielding than the nucleophilic or electrophilic thiations. Although the thiostannanes and ArI have not been widely studied, the author suggested that the process could be general.

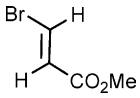
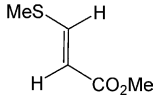
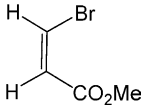
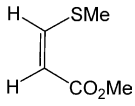
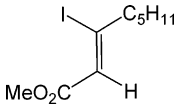
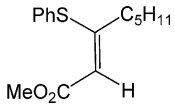


(81)

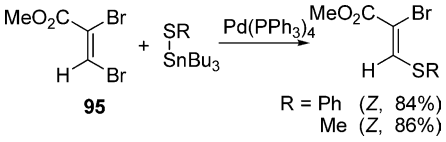
Taking into account the results obtained in the regioselective Pd-catalyzed C–C bond formation reactions with C^2_{sp}-hybridized compounds; C–S bond formation between C^2_{sp}-hybridized mono or dihalides and organotin sulfides was studied [109].

The reaction of methyl (*Z*)-2,3-dibromopropenoate (**95**) with Bu_3SnSR (R = Ph or Me) in the presence of catalytic amounts of $Pd(PPh_3)_4$ has been reported [109c]. The reaction was regio- and stereo-selective to afford the alkyl (*Z*)-3-(arylthio)- and 3-(alkylthio)-2-bromopropenoates in good yields (Eq. (82)).

Table 4
Palladium-catalyzed reaction of Bu_3SnSR with substituted or unsubstituted alkyl 3-halopropenoates[a]

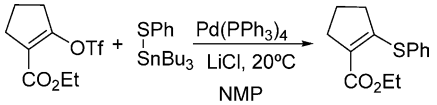
Entry	Tributylstannyl derivative	3-Halopropenoate	Reaction time (h)	Products	Yields[b] (%)
1	Bu_3SnSMe		5		63
2	Bu_3SnSMe		5		45
3	Bu_3SnSPh		38		86

[a] The reactions were carried out in NMP at rt using 1.15 equivalent of tributylstannyl reagents and 5 mol% of $Pd(PPh_3)_4$.
[b] Isolated yields.

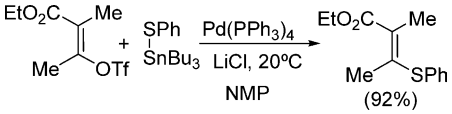


(82)

Under similar conditions, the reaction between Bu_3SnSR (R = Me, Ph) and substituted or unsubstituted alkyl 3-halopropenoates were reported (Table 4) [109b]. The reactions gave the desired stereoisomerically pure substitution products. Similarly, 3-halopropenoates, which contains a (trifluoromethyl)sulfonyloxy group in their 3-position, gave regioselective and stereospecific C–S bond formation. The reaction of ethyl 2-[(trifluoromethyl)sulfonyloxy]-l-cyclopentene-l-carboxylate under the experimental conditions described above, and with 2 equivalent of LiCl gave the ethyl 2-(phenylthio)-1-cyclopentene-1-carboxylate in 96 % yield (Eq. (83)) [109b]. Also, the cross-coupling product ethyl (*E*)-2-methyl-3-(phenylthio)-2-butenoate was obtained regioselectively and stereospecifically under very similar conditions (Eq. (84)) [109b].



(83)

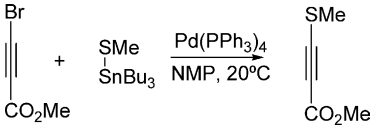


(84)

7.4. Addition to alkynes

The first example of a Pd-catalyzed C_{sp}-heteroatom bond formation was reported by Rossi et al. [109b]. Methyl 3-bromopropiolate reacted with Bu_3SnSMe in the presence of catalytic amount of $Pd(PPh_3)_4$ to give methyl(methylthio)propiolate in 41% yield (Eq. (85)).

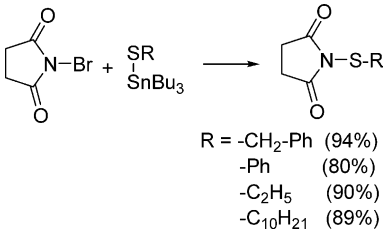
Recently, derivatives of R_3SnSR^1 (R = Me, Ph) have been prepared from the disproportionation of the distannane $(R_3Sn)_2$ and disulfides $(R^1S)_2$ by room light in almost quantitative yields via a radical mechanism [110].



(85)

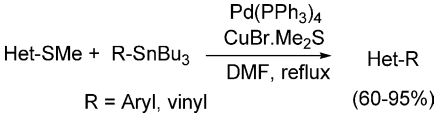
7.5. Other reactions

Derivatives of Bu_3SnSR (R = aryl or alkyl) were also prepared from the corresponding thiols and Bu_3SnCl in yields averaging 90% [111]. The coupling reaction of Bu_3SnSR with either *N*-chloro- or *N*-bromosuccinimide was described to give the *N*-alkylthio or *N*-arylthioimides (Eq. (86)) [112].



(86)

An efficient method for the construction of C–C bonds via a Stille-type reaction was carried out with methylthioether as an electrophile with vinyl- and arylstannanes [113]. The Pd-catalyzed cross-coupling reaction took place with π-electron-deficient heteroaromatics methylthioethers in the presence of a $CuBr{\cdot}Me_2S$ complex and vinyl- or arylstannanes to give the heteroaromatic vinyl- or aryl compounds (Eq. (87)).



(87)

A study of the chemical bond in $Me_nSn(SMe)_{4-n}$ ($n = 0$–3) by ^{119}Sn and ^{13}C NMR spectra has been reported [114]. The inductive and magnetic anisotropy effects seemed to govern the chemical shifts. The dipole moments of compounds $Me_3SnSC_6H_5$, *m*- and *p*-$ClC_6H_4SSnMe_3$ and $(Me_3Sn)_2S$ have also been measured [115].

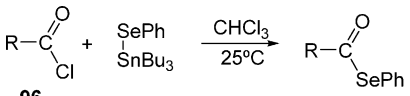
8. Stannylselenides

Derivatives of Ar_2Se have attracted considerable interest because of their potential as anticancer and antioxidant agents [116,117]. Several synthetic methods are available for the formation of aromatic C–Se bonds. A new alternative to obtain Ar_2Se includes organotin selenides, as $R_3SnSeAr$ are more convenient in handling than commonly used selenols, because of their sensitivity to air and moisture, and their unpleasant odors.

Organostannyl selenides undergo similar reactions to the corresponding organosilyl selenides. However, due to the more favorable orbital overlaps between tin and selenium, organostannyl selenides are more stable and reactive than organosilyl selenides [99]. The trialkytinselenides can be obtained in situ by daylight irradiation of a mixture of the distannane $(R_3Sn)_2$ and the diselenide $(RSe)_2$ [110,118].

8.1. Nucleophilic substitution reactions

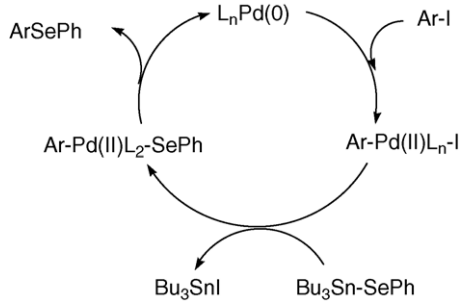
Derivatives of $Bu_3SnSeAr$ are an excellent source of ArSe moieties in nucleophilic substitution reactions [119]. Activated aryl fluoride and $Bu_3SnSePh$, in the presence of catalytic amount of F^- ions, underwent nucleophilic substitution. Unsymmetrical diarylselenides were obtained in high yields [119a]. In other nucleophilic substitution reactions, $Bu_3SnSePh$ reacted with acid chlorides **96** to form corresponding phenylselenoesters **97** in almost quantitative yields (Eq. (88)) [119b].



R = Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4; R = 4-$(COCl)C_6H_4$, (*E*)-PhCH=CH, (*E*)-4-$NO_2C_6H_4CH$=CH, Me (88)

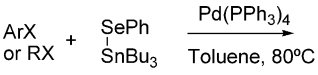
8.2. Cross-coupling reactions

It was shown that derivatives of $R_3SnSeAr$ could be also used as a source of ArSe group in the arylselenylation of ArX and/or ArOTf catalyzed by Pd [120,121], Ni [120,122] and Cu [123]. Sonoda et al. have reported that $Pd(PPh_3)_4$ catalyzed the reaction of $Bu_3SnSePh$ with ArX and RX giving



Scheme 19.

the corresponding diaryl and alkylarylselenides in moderate to good yields (Eq. (89)) [120]. Table 5 shows the reported results with various aryl and alkyl halides in the presence of catalytic amount of $Pd(PPh_3)_4$ in toluene. The catalytic cycle proposed for the cross-coupling reactions, is presented in Scheme 19 [120].



PhSeAr (47-88%) or PhSeR (57-62%) (89)

$Bu_3SnSeBu$ also acted as reagent for introducing the BuSe-group and gave PhSeBu in 79% yield [120]. When $(Bu_3Sn)_2Se$ was allowed to react with two equivalents of PhI, Ph_2Se was obtained in 53% yield (Eq. (90)) [120].

$$(Bu_3Sn)_2Se + PhI \xrightarrow[PhMe,80\,^{\circ}C]{Pd(PPh_3)_4} \underset{(53\%)}{Ph_2Se} \quad (90)$$

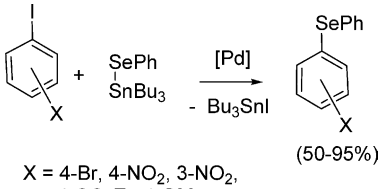
Unsymmetrical diarylselenides were also obtained by the Pd-catalyzed cross-coupling reaction of ArI with the in situ prepared $Bu_3SnSePh$ (Eq. (91)) [120]. The same compounds can be obtained by the non-catalyzed reactions of $Bu_3SnSePh$, ArN_2BF_4 and $(ArN_2)_2ZnCl_4$ in very good yields (85–98%) [120]. The reaction of PhOTf with $Bu_3SnSePh$,

Table 5
Synthesis of diorganyl selenides

Entry	RX	Time (h)	Product	Yields[a] (%)
1	4-$CH_3C_6H_4I$	2	4-$CH_3C_6H_4SePh$	81
2	4-$CH_3OC_6H_4I$	4	4-$CH_3OC_6H_4SePh$	88
3	4-$NO_2C_6H_4I$	0.5	4-$NO_2C_6H_4SePh$	70
4	4-OHC_6H_4I	5	4-OHC_6H_4SePh	50
5	4-$NH_2C_6H_4I$	5	4-$NH_2C_6H_4SePh$	53
6	2-$CH_3C_6H_4I$	5	2-$CH_3C_6H_4SePh$	47
7	C_6H_5Br	8	C_6H_5SePh	(79)[b]
8	C_6H_5Cl	8	C_6H_5SePh	(60)[b]
9	$C_6H_5CH_2Br$	2	$C_6H_5CH_2SePh$	57
10	$C_8H_{17}I$	24	$C_8H_{17}SePh$	62

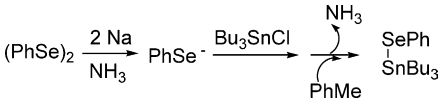
[a] Isolated yields.
[b] GC yields.

catalyzed by $NiCl_2(PPh_3)_2$ in the presence of LiBr, led to the Ph_2Se in good yields (80%) [120].

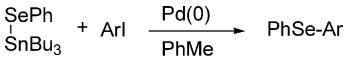


X = 4-Br, 4-NO_2, 3-NO_2, 4-CO_2Et, 4-OMe, 4-Me_2N, 4-I, 4-Ac, 4-SePh (91)

The "one-pot" Pd-catalyzed cross-coupling seleniation with $Bu_3SnSePh$ has recently been reported [124]. $Bu_3SnSePh$ was synthesized using $(PhSe)_2$ as the initial reagent. After formation of the anion $PhSe^-$ with Na metal in dry liquid ammonia, Bu_3SnCl was added, the ammonia was allowed to evaporate and PhMe was added (Eq. (92)). The Pd-catalyzed cross-coupling reaction was carried out with the solution of $Bu_3SnSePh$ in toluene and the ArI, in the presence of a Pd catalyst (Eq. (93)).



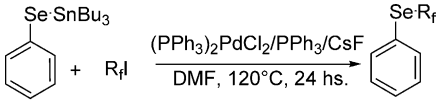
(92)



Ar = 1-Naph	94%
p-ClC_6H_4	96%
p-$CH_3COC_6H_4$	98%
p-$H_2NC_6H_4$	78%
p-$O_2NC_6H_4$	38%
p-HOC_6H_4	50%

(93)

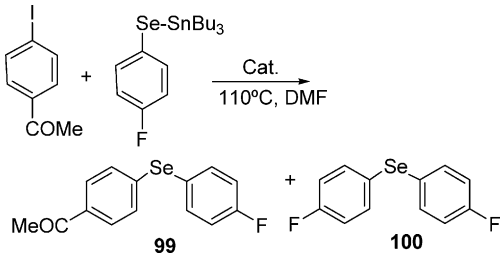
This method was found to be compatible with many functional groups, and a variety of functionalized selenides were obtained in very good yields (Eq. (93)). ArOTf also reacted under these conditions. Also, this method provides a convenient route to obtain perfluoroalkyl selenides [124]. The synthesis of perfluoroalkyl selenides by the Pd-catalyzed cross-coupling reaction of $Bu_3SnSePh$ with perfluoroalkyl iodides as electrophiles was described (Eq. (94)) [124]. This was the first report of this type of reaction for heteroatom-R_f bond formation.



R_f = C_8F_{17}	70%
$C_{10}F_{21}$	90%

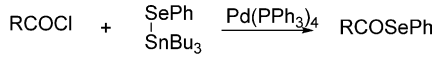
(94)

A new approach to prepare $ArSeAr^1$ using ArI and ArBr with $Bu_3SnSeAr^1$ catalyzed by Cu(I) has been reported by Beletskaya et al. [123]. In the reaction of 4-iodoacetophenone with 4-$FC_6H_4SeSnBu_3$, the catalyst $Pd(Ph_3P)_2Cl_2$ efficiently and selectively catalyzed the reaction yielding **99** (96% yield, Eq. (95)). The Ni complexes were ineffective and lead to disproportion product **100** together with the cross-coupling product **99**. Excellent results were achieved with the copper complexes CuI·phen and (Ph_3P)CuI·phen (**99** in 94 and 82% yield, respectively, Eq. (95)).



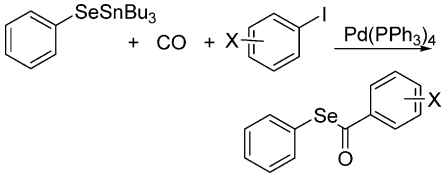
(95)

Several derivatives of ArBr or HetArBr, having electron withdrawing and electron donating substituents, reacted with 4-$FC_6H_4SeSnBu_3$ and Cu catalyst to afford unsymmetrical diarylselenides in high yield [123]. The synthesis of Se-phenyl selenol esters by reaction of $Bu_3SnSePh$ with acyl or aroyl chlorides in the presence of a catalytic amount of $Pd(PPh_3)_4$ has been reported (Eq. (96)) [125].



R = Ar, alkyl (96)

The aroyl chlorides afforded the corresponding Se-aryl selenol esters in 71–97% yields. Similarly, the coupling reaction with acyl chloride having a linear alkyl chain or benzylic group was successfully carried out and the selenol esters were obtained in 51–92%. Also, the cross-coupling reaction of $Bu_3SnSePh$ with α-halo carbonyl compounds to afford the corresponding α-phenylseleno carbonyl compounds in moderate yields was described [125]. On the other hand, selenol esters were obtained by the Pd-catalyzed three-component coupling of $Bu_3SnSePh$ with ArI and CO under neutral conditions (Eq. (97)) [126]. When $Bu_3SnSePh$ was allowed to react with PhI under a pressure of CO (5 atm) in the presence of catalytic amount of $Pd(PPh_3)_4$ the corresponding Se-phenyl selenobenzoate was formed in 89% yield. The reaction proceeded with other ArI or HetAr-I to afford the corresponding selenol esters in moderate to good yields (41–89%).

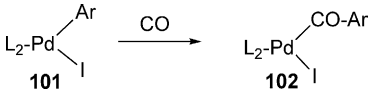


X = H	89%
o-CH_3	57%
m-CH_3	67%
p-CH_3	73%
p-CH_3O	70%
p-Cl	85%
p-NO_2	41%

(97)

The author proposed that based on the catalytic cycle of the cross-coupling reactions, the aryl palladium complex **101**

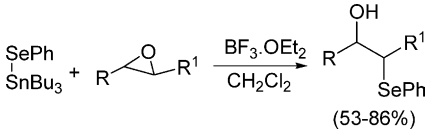
is easily converted to the palladium complex **102** under an atmosphere of CO (Eq. (98)) [126].



(98)

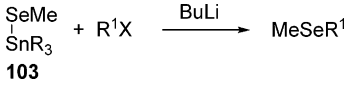
8.3. Other reactions

Other synthetic applications of organselenium compounds having a Sn–Se bond is the regioselective ring opening reaction of epoxides with $Bu_3SnSePh$ [127]. When $Bu_3SnSePh$ was allowed to react with epoxides in the presence of $BF_3{\cdot}OEt_2$ as a Lewis acid, the ring opening reaction of the epoxides proceeded with complete regioselectivity to afford the β-hydroxy phenylselenides in moderate to good yields (Eq. (99)). In the presence of a Lewis acid as boron trifluoride etherate, $Bu_3SnSePh$ reacts with acetals to give monoselenoacetals [128].



(99)

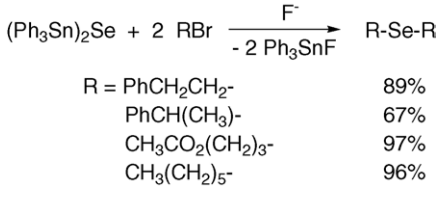
Trialkylstannyl selenides **103** (R = Me or Bu) are also useful nucleophilic selenium reagents; **103** reacts with alkyl halide by treatment with BuLi to form the corresponding unsymmetrical selenides in good yields (Eq. (100)) [129].



(100)

8.4. Reactions with bis(trialkylstannyl)selenides

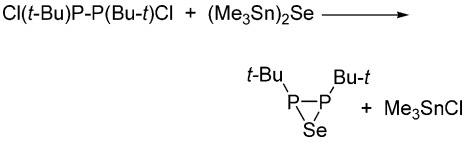
On the other hand, $(R_3Sn)_2Se$ can be easily prepared and used to obtain organoselenides. In the presence of RX, $(Ph_3Sn)_2Se$ is smoothly destannylated using CsF with crown ether or $(Bu)_4NF$ under neutral solvent conditions to afford the organoselenides in excellent yields (Eq. (101)) [99]. The F^- ion attacks the organotin selenide to liberate a nucleophilic selenolate species.



(101)

Selenoaldehydes substituted with EWG were obtained in the same way, with the selenium dianion generated by the treatment of $(Bu_3Sn)_2Se$ and $(Bu)_4NF$ [130]. Thus, the reaction of the corresponding *gem*-dichlorides with Se^{2-} afforded the selenoaldehydes, which were trapped in situ by 1,3-dienes to give Diels-Alder adducts (Scheme 20).

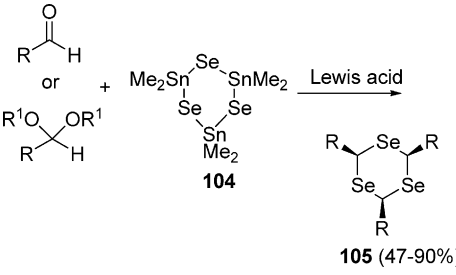
The reaction of *N*-monosubstituted and *N*,*N*-disubstituted formamides with $(Me_2Al)_2Se$, prepared in situ via transmetalation reaction of $(Bu_3Sn)_2Se$ with Me_3Al, afforded the corresponding selenoformamides in 31–91% yield [131]. On the other hand, di-*tert*-butylselenodiphosphirane was synthesized from 1,2-di-*tert*-butyl-1,2-dichloro-diphosphane and $(Me_3Sn)_2Se$ (Eq. (102)) [103]. Also, $(Ph_3Sn)_2Se$ is a reagent that promotes the dehalogenation of α-halo ketenes in the presence of F^- ion and under mild conditions [132].



(102)

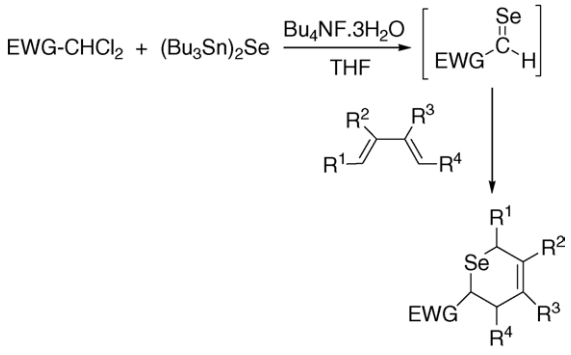
Tin assisted seleniation has been reported by treating bis(tricyclohexyltin) selenide with BCl_3 in the presence of carbonyl contained compound [101]. The carbonyl compounds were converted into the corresponding selenoketone and aldehydes.

An efficient synthesis of 2,4,6-trisubstitued 1,3,5-triselenanes (**105**) was achieved by treatment of aldehydes or their acetals with 2,2,4,4,6,6-hexamethyl-1,3,5-triselena-2,4,6-tristanacyclohexane (**104**) in the presence of a Lewis acid like $BF_3{\cdot}OEt_2$ or $AlCl_3$ (Eq. (103)) [133]. In **104**, the reactivity to the carbonyl group was enhanced with respect to the bis(trialkylstannyl) selenides by minimizing the steric bulkiness of the alkyl moieties.

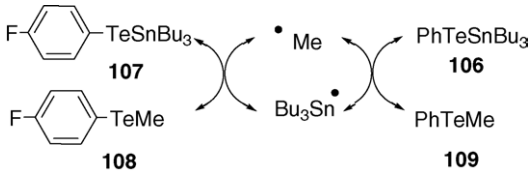


(103)

α-Bromo esters can react with diselenides in the presence of metallic tin to give α-selenoesters in good yields (Eq.



Scheme 20.



Scheme 21.

(104)) [134]. The reaction mechanism is still unclear.

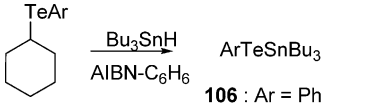
$$\underset{\text{Br}}{\text{RCHCO}_2\text{R}^1} + (\text{R}^2\text{Se})_2 \xrightarrow[\text{THF/H}_2\text{O}]{\text{Sn}} \underset{\text{SeR}^2}{\text{RCHCO}_2\text{R}^1} \quad (104)$$

The catalysis of stannanes-mediated radical chain reactions by selenols (ArSeH) has been described [135]. In this chemistry, the conveniently handled solid $(PhSe)_2$ was first reduced in situ by the stannane, thereby eliminating the need to handle PhSeH itself (Eq. (105)).

$$\text{R}_3\text{SnH} + (\text{PhSe})_2 \longrightarrow \underset{\text{SnR}_3}{\text{SePh}} + \text{PhSeH} \quad (105)$$

9. Stannyltellurides

Organotellurium compounds have attracted a great deal of attention because of their synthetic utility and the roles they play in organic radical reactions [136]. Various stannyltellurides have been synthesized. $PhTeSnBu_3$ [137] and $4\text{-}FC_6H_4TeSnBu_3$ [138] were prepared by reaction of phenyltellurocyclohexane or (4-fluorophenyl)tellurocyclohexane with tributyltin hydride in benzene and AIBN as initiator (Eq. (106)). The tellurides **106** and **107** proved to be light sensitive and generally unstable. In benzene, under nitrogen and in the dark, they appear to have an indefinite lifetime.



(106)

The chemistry of these tellurides as aryltelluride free-radical precursors was investigated [137,138]. As an example, when one equivalent of $4\text{-}FC_6H_4TeMe_3$ (**108**), Bu_3SnH and AIBN were introduced into a solution of **106** and the solution was heated at 80 °C, the NMR spectroscopy revealed the presence of PhTeMe **109** and **107** (Scheme 21). Without initiator (AIBN) no reaction was observed.

It was postulated that the formation of **107** and **109** involved homolytic substitution by $CH_3^\bullet$ radicals, generated by reaction of **108** with $Bu_3Sn^\bullet$ radical at the tellurium atom in **106** with expulsion of further chain-carrying $Bu_3Sn^\bullet$ radical (Scheme 21) [137,138] The conclusion was that primary and secondary alkyl radicals were capable of displacing $Bu_3Sn^\bullet$ radicals from tellurium atom. Consequently, reactions involving aryltellurides as radical precursors together with chain carrying species such as Bu_3SnH may involve reversible homolytic substitution at tellurium leading to reduce reactions yields.

Chalcogenides of heavier group XIV metals, R_3MZR^1 (M = Sn, Pb and Z = S, Se, Te) decompose upon heating to give chalcogenides, which are useful for solar cells and other semiconductor applications [139]. As a route to a source of semiconductors, the $(Bu_3Sn)_2Te$ was synthesized from $Te=PBu_3$ and Bu_3SnH by titanium-mediated heterodehydrocoupling (Eq. (107)).

$$2\ \text{Bu}_3\text{SnH} + \text{Te=PBu}_3 \xrightarrow[\text{C}_6\text{D}_6,\ 25^\circ\text{C}]{\text{Cp}^*_2\text{TiH},\ 2\text{-}10\ \text{mol}\ \%} (\text{Bu}_3\text{Sn})_2\text{Te} + \text{H}_2 \quad (107)$$

With the same methodology, $Me_3SnTePh$ was obtained from the disproportionation of organoditin and $(PhTe)_2$ by room light in high yields (93%) via a radical mechanism [110]. On the other hand, $(Ph_3Sn)_2Te$ [140] was employed as a reagent for telluration [141]. When alkyl halides were treated with $(Ph_3Sn)_2Te$ in the presence of F^- ion RTeR were obtained in good yields (33–100%; Eq. (108)). While benzylic halides reacted directly with the stannyltelluride, others halides needed to be activated with CsF. Although RI and RBr reacted easily, ArX and RCl did not react [141].

$$(\text{Ph}_3\text{Sn})_2\text{Te} + 2\text{R} - \text{X} \xrightarrow{\text{F}^-} \text{R} - \text{Te} - \text{R} + \text{Ph}_3\text{Sn} - \text{X} \quad (108)$$

The reactivity of the Sn–Te bond toward transition metal species remains unexplored. The only example reported in this matter was the oxidative addition reaction in C_6D_6 of $PhTeSnMe_3$ to $Pt(PEt_3)_3$ [142]. The *trans*-$Pt(PhTe)(SnMe_3)(PEt_3)_2$ complex as well as the silyl and germyl analogues were obtained in high yield as red solids, though they are extremely air and moisture sensitive.

Acknowledgments

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