CHAPTER 1

THE STILLE REACTION

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INTRODUCTION

Examples of the palladium-catalyzed coupling of organotin compounds with carbon electrophiles were first reported in 1977 by Kosugi, Shimizu, and Migita.[1-3] The first study by Stille appeared in 1978.[4] The early work of Beletskaya, using "ligandless" catalysts in cross-coupling reactions, also often employed organostannanes.[5] In recognition of Stille's comprehensive synthetic and mechanistic studies, this coupling is now referred to as the Stille reaction.[6] The Stille reaction is schematically defined in Eq. 1.

$$R^1Sn(R^2)_3 + R^3X \xrightarrow{Pd(0)L_n} R^1\text{-}R^3 + (R^2)_3SnX \qquad \text{(Eq. 1)}$$

In Eq. 1, R^1 is typically an unsaturated moiety (e.g., vinyl, aryl, heteroaryl, alkynyl, allyl) or less often an alkyl group, and R^2, the nontransferable ligand, is almost always butyl or methyl. Electrophiles participating in the coupling include halides (almost always bromides or iodides) and sulfonates (most often used are the triflates). Other leaving groups have been used in special cases.

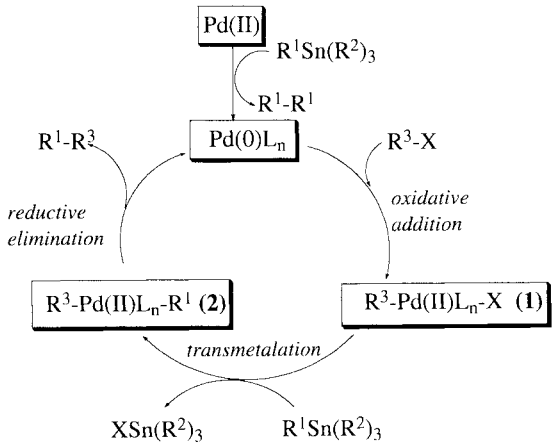
The Stille reaction belongs to the larger family of palladium- and nickel-catalyzed cross-coupling reactions which features, e.g., organomagnesium,[7] organozinc,[8] organoboron,[9] and organosilicon reagents.[10]

Organotin reagents are air- and moisture-stable organometallics, and can be conveniently purified and stored. Since they do not react with most common functional groups, the use of protecting groups is almost always unnecessary in conjunction with the Stille reaction. This is a very unusual and attractive feature for an organometallic process. Also, the reaction is often neither air nor moisture sensitive. In some cases, water and oxygen have actually been shown to promote the coupling. Although the reaction as initially described by Stille is often carried out under rather drastic conditions (temperatures of $\geq 100°$ are not uncommon), newly developed ligands[11] and the addition of copper(I) salts[12] have solved some of the problems associated with low reactivity. The utility and mildness of the Stille reaction are demonstrated by its frequent use in the final stages of complex natural product syntheses.

This review attempts a critical and comprehensive coverage of the reaction scope. Our mechanistic description of the reaction is rather brief, and we refer the reader to the pertinent literature for a more detailed analysis. All of the relevant literature is covered up to the end of 1994. The reaction was reviewed by Stille in 1986,[6] and by Mitchell in 1992;[13] a rather comprehensive account by Farina and Roth has appeared more recently.[14] Developments that occurred in 1995, as this work was in progress, and that were deemed important were incorporated as much as possible in this review.

MECHANISTIC CONSIDERATIONS, REGIOCHEMISTRY, AND STEREOCHEMISTRY

The three-step catalytic cycle proposed for the Stille reaction follows the general principles of transition metal-mediated cross-coupling reactions and is shown in Scheme 1.[6]



Scheme 1. Catalytic cycle of the Stille reaction.

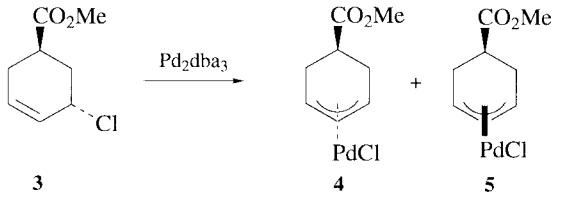
When the catalyst is introduced as Pd(II), fast reduction by the stannane to a Pd(0) complex ensues, and the resulting Pd(0) species enters the cycle. Alterna-

tively, the catalyst can be introduced directly as Pd(0). The rate or yield differences sometimes observed between Pd(II) and Pd(0) catalysts are not likely to be due to the initial difference in oxidation state, but rather to the stoichiometric ratio of palladium to ligand or other factors.[11]

The first step of the cycle is termed *oxidative addition* and is a quite general process for low-valent transition metal complexes.[15] The reaction is represented as a simple process in Scheme 1, but is likely to be a rather complex one. There is substantial evidence that a coordinatively unsaturated Pd(0) species, for example $Pd(PPh_3)_2$, is responsible for the oxidative process.[16] When the substrate is an aryl iodide, the reaction is accelerated by electron-withdrawing substituents on the ring ($\rho = +2$).[17] Oxidative additions are also accelerated by electron-rich phosphorus ligands on the palladium center.[18] In the coupling of aryl bromides with tetramethylstannane, the overall rate is strongly enhanced by electron-withdrawing groups on the aryl moiety ($\rho = +3.38$), suggesting that in this case the oxidative addition is rate limiting.[19]

At least with alkenyl halides, the oxidative addition may be a reversible process. Such a reaction generally proceeds with retention of olefin geometry.[20] Benzylic bromides undergo oxidative addition with partial or total racemization;[21] this has been explained by invoking a one-electron transfer process for this oxidative addition,[22] and CIDNP studies have supported the suggestion.[23] In these cases, the oxidative addition may be accelerated by the presence of oxygen in solution.[19] Intermediate **1** (Scheme 1) is generally formed as a *trans* square-planar complex, i.e., the two phosphine moieties are *trans* to each other, although the intermediacy of the less stable *cis* complex is assumed.[6]

In allylic systems, i.e., allylic chlorides, the oxidative addition was initially shown to proceed with complete inversion of configuration, through the intermediacy of η^3-complexes,[24] but subsequent studies have revealed a more complex situation (Eq. 2).[25]



3 **4** **5**

Solvent	**4:5**
Benzene	100:0
THF	95:5
Acetone	75:25
DMF	29:71
DMSO	3:97

(Eq. 2)

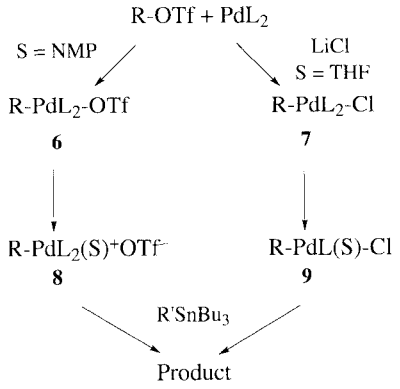
Specifically, it was shown that, in the absence of strong coordinating ligands, the stereochemistry depends on the solvent, nonpolar solvents favoring retention and polar ones leading to inversion. Furthermore, olefin ligands promote *syn* oxidative addition, and phosphines favor the *anti* pathway.[26]

Although it is known that the transmetallation is very often the rate-determining step of the Stille reaction, much less is known mechanistically about this metathesis reaction.

In early studies, Stille et al. showed that, in the coupling of benzylic stannanes with acid chlorides, electron-releasing substituents slightly increased the transmetallation rate ($\rho = +1.2$), suggesting that carbon-tin bond breaking precedes palladium-carbon bond formation. The stereochemical outcome with benzylic stannanes is predominantly inversion at the tin-bearing carbon, suggesting an "open" S_E2 mechanism.[27]

More recently, it has been shown that the transmetallation of **1** to **2** proceeds via prior ligand dissociation and that ligands with lower donicity toward Pd(II) than PPh_3 [i.e., tri(2-furyl)phosphine and triphenylarsine] can lead to major (up to 1,000-fold) rate enhancements in the transmetallation.[11] With these ligands, many Stille couplings previously requiring vigorous conditions can be performed at room temperature.

In studies of the synthetically important coupling of organic triflates,[28,29] LiCl is necessary to induce coupling of organic triflates in THF as solvent. This has been rationalized by postulating that the initial oxidative addition product (**6**, Scheme 2), which was isolated in one case, is catalytically incompetent, whereas ligand substitution with chloride ion leads to the reactive species **7**.[28]



Scheme 2. Two possible pathways in the Stille coupling with organic triflates.

More recently, it has been found that addition of LiCl is often not necessary when operating in highly polar solvents like NMP, and in many cases LiCl is actually an inhibitor of the coupling. This was explained by invoking two pathways in the transmetallation, i.e., a faster one proceeding via cationic species **8** and a slower one (with $L = PPh_3$) proceeding via ligand dissociation (through **9**). Hammett studies confirmed that there are two pathways with opposite electronic demands. Thus, in the absence of chloride the reaction is faster when the arylstannane contains electron-releasing groups ($\rho = -0.89$), whereas in the presence of LiCl, electron-withdrawing substituents also enhance the rate. The transmetallation is affected in a complex way by the combination of LiCl, ligands, and solvent, and the highest rates are obtained with $AsPh_3$ as ligand. With

this superior ligand, the effect of halide additives on the rate of the transmetallation is minimal.[30]

Intramolecular couplings of triflates with stannanes do not require LiCl even in THF.[31] The recently reported ability of Ag(I) salts to improve some Stille couplings may also be explained by a switch of the transmetallation pathway via **8** and away from **9** (Scheme 2).[32]

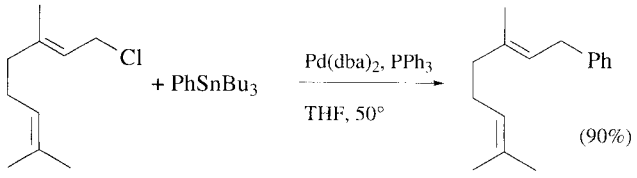
The cocatalytic effect of Cu(I) in the Stille coupling was first reported by Liebeskind and Fengl.[12] Later studies have shown that Cu(I) performs a dual role: In ethereal solvents (THF, dioxane) and in conjunction with highly coordinating ligands (PPh_3), Cu(I) acts as a ligand scavenger to facilitate formation of the coordinatively unsaturated Pd(II) intermediate (**9** in Scheme 2) needed to effect transmetallation, whereas in highly dipolar solvents (NMP) in the presence of "soft" ligands ($AsPh_3$) formation of an organocopper species is likely.[33] Thus, it seems simply that in the presence of inorganic Cu(I) salts, an organostannane may be in equilibrium with an organocopper species (Eq. 3). Another important role of Cu(I), enhancing the selectivity of group transfer in the Stille reaction, is discussed in a later section.

$$RSnBu_3 + CuI \underset{\longleftarrow}{\overset{NMP}{\rightleftharpoons}} RCu + ISnBu_3 \qquad \text{(Eq. 3)}$$

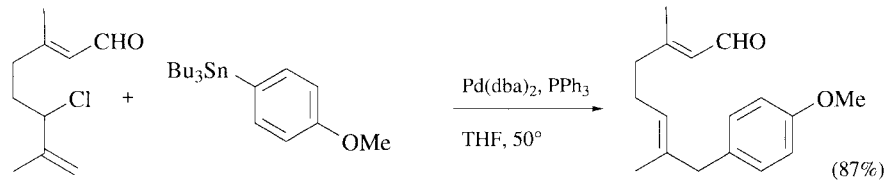
Similar transmetallations have been postulated in order to explain the beneficial effect of stoichiometric Zn(II) salts on certain Stille couplings, but no experimental evidence is available.[28]

From the standpoint of the stereochemistry at Pd(II), the transmetallation usually proceeds with retention of configuration and is probably followed by *cis-trans* isomerization. The reductive elimination that follows probably proceeds through a T-shaped intermediate via prior ligand dissociation at Pd(II).[15] Pd(IV) species have been implicated as intermediates in the reductive elimination,[34] but factors that influence this step are not discussed further since reductive elimination is not rate determining in the Stille coupling. In the coupling of allylic electrophiles, however, reductive elimination will determine the regiochemistry of coupling, and in this case detailed understanding of this step is very important.

Allylic halides, typically chlorides, couple smoothly with organostannanes under normal conditions, and the regiochemistry of the coupling is usually the one resulting from attack of the organostannane at the less hindered terminus of the allylic moiety (Eqs. 4 and 5).[24]



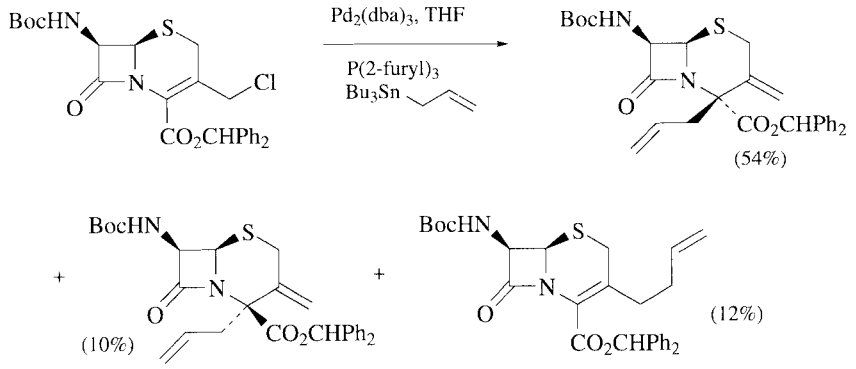
(Eq. 4)



(Eq. 5)

When the organostannane is also allylic, the situation is more complicated. Apparently, the coupling is somewhat regiospecific, and the C-C bond is formed between the more substituted end of the allylic stannane and the less substituted one in the allylic halide.[35,36] To explain the predominant allylic transposition of the stannane, both Stille and Trost postulated a direct attack of the stannane at the carbon terminus of an intermediate π-allyl complex, but there is no proof for such a mechanism. Indeed, indicator substrates for nucleophilic attack at π-allyl complexes classify allylstannanes as reacting directly at Pd(II) and not at carbon.[37] This mechanistic issue is still unresolved, even though a simple stereochemical probe could resolve the issue. On the other hand, in the presence of maleic anhydride the coupling takes place in a preferred head-to-head mode, and the stereochemistry indicates attack of the stannane at the Pd center of the π-allyl complex, followed by reductive elimination with retention of configuration.[38,39]

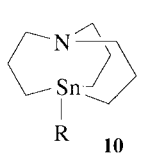
Exceptions to these regiochemical trends, however, can be found in the literature. One is shown in Eq. 6 and is mechanistically difficult to explain. One must also note that the two regiochemistries are interconvertible by Cope rearrangement.[40]



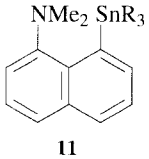
(Eq. 6)

An important mechanistic issue that has recently begun to be addressed by several investigators concerns the effect of nucleophilic assistance at tin(IV) during the transmetallation. Two studies[41,42] have independently shown that a nucleophilic moiety placed within the stannane considerably enhances transmetallation rates, whereas other studies in related systems have failed to de-

tect such enhancements.[30] The increased reactivity of stannanes **10** has been explained by invoking internal N-Sn coordination in the transition state,[41] and a similar rationalization has been applied to the increased reactivity of systems such as **11**.[42]



10



11

These stannanes are able to effect transfers of alkyl moieties, which occur sometimes with difficulty or not at all using traditional Stille chemistry. The mechanistic and synthetic significance of these intriguing observations should be further explored.

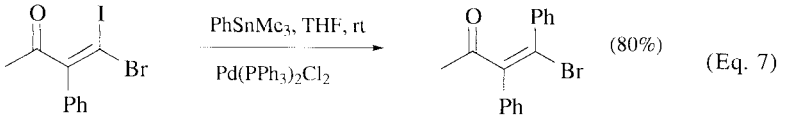
SCOPE AND LIMITATIONS: THE ELECTROPHILE

In this section, the range of electrophiles used in the Stille coupling is surveyed. Details of experimental conditions and side reactions are more fully described in separate sections. The examples discussed are a select few. A complete survey is found in the tables. Limitations are discussed whenever carefully documented in the literature. Occasionally, low yields are reported in a number of isolated Stille couplings. These may be due to incomplete optimization of the reaction. Therefore, these examples are considered a real limitation only if the authors reported a thorough study exploring a comprehensive list of catalysts and conditions.

Alkenyl Halides

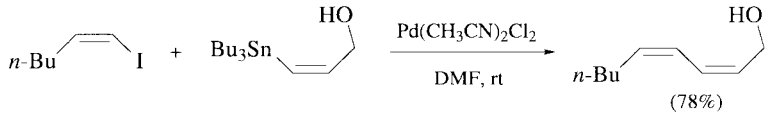
Alkenyl chlorides have been used very little in Stille couplings, presumably because of their lack of reactivity in the oxidative addition with Pd(0). Scattered examples of successful coupling exist, but appear limited to activated systems.[43,44]

Alkenyl bromides and iodides are generally useful partners. Their coupling is often stereospecific. Since bromides undergo oxidative addition only at elevated temperatures, *E/Z* isomerizations are sometimes observed. More consistently stereospecific is the coupling with vinyl iodides, which takes place at room temperature or slightly above. The higher reactivity of the iodides vs. the bromides is nicely illustrated in Eq. 7, where under the mild conditions employed the bromide moiety is left unreacted.[45]



(Eq. 7)

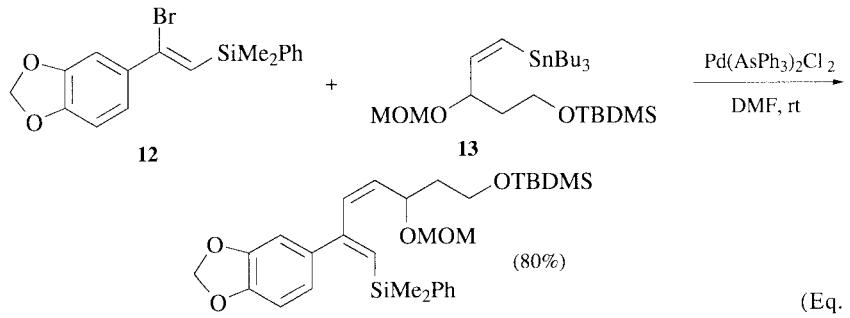
Two general studies on the cross-coupling between simple alkenyl iodides with both alkenyl[46] and alkynyl[47] stannanes are reported. Bromides also couple, but in lower yield. In each case, the preferred catalyst is the "ligandless" species $Pd(CH_3CN)_2Cl_2$. The reaction proceeds in DMF or THF at room temperature, and *E/Z* isomerization is negligible (Eq. 8).



(Eq. 8)

The palladium-catalyzed reduction of vinyl iodides with tributyltin hydride or other hydride reagents can be loosely classified as a Stille coupling. The reaction is highly stereospecific, in contrast with the radical-induced reduction, which leads to geometrical isomerization.[48]

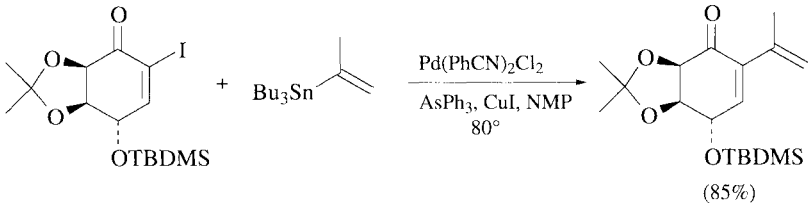
Very few limitations of this coupling reaction have been clearly documented. Even tetrasubstituted vinyl iodides couple in good yields.[49,50] However, β-silyl vinyl bromide **12** couples with stannane **13** to yield only a completely isomerized product even under the mildest conditions.[51] This lack of stereospecificity is attributed to the bulky silyl group (Eq. 9).



(Eq. 9)

Special classes of alkenyl halides that have been made the objects of specific studies include β-halo-α,β-unsaturated ketones and esters, which couple smoothly with a variety of stannanes,[52-54] quinone halides, which also couple well (preferentially using CuBr as cocatalyst),[55-58] and β-halo-α,β-unsaturated sulfoxides, which couple with alkenyl-[59] and alkynylstannanes[60] without *E/Z* isomerization and without epimerization at the chiral sulfur center.

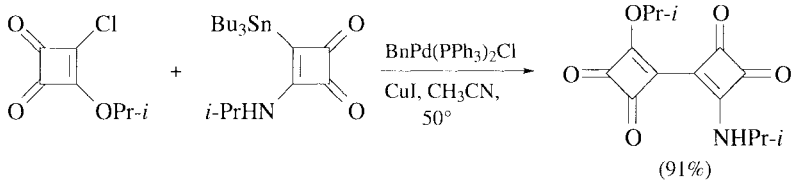
Certain systems, on the other hand, appear difficult to couple and require carefully optimized conditions. For example, α-iodo-α,β-unsaturated ketones must be coupled using the "soft" ligand $AsPh_3$ and cocatalytic Cu(I). Even under these conditions, high temperatures are required, but the reaction is general and gives very good yields (Eq. 10).[61]



(Eq. 10)

On the other hand, α-bromo-α,β-unsaturated ketones can be coupled with aryl stannanes using P(*o*-Tol)$_3$ as ligand in the absence of Cu(I) additives.[62]

Halocyclobutenediones couple with stannanes, and CuI cocatalyst is necessary to obtain good yields (Eq. 11).[63,64]

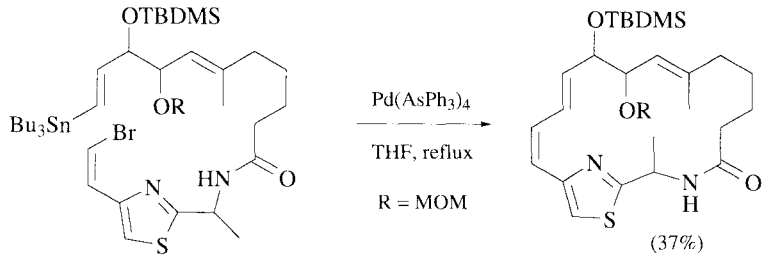


(Eq. 11)

Cyclooctatetraenyl bromide couples with stannanes at room temperature, and P(2-furyl)$_3$ or AsPh$_3$ are the ligands of choice.[65,66]

Bromotropolones can be coupled with a variety of arylstannanes, to yield analogs of the antimitotic agent colchicine.[67]

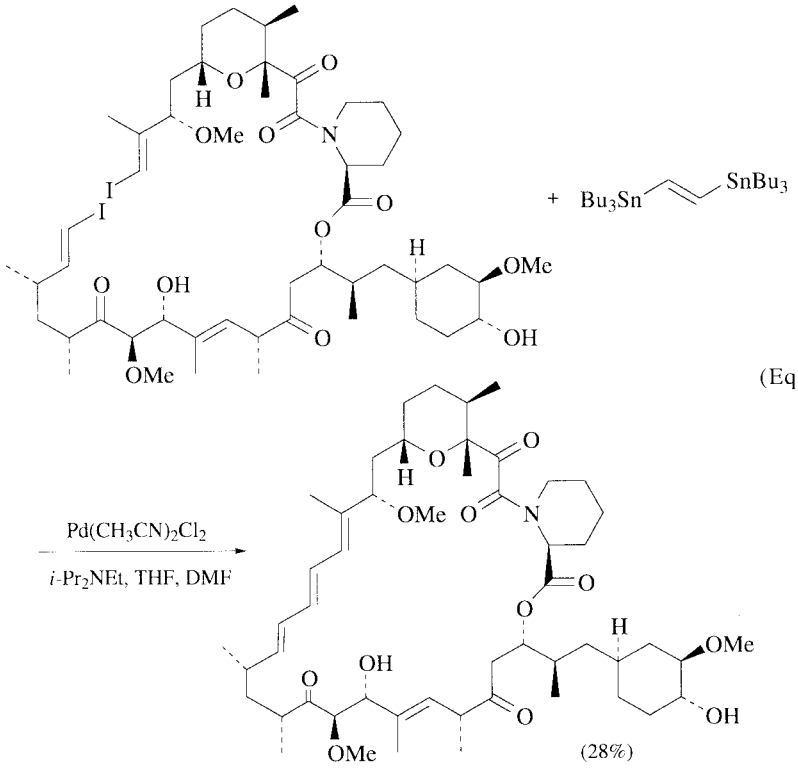
Intramolecular versions of this coupling reaction yield a variety of ring sizes, from four[68] and five[69] to medium-size rings,[70–74] and even macrocycles.[75] Equation 12 illustrates the key step in the total synthesis of leinamycin.[76] The



(Eq. 12)

mildness and generality of this method is demonstrated by its frequent application to the late stages of complex natural product syntheses. Thus, the alkenyl halide/organostannane coupling has been applied in recent years to the total syntheses of neooxazolomycin,[77] onnamide A,[78] 22,23-dihydroavermectin,[79] calyculin A,[80–82] lankacidin C,[83] lepicidin A,[84] and rapamycin.[85]

Probably the most spectacular application of this reaction is represented by the final step of Nicolaou's total synthesis of rapamycin, in which a tandem Stille coupling is carried out on the fully functionalized skeleton.[86] The yield is modest, but an intermediate iodostannane could be isolated and resubjected to the reaction conditions, affording more cyclized product and thereby increasing the overall yield to 46% (Eq. 13).

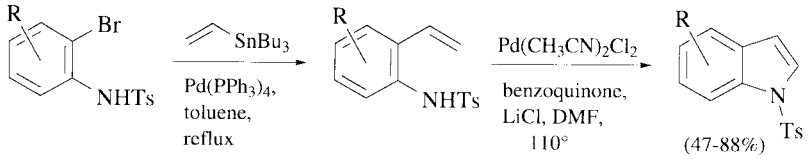


(Eq. 13)

Aryl and Heterocyclic Halides

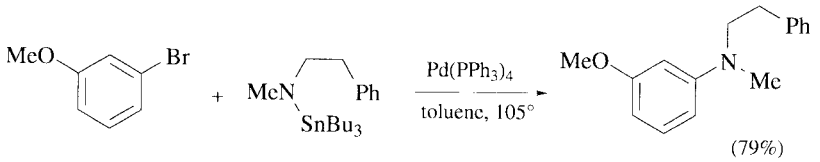
An early study reports that in the coupling of aryl halides with organostannanes, aryl bromides are the optimal electrophiles in the coupling reaction with allyltributylstannane. Aryl chlorides react only if strongly activated toward oxidative addition (e.g., *p*-nitrochlorobenzene), whereas aryl iodides couple only in low yields.[3]

In independent studies of the scope and utility of the reaction, it was found that both aryl bromides and iodides couple with a number of stannanes in high yield.[19,87] The coupling of aryl bromides requires more vigorous conditions and is facilitated by electron-withdrawing substituents in the *para* position of the halide derivative, indicating that oxidative addition is the rate-determining step. A specific study deals with the preparation of styrene derivatives.[88] The method was applied to the synthesis of indole derivatives (Eq. 14).[89]



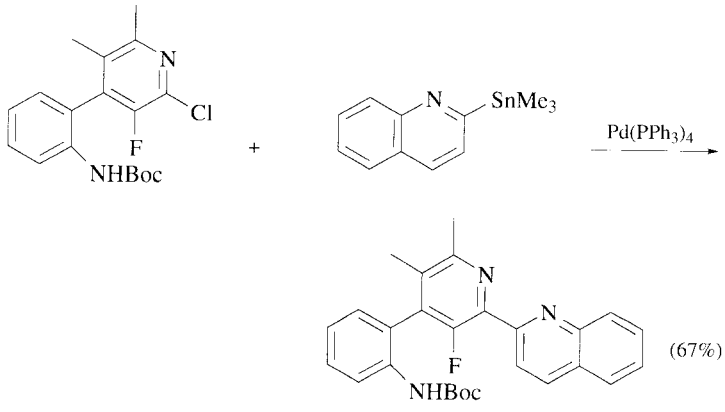
(Eq. 14)

A synthetically useful variant of the Stille reaction is the coupling of aryl halides with aminostannanes.[90-92] The reaction so far is limited to aryl bromides. Secondary amines can generally be coupled, whereas among primary amines, only anilines have been reported to couple. The aminostannanes can be conveniently generated in situ from the corresponding amines and (diethylamino)tributylstannane. This is obviously a reaction with much potential, and it is likely that its scope will grow after further scrutiny. An example is shown in Eq. 15.[91] Other carbon-heteroatom bonds can be made through the intermediacy of organostannanes, as detailed later in the section describing the scope and limitation with respect to the types of stannanes that can be used.



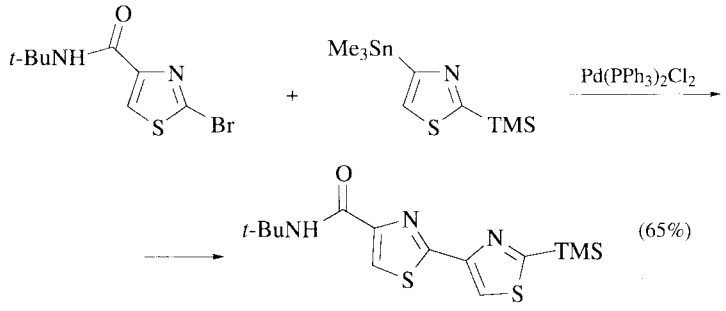
(Eq. 15)

Heteroaryl halides also couple with organostannanes. Although the scope of these reactions has generally not been studied in detail, many examples in the literature exist to support some generalizations. For example, 2-, 3-, or 4-bromopyridines couple well with aryl and heteroaryl stannanes,[93-95] whereas 3-iodopyridines couple in only fair yields.[96] 2-Chloro-3-fluoropyridine derivatives couple specifically at the 2 position with a variety of alkenyl stannanes.[97] Even 4-chloropyridine can be coupled. 3-Bromoquinolines also couple with stannanes.[93,98] Equation 16 illustrates the key step in the synthesis of a lavendamycin analog.[99]

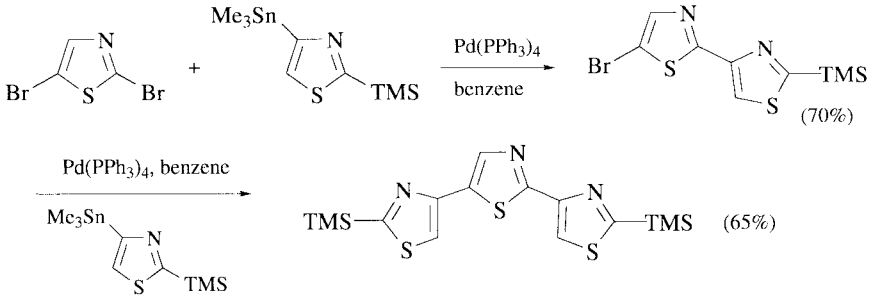


(Eq. 16)

2- and 3-Furyl[100] and thienyl[96,101–106] halides are easily coupled with stannanes. 2-Halothiazoles couple smoothly, as illustrated by a key step in a recent synthesis of micrococcinic acid (Eq. 17).[107] 2,5-Dibromothiazole couples first at the 2 position, then at C-5 (Eq. 18).[108]

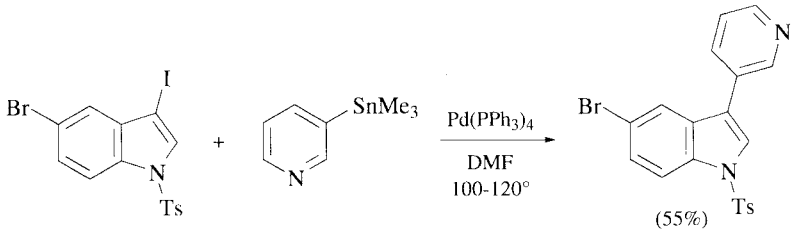


(Eq. 17)



(Eq. 18)

Both 2-[109] and 3-indolyl[110] halides have been coupled with stannanes. Interestingly, 5-bromo-3-iodotosylindole couples specifically at C-3 (Eq. 19).[110]

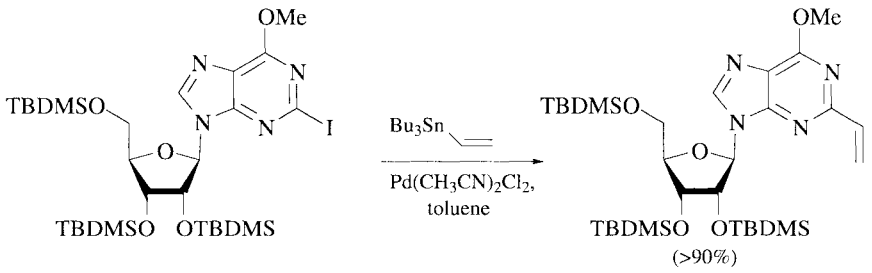


(Eq. 19)

2-Imidazolyl bromides couple with phenyltrimethylstannane, and 2,4-imidazolyl dibromides couple selectively at the 2 position with aryl stannanes, contrary to the corresponding arylboronates, which couple at both positions without selectivity.[111]

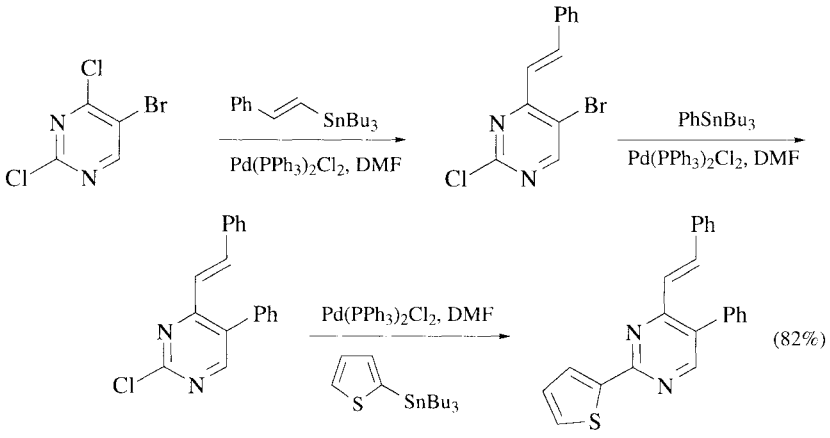
4(5)-Imidazolyl iodides, however, can be successfully coupled.[112,113] 4-Iodoisoxazoles can be coupled with a large number of stannanes.[114] 2,5-Dibromosiloles couple with alkynylstannanes,[115] and 2-bromo- and 2,4,6-tribromophosphinines couple with stannanes in an interesting selectivity pattern.[116]

Many applications of the Stille reaction to nucleoside chemistry have been made since the first application of the reaction to 2-iodopurines (Eq. 20).[117–120]



(Eq. 20)

Similar chemistry has been reported for 5-iodouridines,[121–125] and 5-bromo- or 5-iodouracil[126–128] derivatives. 5-Arylcytosines have been prepared from the corresponding 5-iodo derivatives by Stille coupling.[129] Stannane coupling in purine chemistry has been extended to 8-bromoadenosines,[130] 8-iodoadenosines,[131] 6-iodouridines,[132] and 6-chloropurines.[133,134] A number of 4- and 5-halopyrimidines (halo = Cl, Br, I) have been coupled with stannanes.[135–140] In polyhalogenated pyrimidines the order of reactivity in the coupling is C-4 > C-5 > C-2, regardless of the halide (Eq. 21).[141]



(Eq. 21)

2-Chloropyrazines can be coupled with stannanes,[142] and even bromo-substituted porphyrins have been subjected to the Stille coupling.[143,144] Finally, aryl io-

dides attached to a polymer have been subjected to Stille couplings in relation to the building of combinatorial libraries.[145]

Acyl Chlorides

It was reported in 1977 that stannanes can be coupled with acyl chlorides under palladium[1] or rhodium catalysis.[2] Stille subsequently explored the scope of the reaction and showed that it is general for a wide variety of acyl chlorides (Eq. 22).[146]

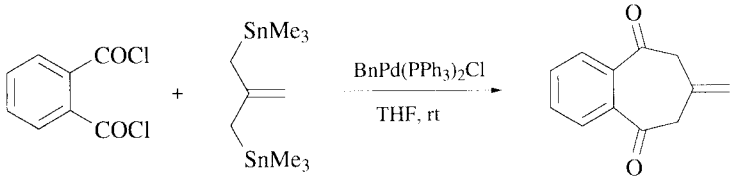
$$R^1COCl + R^2SnBu_3 \xrightarrow[CHCl_3,\ reflux]{BnPd(PPh_3)_2Cl} R^1COR^2 \qquad \text{(Eq. 22)}$$

R^1= Aryl, alkyl, alkenyl; R^2= Alkyl, alkenyl, alkynyl, aryl

Few limitations are encountered in this reaction. Allylstannanes may react further with the ketone products in a nonpalladium catalyzed nucleophilic carbonyl addition. Decarbonylation is seen in some cases, but can be avoided by running the reaction under a CO atmosphere. Product isomerization is a complication when allyl- and alkenylstannanes are employed. This reaction can be run under milder conditions (room temperature) by using tri(2-furyl)phosphine or $AsPh_3$ as ligands.[11] Use of the former often prevents the unwanted geometric isomerization. Oxalyl chloride is not a good substrate for this reaction.[147] Coupling with β-stannyl enones yields butene-1,4-diones, which are directly reduced to 1,4-diketones under the reaction conditions.[148]

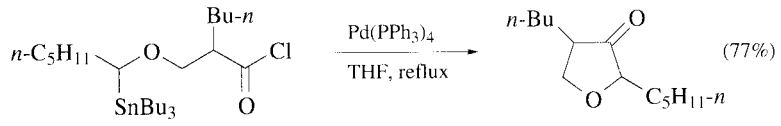
The coupling of acyl chlorides and alkynylstannanes is quite general and affords good yields of α,β-acetylenic ketones.[149]

Examples of this reaction in the absence of palladium are well known,[150] and, although the uncatalyzed reaction is outside the scope of this chapter, in some cases it is claimed to be higher yielding than its palladium-promoted counterpart.[151] Acyl chlorides from dicarboxylic acids also participate in the coupling. If a distannane is used, an annulation reaction results (Eq. 23).[152]



(Eq. 23)

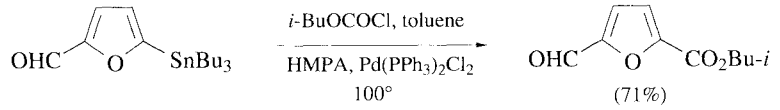
Intramolecular couplings are also quite useful synthetically.[153,154] An example is shown in Eq. 24.[155]



(Eq. 24)

When the stannane used is tributyltin hydride, a general synthesis of aldehydes results.[156]

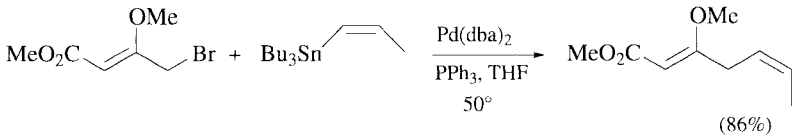
Chloroformates and carbamoyl chlorides also couple with stannanes[157] to yield esters and amides, respectively, in good yields (Eq. 25).[158] Intramolecular examples have been reported.[159]



(Eq. 25)

Allylic, Benzylic, and Propargylic Electrophiles

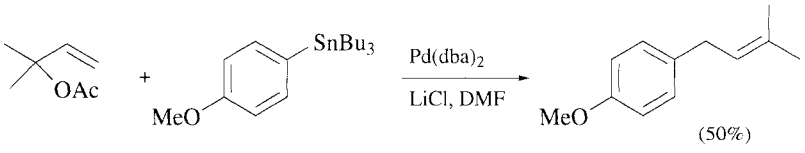
The coupling of allylic electrophiles with organostannanes is a reaction of general utility. Stille studied the scope of the reaction of allylic chlorides and bromides with organostannanes. With allylic electrophiles, a regiochemical issue exists: Since these couplings probably proceed via η^3-allylpalladium intermediates, coupling at either the α or the γ position is possible. Stille reports that coupling generally occurs at the less substituted terminus of the allyl moiety. An example is shown in Eq. 26.[24]



(Eq. 26)

Aryl- and alkenylstannanes couple in good yields. Allylic stannanes react to yield mixtures in which coupling at the more substituted terminus of the stannane is favored.[36,37] Among the applications to compounds of biological interest, the coupling of chloromethylcephems with stannanes constitutes a versatile approach to novel semisynthetic cephalosporins.[41]

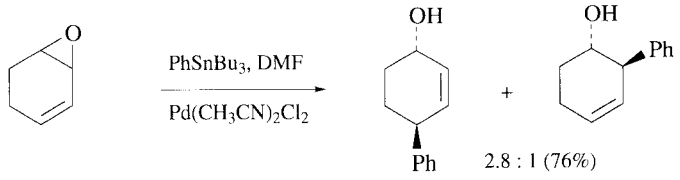
Allylic acetates[36,160,161] and allylic phosphates[162] also couple with stannanes under special conditions. A study on the cross-coupling of allylic acetates showed that the reaction is quite general and is best carried out in the absence of phosphine but in the presence of LiCl. Again, coupling takes place at the less substituted allyl terminus, and both alkenyl- and arylstannanes couple in high yields. An example is given in Eq. 27.[163]



(Eq. 27)

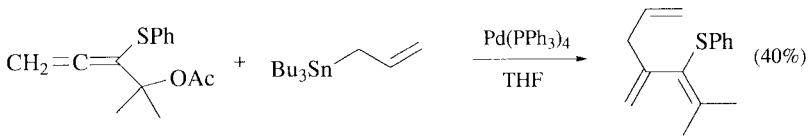
Alkenyl epoxides can be considered allylic electrophiles. They also undergo coupling with aryl- and alkenyl- (but not allyl-, benzyl-, alkyl-, and alkynyl-) stannanes to yield mixtures of 1,2 and 1,4 coupling products.

As with allylic acetates, the less substituted terminus is the more reactive. Added water increases the yield and the regioselectivity, but further work aimed at better control of the regiochemistry is necessary to make this reaction synthetically useful. Equation 28 shows a typical example.[164]



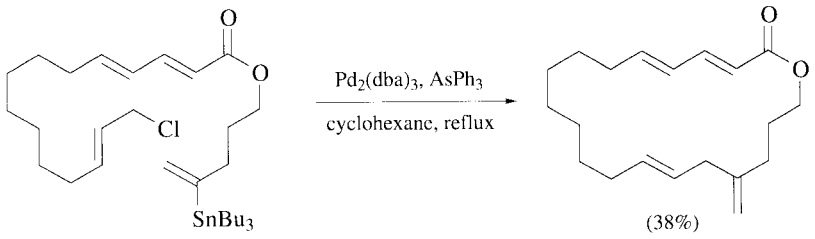
(Eq. 28)

Propargylic acetates do not couple with organostannanes,[165] and alkynylstannanes may undergo anomalous coupling with allyl halides.[41] Allenyl acetates have been coupled with stannanes to yield polysubstituted 1,3-dienes (Eq. 29).[166]



(Eq. 29)

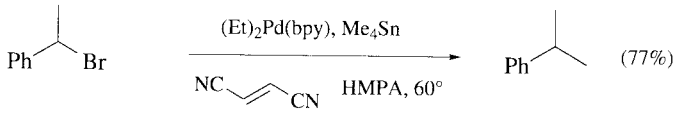
Intramolecular examples of the coupling of organostannanes with allylic electrophiles have also been reported. Under optimized conditions, large rings can be constructed in fair yields (Eq. 30).[167]



(Eq. 30)

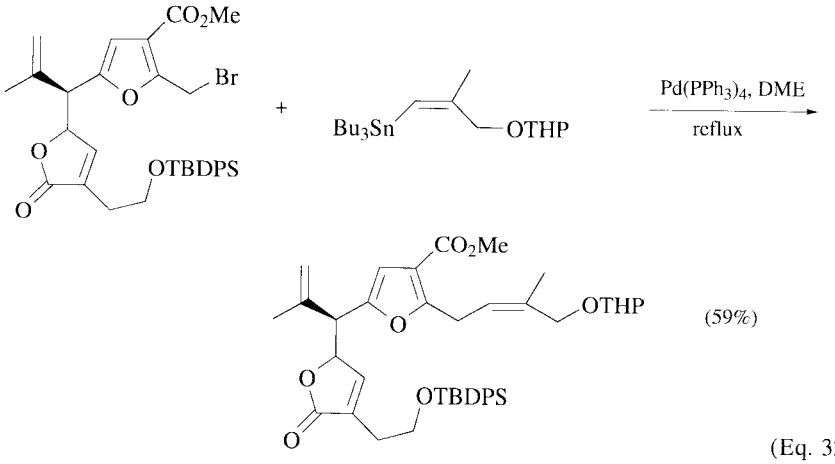
Allyl esters and carbamates are important in the protection of carboxy and amine functional groups. Deprotection conditions sometimes involve use of Pd(0) catalysts in conjunction with tributyltin hydride.[168] Specific examples are not discussed, since they are outside the scope of this review.

Few studies on the coupling of benzyl halides with stannanes have appeared. Benzyl bromide itself couples with tetramethylstannane, vinyltributylstannane, and tetraphenylstannane in good yields under the catalysis of $BnPd(PPh_3)_2Cl$ in HMPA.[19] Reaction with hexaalkyldistannanes yields benzylic stannanes in fair to good yields.[169] Propargyl halides have not generally been used as substrates in the Stille reaction. Propargyl bromide couples to some stannanes to yield allene derivatives.[170] The coupling of benzylic bromides containing β hydrogens takes place smoothly, without substantial β elimination, in the presence of the catalyst (2,2′-bipyridine)fumaronitrile palladium(0) (Eq. 31)[171]. Further applications of



(Eq. 31)

this interesting catalyst to other cross-coupling chemistry have not been reported. Finally, a nice application of this coupling to natural product synthesis is found in an approach to furanocembranolides (Eq. 32).[172]

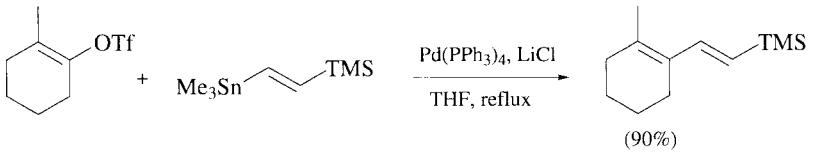


(Eq. 32)

Alkenyl Sulfonates and Other Electrophiles

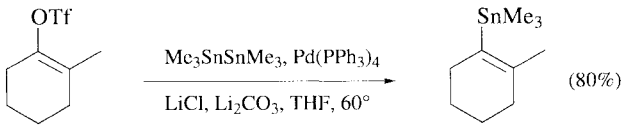
The coupling of vinyl sulfonates is, in general, limited to triflates. In a few special cases where extra activation is present, mesylates[173] and tosylates[174] can be used, but these substrates have limited utility and are not discussed further. The coupling of vinyl triflates with organostannanes is a truly general reaction of paramount importance in organic synthesis, owing in part to the ready availability of isomerically pure alkenyl triflates.[175] An initial study shows that the coupling takes place in high yield in THF with alkenyl-, alkynyl-, and

allylstannanes, but arylstannanes do not react.[28] The reaction requires addition of excess LiCl (Eq. 33).



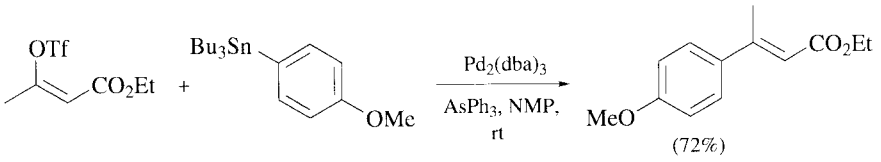
(Eq. 33)

The reaction of alkenyl triflates with hexamethyldistannane constitutes an important approach to alkenylstannanes (Eq. 34).[176]



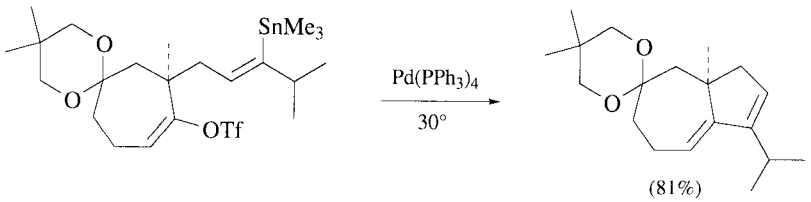
(Eq. 34)

A more recent study has shown that even arylstannanes couple smoothly under optimized conditions, using the "soft" ligand $AsPh_3$ and highly polar solvents such as NMP.[30] A careful reexamination of the LiCl effect has shown that this additive is often unnecessary for the reaction to proceed if one operates in NMP as solvent. LiCl is generally an inhibitor of the reaction in NMP when strong ligands (PPh_3) are used , but has little effect on the rate when "soft" ligands ($AsPh_3$) are employed. For a discussion of this complex behavior, the reader is referred to the mechanistic section. *E/Z* isomerization of the product can be a problem with these couplings (Eq. 35).[30] Use of CuI as a cocatalyst often reduces such isomerization.[177]



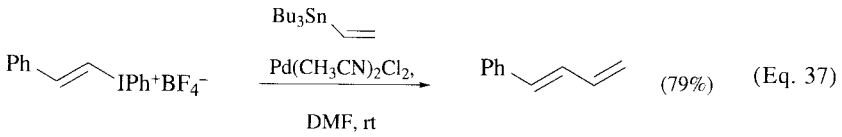
(Eq. 35)

The intramolecular version of this reaction has been developed. The cyclization precursors were assembled using an array of tin-containing bifunctional synthons developed for this purpose. A variety of small- and medium-size rings was assembled, and applications to the total synthesis of terpenoids were reported.[31,69,178–183] Once again, LiCl behaved as an inhibitor of the coupling. An example of this powerful methodology is shown in Eq. 36.[184] An extension to macrocyclizations is reported.[185,186]



(Eq. 36)

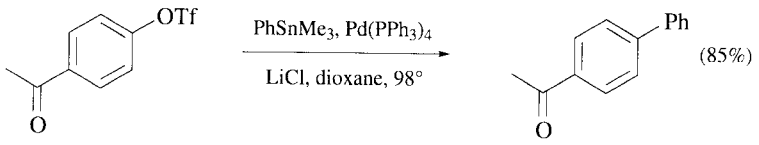
Alkenyl phenyliodonium salts also couple with alkenylstannanes under mild conditions, as shown in Eq. 37.[187,188]



(Eq. 37)

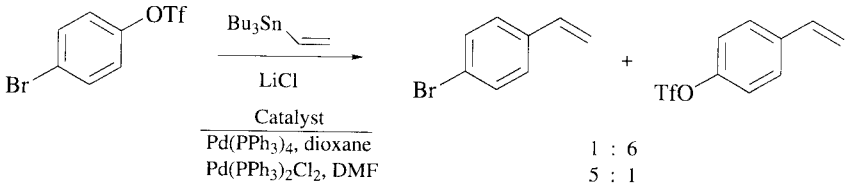
Aryl and Heterocyclic Sulfonates and Other Derivatives

The Stille coupling of aryl triflates has been extensively studied. In the presence of LiCl, these substrates couple with alkyl-, alkenyl-, allyl-, alkynyl-, and arylstannanes in high yields under relatively harsh conditions (ca. 100°). Dioxane and DMF are the solvents of choice. Equation 38 shows a typical example.[189]



(Eq. 38)

Aryl triflates are less reactive than aryl iodides, but their reactivity is comparable to that of aryl bromides. A direct competition experiment showed that product distribution depends strongly on the coordinative level of the catalyst used (Eq. 39). Unfortunately, no firm conclusions can be drawn about the mechanistic

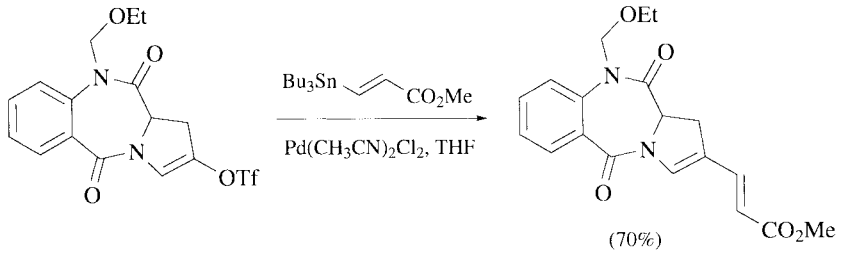


(Eq. 39)

basis for this dichotomy, since the two catalysts were used in different solvents, and it is likely that the solvent is also a key factor in the ease of oxidative addi-

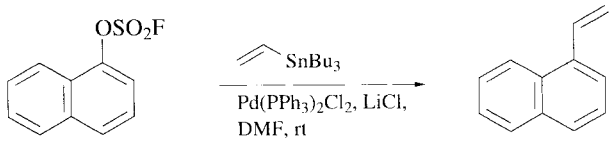
tion.[30] Ether, nitro, amido, and carbonyl groups (even aldehydes) are tolerated on the aryl triflate. Because of the harsh conditions employed, double bond migrations and isomerizations are recurring problems. As for vinyl triflates, a reexamination of the reaction showed that the coupling of aryl triflates is best carried out in NMP with $AsPh_3$ as ligand. In this solvent, LiCl reduces the coupling rate, but is sometimes beneficial to catalyst stability. An *ortho* methyl group on the aryl triflate slows the coupling by a factor of 3.[30]

Separate studies have shown that electron-rich aryl triflates also couple in good yields, especially with Cu(I) cocatalysts.[190,191] Both 1- and 2-naphthyl triflates couple as expected,[192] as do indolyl,[193] quinolyl, and isoquinolyl triflates.[194,195] Pyrimidyl triflates couple with organostannanes in good yields.[196] Among the derivatives of medicinal interest as targets, one must note the utility of the coupling of cephem,[40] carbacephem,[197] and carbapenem[198] triflates with stannanes for the synthesis of antibacterial β-lactams, the coupling of uridine triflates with stannanes,[199] and an application to the synthesis of anthramycin (Eq. 40).[200]



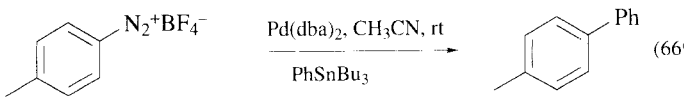
(Eq. 40)

In addition to triflates, other sulfonates can be used, including long-chain polyfluorinated sulfonates,[29,201] *p*-fluorophenyl sulfonates,[202] and fluorosulfonates.[203] The last appears to be of practical utility, considering the low cost of fluorosulfonic acid vs. the expense of triflic acid (Eq. 41).



(Eq. 41)

Among the aryl electrophiles, diazonium salts participate in the Stille coupling with alkenyl-, alkyl-, and arylstannanes, and an example is shown in Eq. 42.[204] Given their ready availability, the under-utilization of these substrates is hard to understand.

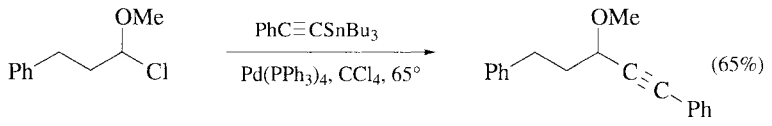


(Eq. 42)

Even some ether derivatives, notably some *pseudo*-saccharyl *O*-ethers, couple with stannanes in low to fair yield, especially under Ni(0) catalysis, but this reaction is restricted to tetramethylstannane so far, and therefore its scope is still to be fully explored.[205] Diaryliodonium salts also participate in the Stille reaction.[206]

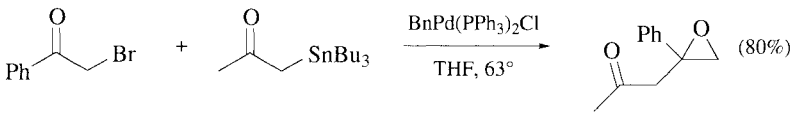
Miscellaneous Electrophiles

Alkyl halides do not normally cross-couple with organostannanes, but some α-activated substrates do undergo the Stille coupling. Among them, the α-halo ethers and α-halo thioethers couple smoothly, even if β hydrogens are present (Eq. 43),[207] whereas α-halolactones couple with allylic and acetonyl stannanes.[208]



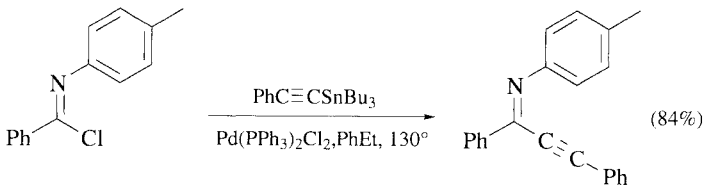
(Eq. 43)

α-Halocarbonyl compounds react with allyl and acetonyl stannanes in an anomalous fashion, i.e., by attack at the carbonyl followed by oxirane formation (Eq. 44).[209]



(Eq. 44)

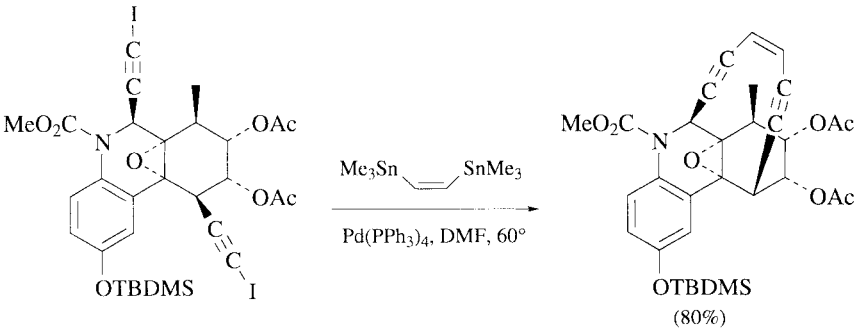
Perfluorinated alkyl iodides, in which β-hydride elimination after oxidative addition is impossible, couple with stannanes in good yields, although the reaction is proposed to be radical mediated.[210] Imidoyl chlorides couple with stannanes in low to fair yields, thus providing a route to imines from amides. An example is shown in Eq. 45.[211] Alkynylstannanes react in particularly good yields.[212]



(Eq. 45)

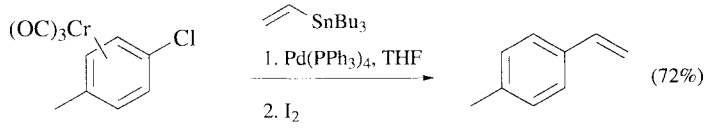
Although no general study has appeared on the use of alkynyl halides in the Stille reaction, sporadic but useful applications of these electrophiles have been

recorded.[213-215] A remarkable result is reported in a dynemicin total synthesis (Eq. 46).[216]



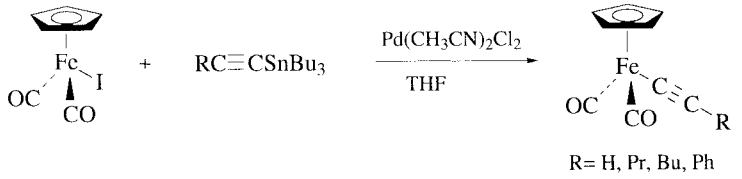
(Eq. 46)

Many examples of arene or polyene metallocarbonyls in the Stille cross-coupling have been reported.[217-226] The purpose of the metallocarbonyl moiety is often to activate the aryl electrophile toward oxidative addition, as in Eq. 47.[227]



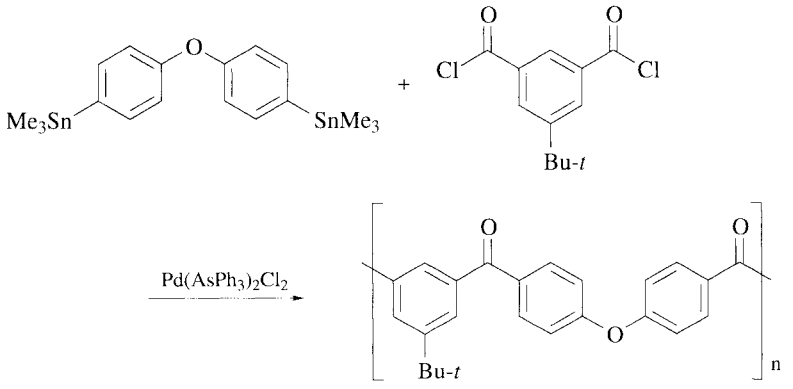
(Eq. 47)

Several heteroatom-halogen bonds can be activated toward coupling by Pd(0) catalysts, including P-Cl,[228] S-Cl,[229] and Fe-I bonds.[230] The last appears to be the first example of the formation of a transition metal-carbon bond under the catalysis of a Pd(0) complex. An example is shown in Eq. 48.[231]



(Eq. 48)

Bifunctional electrophiles and stannanes, when coupled, usually give rise to polymeric materials. Many examples of this strategy have been reported, as is evident from Table XXXI. A typical example is shown in Eq. 49.[232]



(Eq. 49)

SCOPE AND LIMITATIONS: THE STANNANE

Unfortunately, most studies on the Stille reaction emphasize a specific type of electrophile, and very few studies examine a particular class of stannanes. General studies of stannane reactivity are therefore lacking. It is impossible to discuss all examples in which a particular type of stannane has been used. In this section we attempt to focus on a limited number of more general papers in an effort to delineate the current scope and limitations in the use of stannanes for the Stille reaction.

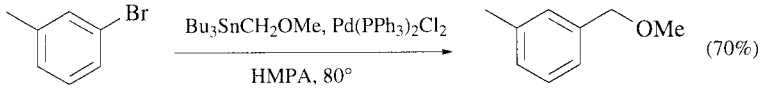
Alkylstannanes

It is generally accepted that transfer of alkyl groups from tin is much slower than that of unsaturated substituents.[6] Indeed, it is this property that makes the methyl and especially the butyl group such excellent "dummy," i.e., "nontransferable," ligands. Nevertheless, in many cases coupling of tetraalkylstannanes occurs in high yields at elevated temperatures. Among the tetraalkylstannanes, tetramethylstannane and tetrabutylstannane are most often used, the former being more reactive. The coupling of these stannanes with aryl and benzyl halides is carried out in HMPA and proceeds in good yields.[19] Use of triphenylarsine as ligand facilitates the coupling of these sluggish nucleophiles with aryl triflates.[30]

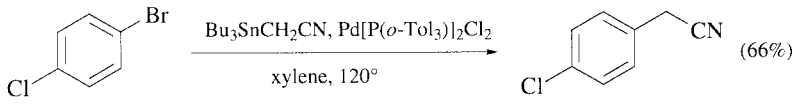
One of the problems associated with the coupling of symmetrical tetraalkylstannanes is that only the first alkyl group is transferred at a sufficient rate to be of synthetic utility,[6] successive transfer becoming more and more difficult with increasing halogen substitution at tin. The need therefore arises for the use of "dummy" ligands; selectivity in the transfer of alkyl groups, however, is quite poor. In special cases, when the alkyl group is activated by particular substituents, some selectivity may be observed. Thus, benzyl trialkylstannanes selectively transfer the benzyl group[27] with inversion of configuration at carbon.

The reaction is facilitated by electron-withdrawing substituents on the aryl ring of the stannane.

Other activated stannanes have been coupled successfully, including transfer of hydroxymethyl,[233] methoxymethyl,[234] and cyanomethyl[235] groups onto a number of aryl bromides (Eqs. 50 and 51).

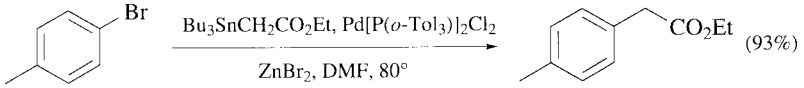


(Eq. 50)



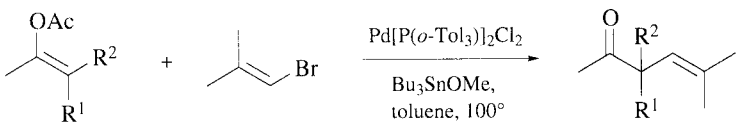
(Eq. 51)

The successful coupling of ethyl α-(tributylstannyl)acetate is reported; the addition of Zn(II) salts is needed for optimum results (Eq. 52).[236] Unfortunately, in none of these studies was a quantitative assessment carried out regarding the transfer selectivity of the activated alkyl vs. the "dummy" butyl group.



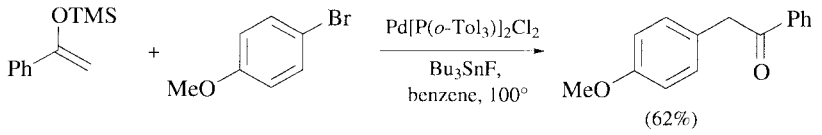
(Eq. 52)

Acetonylation is also possible using acetonyltributylstannane,[237] but in general these α-stannyl ketones are unstable, and their coupling is best carried out by generating them in situ from enol acetates[238–240] or enol silanes.[241] This reaction amounts to a net α-arylation (or alkenylation) of enolates, a rather difficult operation. The above methodology, however, is limited: Only methylene enolates are arylated in good yields, whereas more substituted derivatives couple poorly (Eqs. 53[240] and 54[241]). Further synthetic studies in this important area are warranted.



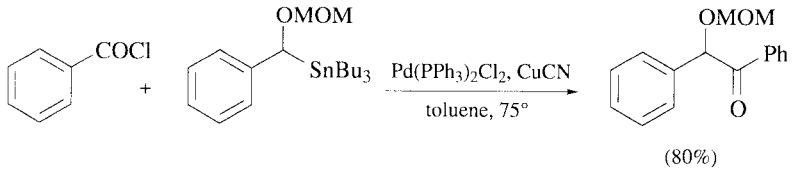
R^1	R^2	
H	H	(62%)
H	Me	(35%)
Me	Me	(8%)

(Eq. 53)



(Eq. 54)

Cyclopropyltributylstannane transfers the cyclopropyl group in low yield.[126] The coupling of α-amino- and α-alkoxystannanes[242] with acyl chlorides takes place in good yields and with retention of configuration at the sp^3 carbon of the stannane, provided Cu(I) salts are added as cocatalysts (Eq. 55).[243] The intermediacy of an organocopper species has been implicated. 4-(Tributylstannyl)-2-azetidinones also couple with acid chlorides.[244]

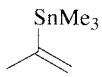


(Eq. 55)

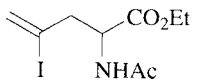
An important advance in the selective transfer of alkyl groups from tin has been reported.[41] Using alkylstannanes **10**, selective transfer of alkyl groups, including *sec*-butyl and α-trimethylsilylmethyl, is achieved under rather mild conditions. Further research is needed to expand the synthetic utility of systems containing a substituent capable of triggering pentacoordination at tin.

Alkenylstannanes

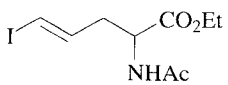
The coupling of alkenylstannanes with a variety of electrophiles is a quite general reaction, and it is difficult to find specific limitations in the literature. Some failures, however, have been reported. Most studies on the cross-coupling of alkenylstannanes are limited to readily accessible 1,2-disubstituted substrates. These couple efficiently and often with good stereospecificity.[47] More heavily substituted or more complex stannanes couple sometimes with difficulty or not at all. In particular, alkenylstannanes that bear another substituent α to tin appear difficult to couple. For example, stannane **14** does not couple with internal alkenyl iodide **15**, but couples normally with its terminal isomer **16**.[244a] This difference is most likely due to steric hindrance.



(14)

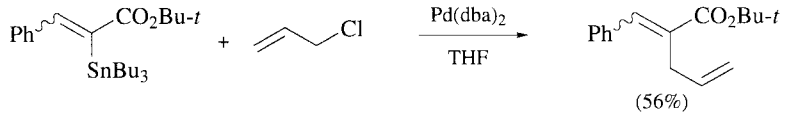


(15)



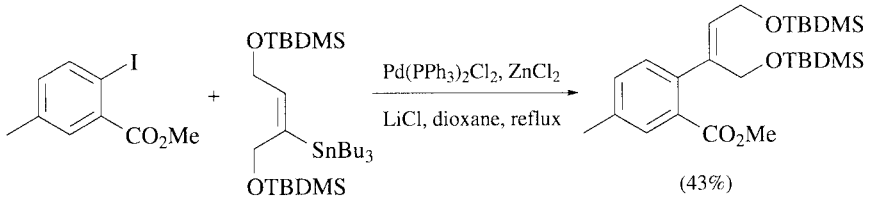
(16)

Methyl α-(tributylstannyl)acrylates couple abnormally with iodobenzene, owing to their tendency to yield cine-substitution products (vide infra).[245] Normal *ipso* reactivity is restored by the addition of Cu(I) salts.[246] β-Substituted α-(tributylstannyl)acrylates, however, couple normally with both acyl chlorides[247] and allylic halides (Eq. 56).[248] Evidently, the β substitution dramatically slows the cine-substitution process.



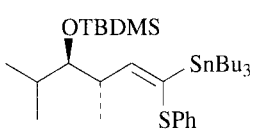
(Eq. 56)

α-Styrylstannanes yield cine substitution when coupled with aryldiazonium compounds (vide infra),[249] but can be coupled with acyl chlorides without side reactions.[250] Again, β substitution restores normal Stille reactivity, although in poor yield.[251] In general, densely substituted stannanes react poorly, and their coupling must be carefully optimized. An example from the total synthesis of lacrimin A is shown in Eq. 57.[252]

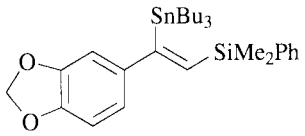


(Eq. 57)

Examples where every attempt to induce coupling fails include stannanes **17**[253] and **18**.[51] Other stannanes with seemingly comparable steric hindrance, however,

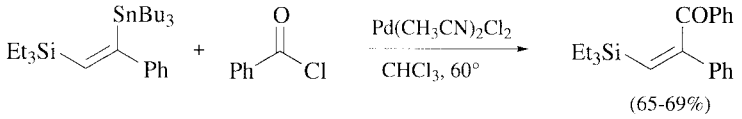


(**17**)



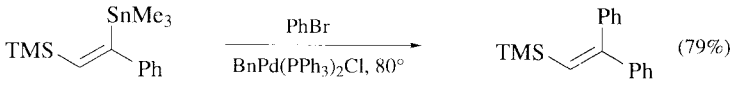
(**18**)

couple under standard conditions. For example, α-trialkylsilyl substitution in alkenyltrimethylstannanes prevents Stille coupling with allyl halides because the methyl groups on tin transfer more rapidly.[254] However, 1-triethylsilyl-2-trialkylstannyl-1-alkenes similar to **18** can be coupled with acyl halides (Eq. 58).[255]

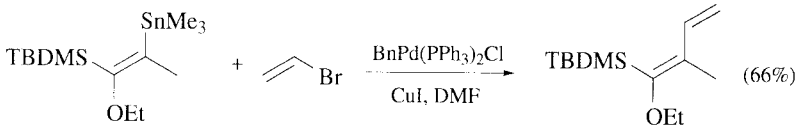


(Eq. 58)

α-Phenyl and α-methyl substitution of olefinic stannanes does not seem to hinder Stille coupling in some cases (Eqs. 59[49] and 60[256]). The latter coupling, however, is successful only in the presence of cocatalytic copper. This may represent a general solution to the problem of coupling hindered alkenylstannanes.

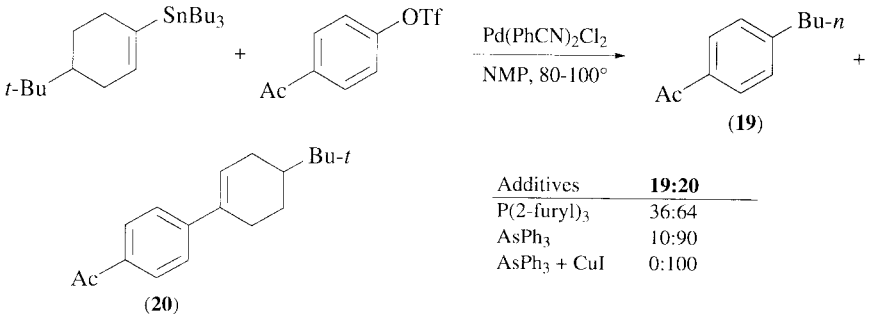


(Eq. 59)



(Eq. 60)

Another example of this trend is shown by the difficult coupling of cyclohexenylstannanes with aryl triflates. Butyl transfer is an important side reaction here, unless one employs cocatalytic copper (Eq. 61).[33]



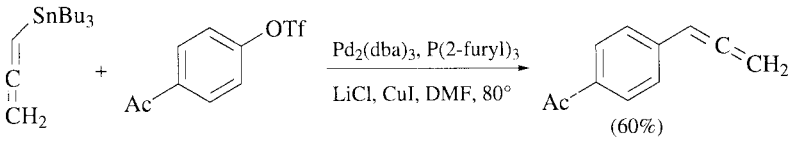
Additives	**19:20**
P(2-furyl)$_3$	36:64
AsPh$_3$	10:90
AsPh$_3$ + CuI	0:100

(Eq. 61)

In general, 1-tributylstannylcycloalkenes couple very sluggishly under Stille conditions,[257,258] and the reason must be attributed to some type of steric hindrance. β-Stannyl enones,[259] β-sulfonyl alkenylstannanes,[260] and 3- (or 4-) tributylstannyl-2-(5*H*)-furanones[261] have been made the objects of special inves-

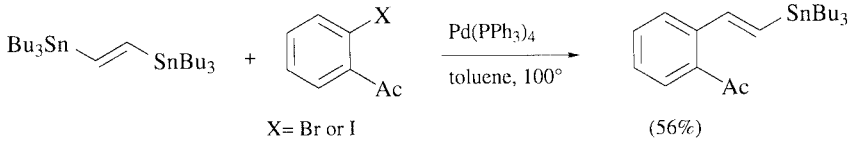
tigations. In each case coupling with electrophiles is successful. Other types of alkenylstannanes that have been separately investigated include a variety of fluorinated alkenyl stannanes,[262-266] cyclobutenone,[267] and cyclobutenedione[12,64,268] stannanes.

α-Alkoxy-substituted alkenylstannanes seem to be especially reactive partners in the Stille reaction.[269-271] β-Alkoxyalkenylstannanes have also been coupled successfully.[272-274] Polyunsaturated alkenylstannanes have been studied in a few sporadic cases. Thus, allenylstannanes couple with aryl iodides[275] and triflates in modest yields (Eq. 62).[276] With allylic electrophiles, these stannanes



(Eq. 62)

yield propargylic derivatives, the result of allylic inversion.[165] A variety of dienyl-[277] and ynenyl-[278] stannanes have also been coupled with a number of electrophiles. 1,1-Distannylalkenes have been coupled with allylic halides, double substitution being the result.[254] With 1,2-bis(stannyl)ethylenes, on the other hand, monocoupling can be controlled to produce substituted alkenylstannanes. A large excess of the bis(stannane) is not necessary, because the first cross-coupling is faster than the second one. The second coupling can be carried out under more forcing conditions (Eqs. 13 and 63[279]).

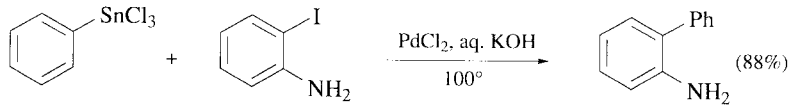


(Eq. 63)

Aryl and Heterocyclic Stannanes

Arylstannanes couple readily with a variety of electrophiles. Both electron-withdrawing and electron-releasing substituents on the aryl ring can accelerate coupling, an indication of a dual mechanism for the transmetallation (see mechanistic section).[30] In general, however, electronic effects in the transmetallation are minor. On the other hand, steric effects can be important. An alkyl group *ortho* to the tin residue can slow the coupling by a factor of ca. 20. An *ortho* methoxy group, which is sterically much smaller, leads to only a 2-fold rate reduction.[30] In general, therefore, coupling with *ortho*-substituted arylstannanes can be difficult, and substantial transfer of the dummy ligand can take place (see section on side reactions). This problem has been tackled successfully by using Cu(I) salts. Under these conditions aryl group transfer is exclusive.[30,280]

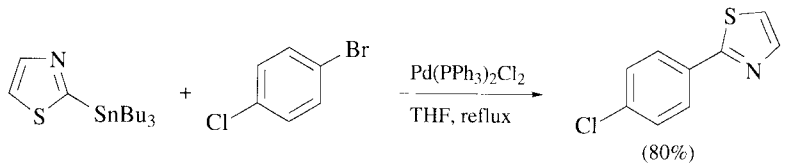
Aryl trichlorostannanes have been used as coupling partners in aqueous media employing vigorous conditions,[281] under which the tin-chlorine bond is probably hydrolyzed to a tin-hydroxy species, because coupling does not take place in organic media (Eq. 64).[282] This protocol obviates the use of organic solvents, but



(Eq. 64)

appears limited to water-soluble electrophiles. In a similar vein, tetrabutylammonium difluorotriphenylstannate can be used to transfer a phenyl group onto vinyl triflates.[283]

Pyridyl-, quinolyl-, and isoquinolylstannanes have been the objects of separate studies. They couple smoothly with acyl chlorides.[284,285] Electron-rich heterocyclic stannanes, such as the 2-furyl-, 2-thienyl-, 2-pyrrolyl-, and 2-thiazolylstannanes, couple with aryl halides under rather mild conditions. An example is shown in Eq. 65.[286]

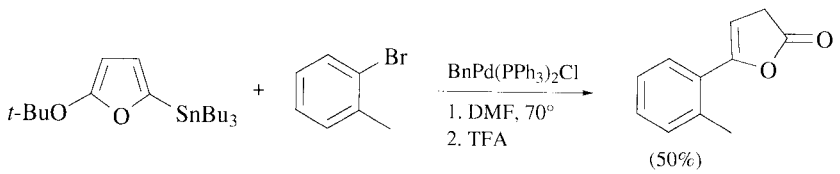


(Eq. 65)

3,4-Distannylfurans have been studied in great detail as bifunctional reagents,[287] and 3-stannylfurans have been used as substrates with acyl chlorides.[288] 2-Stannyl-[289,290] and 3-stannylindoles[291] have also been coupled with a variety of electrophiles. 5-Isoxazolylstannanes have been coupled with aryl iodides.[292,293]

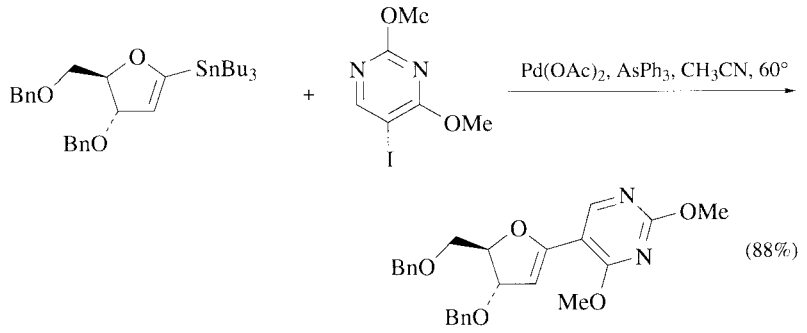
2-Tributylstannylfuran couples with a number of α-chlorocyclobutenones in low yields, and it is postulated that this is due to further attack of the electrophile on the 5 position of the heterocycle, which is very electron-rich. These electrophilic palladations of electron-rich heteroaromatics are indeed precedented.[294] However, 5-trimethylsilyl-substituted stannylfurans couple in excellent yields.[295]

Equation 66 shows the application of the Stille reaction to the synthesis of 5-substituted furanones.[296]



(Eq. 66)

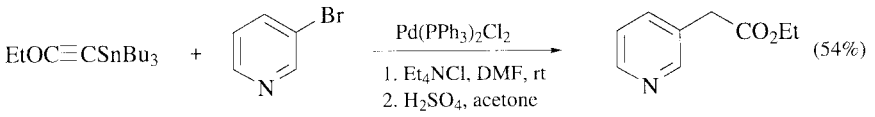
Couplings of nonaromatic, heterocyclic stannanes are often found in the literature. A popular target has been α-substituted glycals.[297–300] One example is shown in Eq. 67.[301]



(Eq. 67)

Alkynylstannanes

Alkynylstannanes couple smoothly with a variety of electrophiles, including alkenyl halides.[47] This class of stannanes is the most reactive of all, according to Stille,[6] and few limitations exist. Alkoxy-substituted alkynylstannanes have been used in an interesting approach to α-aryl and heteroaryl acetates (Eq. 68).[302]



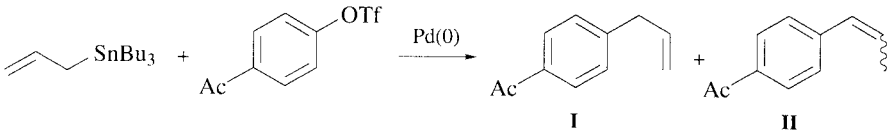
(Eq. 68)

In general, although these stannanes are quite reactive, their use in cross-coupling chemistry is often unnecessary, since terminal alkynes couple directly with organic electrophiles using a palladium catalyst, cocatalytic copper, and amines as bases (Sonogashira coupling).[303]

Allylstannanes

Allylstannanes have been underutilized in the Stille coupling, presumably because of the difficulties with the synthesis of regiochemically defined substrates and their tendency to undergo allylic isomerization, thus making it hard to predict the regiochemistry of the coupling. Simple allylic stannanes couple more slowly than alkenylstannanes,[6] but at acceptable rates in most cases. One problem that has been documented with allylstannanes is the tendency of the double bond to move into conjugation after coupling, especially in reactions with acyl halides[146] and aryl triflates.[189] This can sometimes be prevented by operating

at lower temperatures using tri(2-furyl)phosphine as the palladium ligand (Eq. 69).[11]

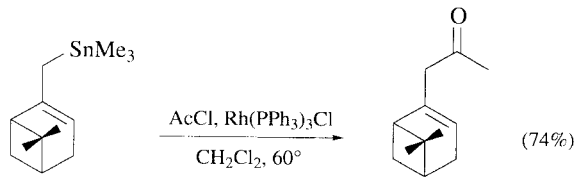


Conditions	
$Pd(PPh_3)_4$, LiCl, dioxane, 98°	**I** (18%) + **II** (54%)
$Pd_2(dba)_3$, LiCl, $P(2\text{-furyl})_3$, NMP, rt	**I** (78%)

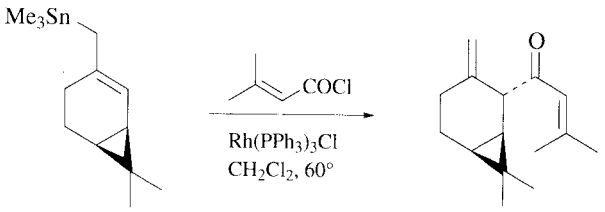
(Eq. 69)

Allylstannanes may couple at the α or the γ position, and not enough data are presented in the literature to draw firm conclusions.[2] Thus, crotyltrimethylstannane couples with acyl chlorides to yield a 1:1 mixture of α and γ products, but the product resulting from γ attack predominates at lower temperatures.[146]

Terpenic allylstannanes undergo regioselective Rh-catalyzed acylation at the α or γ position, depending on the structure of the substrate (Eqs. 70 and 71).[150,304]

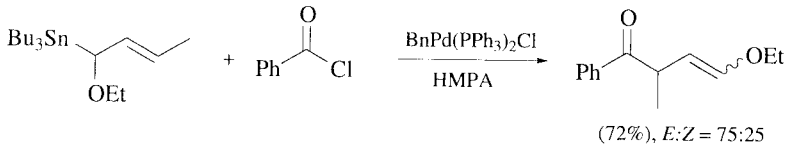


(Eq. 70)



(Eq. 71)

A few special classes of allylstannanes have been described as substrates for the Stille reaction. An interesting one is shown in Eq. 72.[305] Thus, α-alkoxyallyl-

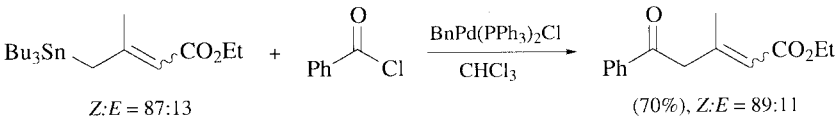


(72%), *E*:*Z* = 75:25

(Eq. 72)

stannanes couple with acyl chlorides to yield the allylically inverted β,γ-unsaturated ketones, which can be further converted to 1,4-dicarbonyl compounds by acid hydrolysis.

On the other hand, γ-carbalkoxy-substituted allylstannanes undergo selective coupling at the α position with alkenyl, aryl, and acyl halides (Eq. 73), but only at



(Eq. 73)

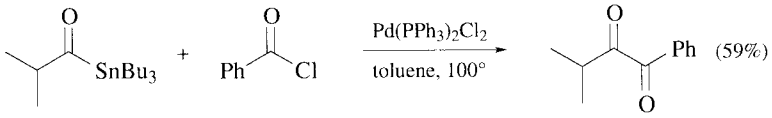
the γ position with allylic electrophiles.[306] This confirms early results, in which allylstannanes were coupled with allylic electrophiles with predominant allylic inversion.[35,36] Further aspects of this reaction are discussed in the mechanistic section.

The use of an allylic bis(stannane) as an annulation reagent has already been discussed (Eq. 23).

In conclusion, although allylstannanes are useful partners in the Stille reaction, they have been used infrequently, probably because the regiochemistry of the coupling is still unpredictable. This area certainly deserves further in-depth research.

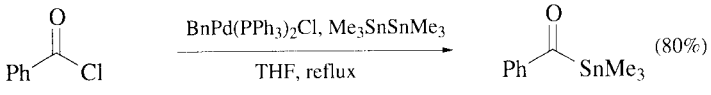
Other Stannanes

Acylstannanes have been coupled in a few cases with acyl chlorides to provide unsymmetrical α-diketones (Eq. 74).[307] A CO atmosphere may help to prevent decarbonylation.



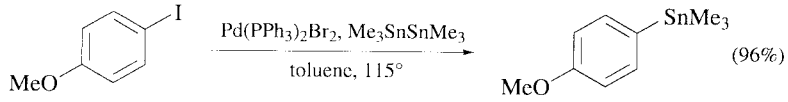
(Eq. 74)

Distannane derivatives are useful reagents in conjunction with a variety of electrophiles. Upon reaction with acyl halides, they yield mixtures of symmetrical ketones and α-diketones. Diketones predominate under a CO atmosphere.[308] Under suitable conditions, the reaction stops at the acylstannane stage, and this is preparatively useful (Eq. 75).[309]



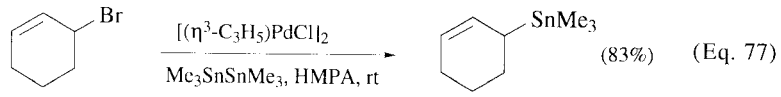
(Eq. 75)

The couplings of hexamethyl- and hexabutyldistannanes with aryl bromides and iodides, and also with benzylic bromides, are high yielding, homocoupling of the electrophile being the only detectable side reaction (Eq. 76). Most substituents on the aryl ring are tolerated except *p*-amino and *p*-nitro. Under these conditions, allyl and alkenyl halides give the corresponding stannanes in low yields.[169]



(Eq. 76)

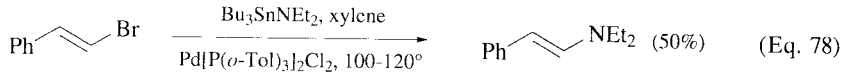
The coupling of distannanes with aryl halides has been studied independently,[310,311] and another investigator found that some of the above limitations can be overcome by using "ligandless" conditions.[312,313] A problem with this protocol is, however, disproportionation of the distannane, and an excess of the reagent must be used. A typical example of this protocol as it applies to allylic acetates, bromides, and chlorides is shown in Eq. 77.[314] Nickel catalysis has also been used in this reaction.[315]



(Eq. 77)

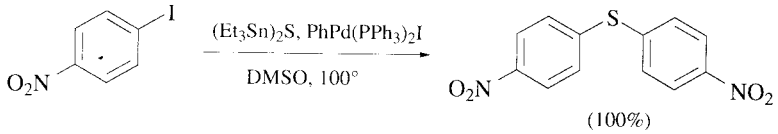
The reaction of distannanes with vinyl triflates is an important route to regiochemically and geometrically defined vinylstannanes, as previously shown (Eq. 34).[176] Even some activated vinylic chlorides couple with hexamethyldistannane.[260]

Aminostannanes react with electrophiles, such as aryl and alkenyl bromides, in variable yields (Eq. 78).[90,316] This process was recently reinvestigated and improved,[91,92] as already illustrated (Eq. 15).



(Eq. 78)

The formation of C-S bonds via organotin sulfides is also well precedented. Alkenyl,[317] aryl,[318] and heteroaryl halides[319] participate. An example is shown in Eq. 79.[320]



(Eq. 79)

Among related reactions that have received only scant attention, (trimethylstannyl)diphenylphosphine couples with iodoaromatics to provide substituted triarylphosphines,[321] and tin alkoxides have been coupled with allylic electrophiles.[322] These methods have not been further applied to organic synthesis.

CARBONYLATIVE COUPLINGS

When a Stille coupling is carried out under a CO atmosphere, carbonyl incorporation under catalytic conditions is possible. The reaction is general for alkenyl, aryl, heteroaryl, and allyl electrophiles (Eq. 80).

$$R^1\text{-}X + CO + R^2SnR^3_3 \xrightarrow{[Pd(0)]} R^1(CO)R^2 + R^3_3SnX \qquad \text{(Eq. 80)}$$

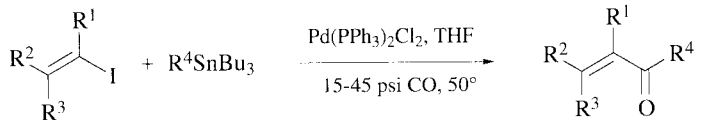
The earliest report of a successful carbonylative coupling between a stannane and an organic halide showed that several simple aryl, alkenyl, and benzyl halides could be coupled with simple stannanes under rather vigorous conditions (Eq. 81).[323] A considerable body of research has been reported as this procedure has been refined and its scope defined.

$$R^1\text{-}X + CO + R^2_4Sn \xrightarrow[\substack{450 \text{ psi CO, } 120^\circ \\ \text{HMPA}}]{PhPd(PPh_3)_2I} R^1COR^2 \qquad \text{(Eq. 81)}$$

R^1 = Ph, $PhCH_2$, PhCH=CH, EtO_2CCH_2; R^2 = Me, Bu, Ph; X= Cl, Br, I

Alkenyl Halides

The palladium-catalyzed carbonylative coupling of alkenyl iodides with alkenylstannanes affords the corresponding dialkenyl ketones in good yield (Eq. 82).[324] The reaction takes place under neutral, mild conditions (40–50°,

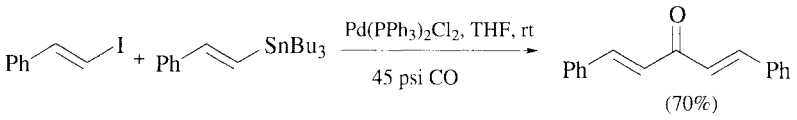


(Eq. 82)

R^4 = alkenyl

THF) and low CO pressure (1–3 atm). One may assume that all of the functional groups compatible with the standard, noncarbonylative cross-coupling reactions are also compatible with the carbonylative conditions, although no comprehensive study has been reported.

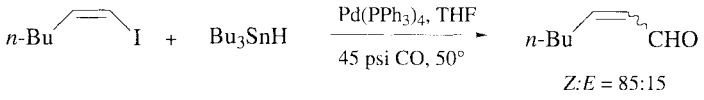
The outcome of the reaction can be sensitive to CO pressure, and slightly elevated pressures (45 psi) typically eliminate the competing direct coupling. An example can been seen in Eq. 83. β-Iodostyrene requires 45 psi CO for exclusive



(Eq. 83)

carbonylative coupling, because under 15 psi CO a 1:1 mixture of direct and carbonylative coupling products is formed.[324] Double bond isomerization can be a problem. Alkenes with *Z* geometry have a propensity to isomerize, especially under harsh reaction conditions.

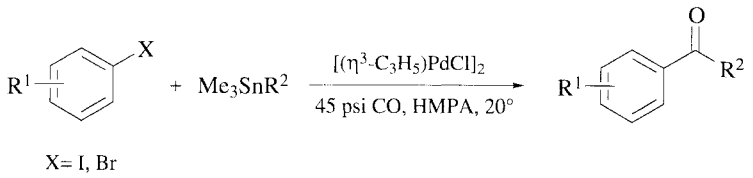
Alkenyl iodides can also be transformed into the corresponding α,β-unsaturated aldehydes through carbonylative cross-coupling using tributyltin hydride as a partner. As with ketone formation, partial *Z/E* isomerization is a problem (Eq. 84).[325]



(Eq. 84)

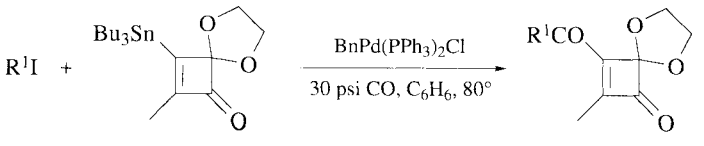
Aryl and Heterocyclic Halides

Aryl iodides and bromides, but not chlorides, can be carbonylatively coupled with organostannanes to furnish ketones. The number of examples in the literature for aryl iodides and bromides is limited, and although bromides couple, the yields are low. The moderate interest in aryl halides is due to the extensive versatility of aryl triflates in this coupling strategy. The protocol using "ligandless" conditions is illustrated in Eq. 85.[326,327]



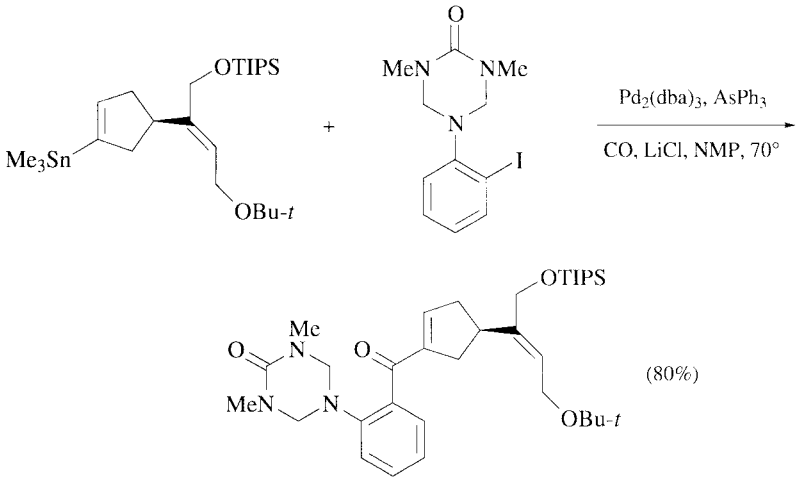
(Eq. 85)

A recent example, which uses more vigorous conditions but employs a nonpolar solvent, is shown in the coupling of aryl and heteroaryl iodides with cyclobutenedionestannanes (Eq. 86).[268]



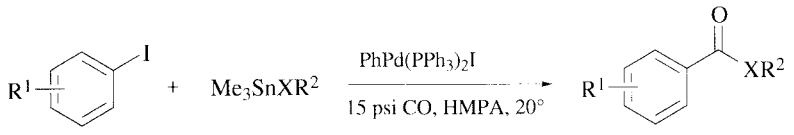
(Eq. 86)

The role of additives, as well as potential ligand effects, has not been experimentally determined for the carbonylation reaction. There is a report on the beneficial effect of $AsPh_3$ in the context of a key step in a total synthesis of strychnine (Eq. 87).[328]



(Eq. 87)

A variety of heterostannanes (R_3Sn-OR′, -SR′, -NR'_2) can also be used as nucleophilic partners in the carbonylative Stille reaction (Eq. 88).[329,330] Esters and

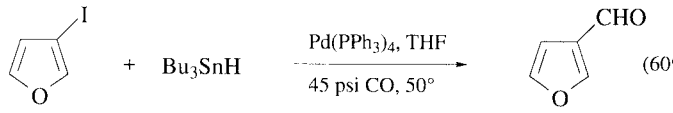


(Eq. 88)

amides are formed under mild conditions using HMPA as solvent. Electron-withdrawing groups on the aromatic ring appear to slow down CO insertion, and when such functional groups are present, there is competing direct coupling between the aryl moiety and the heterostannane.

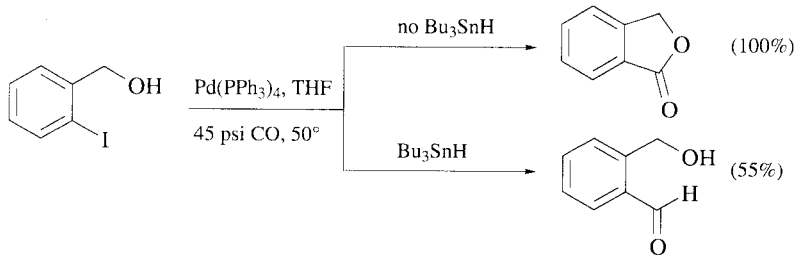
The formylation of aryl iodides appears to be a general process. Aryl bromides furnish the desired aldehydes in moderate to low yield. A competing side reaction is direct reduction of the halide. Aryl iodides containing electron-releasing groups are formylated under 15 psi CO, whereas those containing electron-withdrawing groups need at least 45 psi CO to minimize reduction. Slow addition of tributyltin hydride to the reaction mixture under CO pressure is necessary in

order to optimize the ratio of aldehyde to reduced product. A single example using 3-iodofuran demonstrates that heterocycles can also be formylated in this manner (Eq. 89).[325,331]



(Eq. 89)

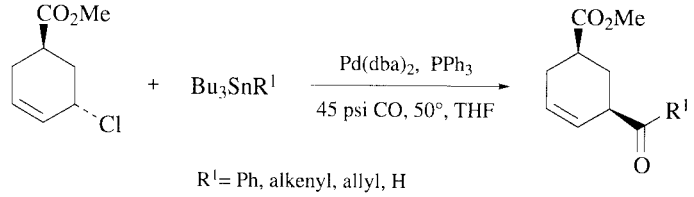
Ortho substituents adversely affect the yield, and those containing a heteroatom also present a unique problem: the potential for competitive alkoxycarbonylation or amidation (Eq. 90).[332]



(Eq. 90)

Allylic and Benzylic Halides

Allyl and benzyl chlorides insert CO when reacted with stannanes, forming the corresponding ketones.[24] Diallylic ketones have been prepared under very mild conditions.[333] Higher pressures of CO favor ketone formation over direct coupling. The major side reaction is the carbonylative homocoupling of the organostannane. Carbonylative couplings occur with inversion of stereochemistry at the halide-bearing carbon, at least under the conditions specified in Eq. 91.[24]



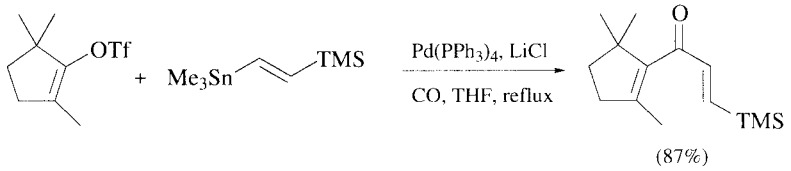
(Eq. 91)

R^1 = Ph, alkenyl, allyl, H

Allyl and benzyl chlorides are also formylated readily. Double bond migration to the α,β-unsaturated aldehyde is a common problem with allylic chlorides, as is competing reduction.[331]

Alkenyl Sulfonates

Alkenyl triflates are popular substrates for carbonylative coupling, which leads to α,β-unsaturated ketones and aldehydes. Many coupling examples can be found in the literature, and the scope of the reaction is broad. This strategy has been used in the total synthesis of natural products such as $\Delta^{9(12)}$-capnellene (Eq. 92)[334] and jatrophone.[335]

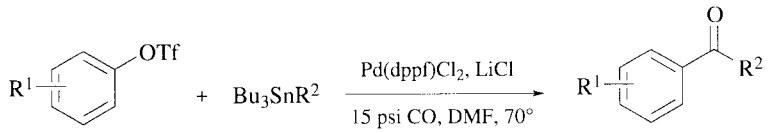


(Eq. 92)

Aryl-, alkynyl-, and alkenylstannanes all couple well, but double bond migration is a problem with allylstannanes. It has been reported that lithium chloride is a required additive for successful reaction. In several examples, the addition of zinc chloride improves the yields.[335] Macrocycles can be effectively prepared through intramolecular carbonylative ketone formation using a polymer-supported palladium catalyst.[186]

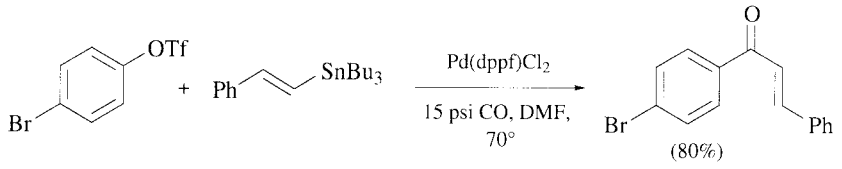
Aryl and Heterocyclic Sulfonates

The palladium-catalyzed carbonylative coupling of aryl triflates to give aryl ketones takes place under mild conditions.[336] Alkenyl-, alkynyl-, and arylstannanes all work well as coupling partners, but the presence of electron-withdrawing groups (e.g., NO_2) in these stannanes adversely affects the reaction because the aryl triflate is cleaved at the oxygen-sulfur bond. Allylstannanes are ineffective, resulting in high proportions of directly coupled products. As with alkenyl triflates, the presence of lithium chloride is required, but here the catalyst dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium gives superior yields (Eq. 93). If a competitive coupling site such as bromide is present on the



(Eq. 93)

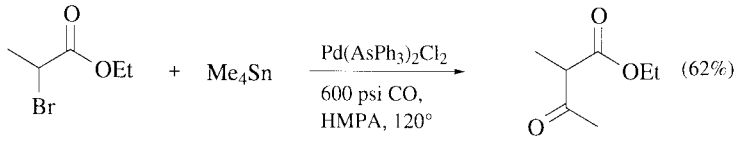
aryl triflate, carbonylative cross-coupling takes place selectively at the triflate moiety even in the absence of lithium chloride (Eq. 94).



(Eq. 94)

Miscellaneous Substrates

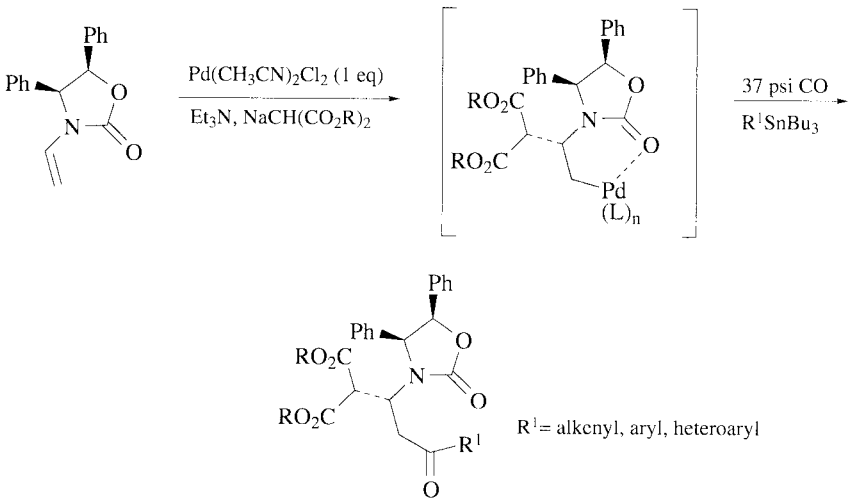
Some activated organic halides containing β hydrogens can be carbonylatively cross-coupled under high CO pressures, and the ligand of choice for this reaction is triphenylarsine (Eq. 95).[337] The reported scope of this reaction is limited to the



(Eq. 95)

use of α-phenethyl bromide, ethyl α-bromopropionate, and α-phenylpropyl bromide as substrates for the formation of methyl ketones, and the major side product is the result of elimination to the corresponding alkene. In a single example tetraphenylstannane has also been coupled.[323]

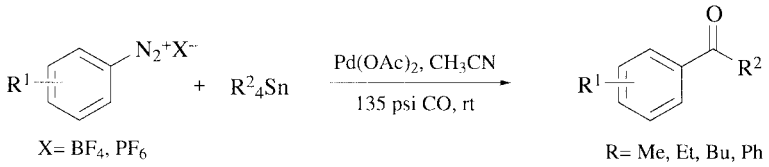
An interesting example of carbonylation has been applied to the synthesis of (+)-negamycin and (−)-5-*epi*-negamycin (Eq. 96).[338] The intermediate from the



(Eq. 96)

palladium-assisted alkylation of an optically active enecarbamate is effectively carbonylated in the presence of an alkenylstannane to furnish the desired optically active ketone. Although this transformation requires a stoichiometric amount of palladium, it appears to be quite general and works well with a variety of alkenyl, aryl, and heteroarylstannanes.[339]

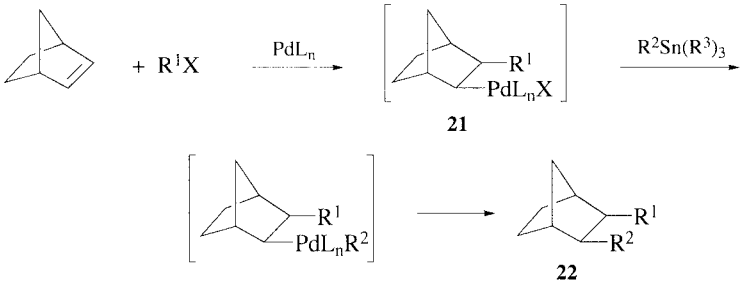
Aryl diazonium salts are also effective substrates for ketone formation (Eq. 97).[340] Diaryl and arylalkyl ketones can be prepared under very mild conditions. The presence of electron-withdrawing and electron-releasing groups on the ring is tolerated, and products from direct coupling are not observed.



(Eq. 97)

COMPLEX SYNTHETIC SEQUENCES INVOLVING TIN-TO-PALLADIUM(II) METATHESIS STEPS

A strategy that is receiving considerable attention in palladium chemistry is the tandem Heck-Stille sequence. Under suitable conditions, the organopalladium(II) intermediate resulting from a Heck insertion can be trapped by an organostannane, resulting in the formation of two C-C bonds at once. This strategy works best when the Heck adduct cannot undergo palladium hydride β elimination. The norbornyl system is used often in this sequence because the initially formed adduct **21** (Scheme 3) has no easily accessible *syn* β hydrogens, which are needed for a stereocontrolled elimination, and it is stable enough to be intercepted by the stannane to yield **22**.

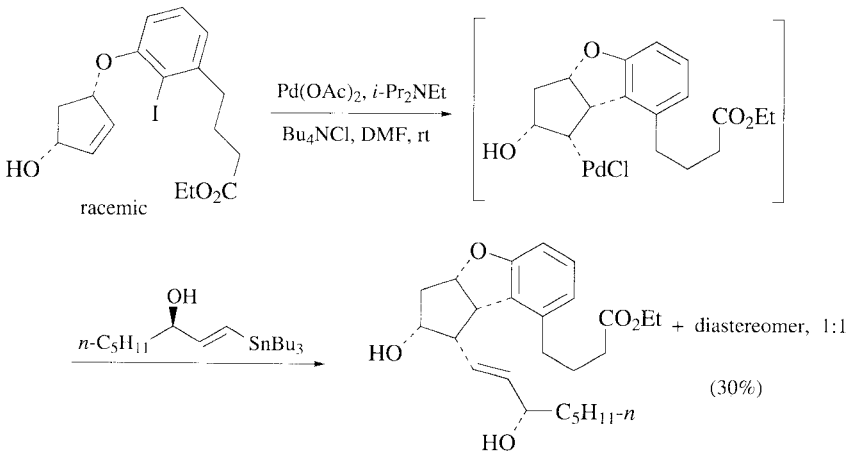


Scheme 3. The Tandem Heck/Stille Strategy.

This strategy can be used in conjunction with $Pd(PPh_3)_4$ as catalyst, alkenyl or aryl bromides as electrophiles, and alkenyl-, alkynyl-, aryl- or allylstannanes as traps. The yields are low to fair, and direct coupling is the major side process.[341]

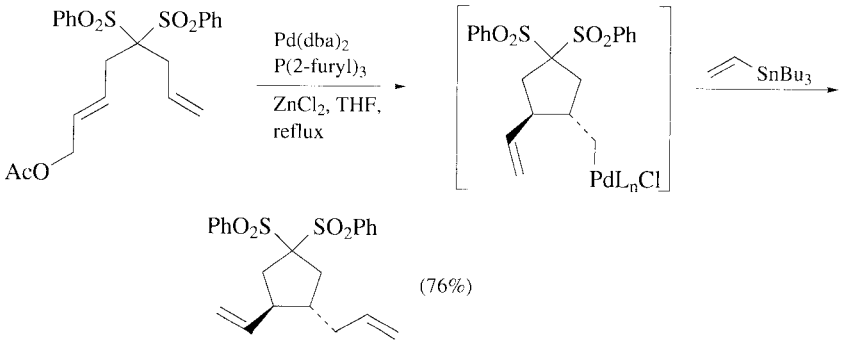
Allyl, benzyl, and acyl halides do not participate in this reaction. Among the stannanes that do not participate are the activated alkylstannanes, aminostannanes, alkoxystannanes, and thioalkoxystannanes.[342] For the analogous reaction with norbornadiene as substrate, the best ligand is (*o*-tolyl)diphenylphosphine. The additive tetraethylammonium chloride is needed for best results.[343]

More generally useful is the analogous sequence in which the initial Heck insertion is intramolecular. An elegant application to the synthesis of benzoprostacyclins is shown in Eq. 98.[344]



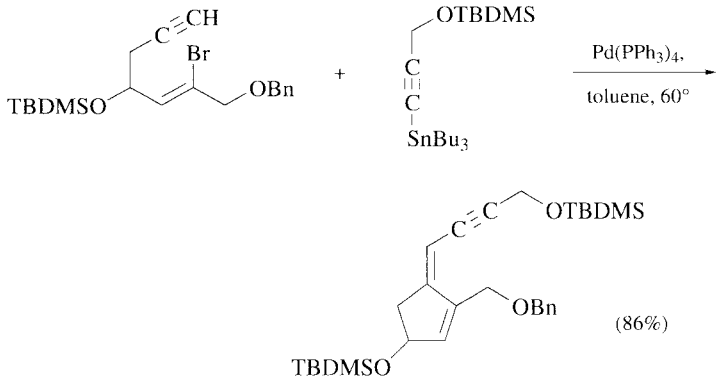
(Eq. 98)

This method can be extended to situations in which the initially formed organopalladium(II) intermediate is, in principle, capable of undergoing ready β-hydride elimination. Nevertheless, fine-tuning of the process with the help of tri(2-furyl)phosphine to accelerate the metathesis, in conjunction with zinc chloride, affords the Heck-Stille coupling product in high yield. The generality of these observations remains to be verified (Eq. 99).[345]



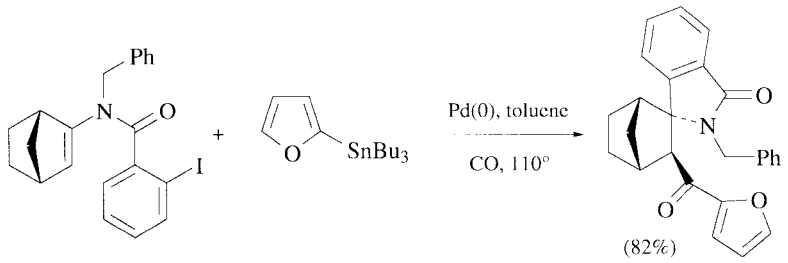
(Eq. 99)

When C-C triple bonds are used as intramolecular traps in this strategy, competing β elimination is not possible, and the tandem process is often successful, the only competition originating from the direct coupling (intermolecular) process. The initial 5-*exo* and 6-*exo* cyclizations are faster than direct coupling, and the tandem process succeeds, even though Al, Zr, and Zn derivatives often yield better results.[346–350] An application of this strategy to a neocarzinostatin synthesis is shown in Eq. 100.[351–353]



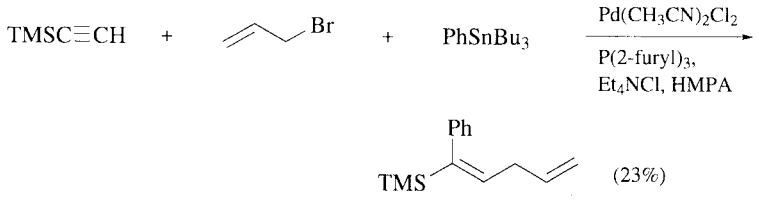
(Eq. 100)

Similar applications to the synthesis of vitamin D are reported.[354] Carbon monoxide insertion can be included in this sequence. An example of this interesting intramolecular Heck-CO insertion-transmetallation strategy is shown in Eq. 101.[355]



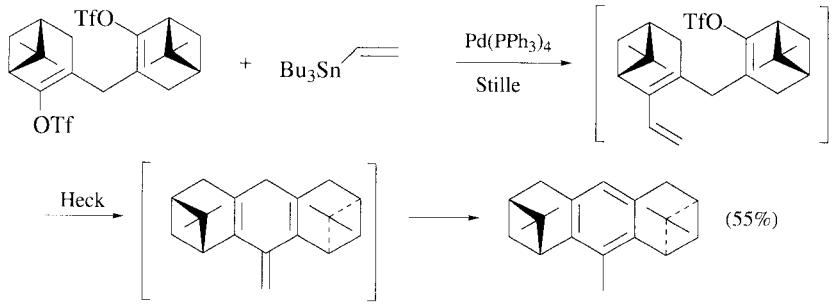
(Eq. 101)

In special cases, even the intermolecular insertion of alkynes can be carried out. When the electrophile is an allylic halide, apparently the direct coupling with stannanes is slow enough that the alkyne is first to react with the intermediate allylpalladium complex. Aryl-, alkenyl-, and alkynylstannanes can be used as traps. The yields, however, are quite modest (10–53%). An example is shown in Eq. 102.[356] A Ni(0)-catalyzed version of this reaction proceeds in higher yields, at least with alkynylstannanes as traps.[357]



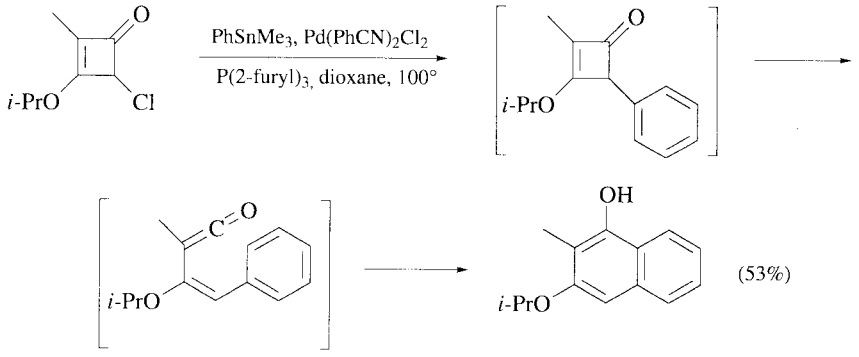
(Eq. 102)

An interesting variant of the tandem Heck-Stille protocol is the reverse strategy. A bis(electrophile) can undergo monocoupling with an alkenylstannane, and this is followed by a fast intramolecular Heck reaction (Eq. 103).[358] This interest-



(Eq. 103)

ing strategy deserves further investigation. There are a number of interesting strategies for the construction of aromatic rings based on the ring opening of complex cyclobutenones, which on thermolysis rearrange to arenes via dienylketenes, as exemplified in Eq. 104.[359] Both alkenyl- and arylstannanes can be

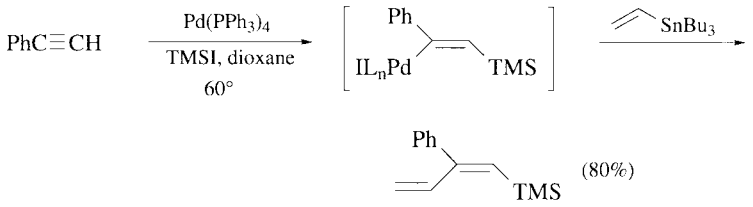


(Eq. 104)

used in this coupling, leading to benzene and naphthalene derivatives, respectively, after electrocyclic ring opening/reclosure.

Variants of this technique are the synthesis of benzofurans and benzothiophenes,[295] an approach to naphthoquinones and anthraquinones,[360] and new routes to benzocyclobutenedione derivatives,[361] azaheteroaromatics,[362] and 2-pyrones, the last involving a carbonylative step.[363]

Finally, the oxidative addition of Pd(0) onto silicon halides can be incorporated in a three-component condensation involving 1-alkynes, TMSI, and alkenyl-, alkynyl-, or allylstannanes. An example of this powerful protocol is shown in Eq. 105.[364]



(Eq. 105)

The use of complex strategies centered on, or terminated by, cross-coupling chemistry is an important and expanding synthetic tool that allows the formation of two or more C-C bonds, usually in a regioselective and stereoselective manner.

SIDE REACTIONS

Homocoupling reactions

Homocoupling of stannanes is apparently the most common side reaction observed when attempting Stille couplings.[30,106,204,286,297,299,365] The reaction may even be synthetically useful when symmetrical dienes[366] or biaryls[30] are desired. An obvious source of small amounts of homocoupled product is the reaction of the stannane with the Pd(II) precatalyst when this is employed. Each molar equivalent of Pd(II) reacts with two equivalents of the stannane to afford a symmetrical product. In many cases, however, larger amounts of homocoupling products are observed than can be accounted for in this way, and homocoupling takes place even when employing preformed Pd(0) catalysts. The reaction involves a catalytic cycle that has a radical component and requires atmospheric oxygen. Insertion of Pd(0) in the carbon-tin bond of the stannane is postulated as the first step of the cycle.[30]

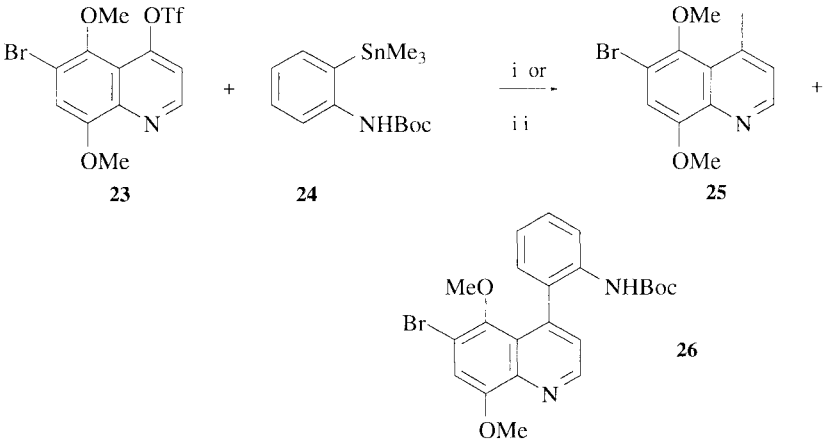
Homocoupling of the electrophile is often observed in transition metal-catalyzed cross-coupling reactions,[367] and there is evidence for a mechanism involving the exchange of organic groups between palladium and tin.[368] These authors used bidentate nitrogen-based ligands, and it is not clear whether this exchange occurs in reactions that use phosphorus-based ligands. A similar phenomenon with PPh_3 as ligand, on the other hand, has been documented.[34]

Transfer of "Nontransferable" Ligands

The Stille reaction usually employs three groups on tin that are not meant to be transferred in the coupling. Overwhelmingly, trialkyl derivatives are used because alkyl groups transfer slowly. Typically, trimethyl- or tributylstannane derivatives are used because of the ready availability of the corresponding trialkyltin halides. Selectivity is not, however, always complete.

For example, phenyltrimethylstannane couples with aryl triflates to yield products resulting from both aryl and methyl group transfer.[189] The selectivity is solvent dependent, dioxane yielding more aryl transfer than DMF or NMP. The phenyl group transfers 37 times more readily than *n*-butyl in NMP, using an aryl triflate as the electrophile. This ratio shows little dependence on the type of ligand. The ratio of the transfer rates of phenyl vs. methyl, on the other hand, is only 5.[30] These data strongly suggest that *n*-butyl groups are preferable to methyl groups as nontransferable moieties. The use of Cu(I) salts as cocatalysts improves this selectivity to >50:1,[33] and this may represent a potentially general solution to the selectivity problem (see also Eq. 61).

An interesting selectivity switch occurs in a hindered Stille coupling using stannane **24**. Whereas exclusive methyl transfer is observed under traditional conditions, use of Cu(I) salts leads to the aryl transfer product **26** in moderate yields (Eq. 106).[280]



Conditions: (i) $PdCl_2$(dppf), DMF, **25** (80%); (ii) $Pd(PPh_3)_4$, LiCl, dioxane, CuBr, 90°, **26** (60-64%).

(Eq. 106)

Other reports of alkyl group transfer in competition with the intended transfer of an aryl group are rather widespread,[55,191,369,370] and alkyl group transfer can sometimes be competitive even with alkynyl[219] and alkenyl coupling.[40,259] Once again, use of Cu(I) has resulted in substantial selectivity improvement in a butyl vs. alkenyl transfer competition.[33]

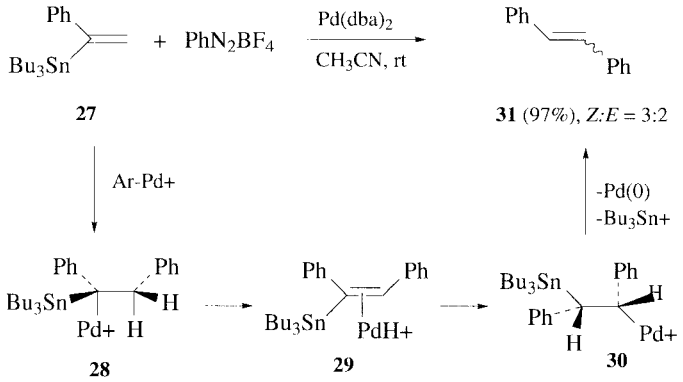
Further studies aimed at more careful quantification of alkyl group transfer as a side process and at discovering new tools to increase selectivity are definitely warranted.

Destannylation

Hydrolytic destannylation, probably brought about by traces of water and/or acids in the reaction medium, has been reported in very few cases, perhaps only because such a process in structurally simple stannanes yields volatile products that are difficult to detect. Organostannanes are quite stable hydrolytically, but when electron-rich aryl- or heteroarylstannanes are employed, destannylation may be a serious side reaction.[371,372]

Cine Substitution

Cine substitution can be a side process in a cross-coupling reaction, and Scheme 4 illustrates an example, together with a proposed mechanism.[204]



Scheme 4. Mechanistic interpretation of cine-substitution.

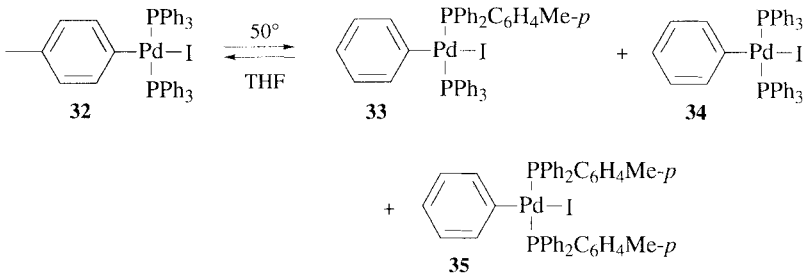
The first step is obviously an insertion of the arylpalladium intermediate across the double bond of the olefin. Evidently, a direct transmetallation is hindered by the α-phenyl substituent on the stannane. The following steps of β elimination and protodestannylation are reasonable and precedented. Another example of cine substitution requires an *anti* β elimination of palladium and hydrogen, which is a stereoelectronically disfavored pathway.[373]

It has been proposed that species like **28** may be able to undergo an unprecedented α elimination of Bu_3SnX to yield a Pd(0)-carbene species. A study of cine substitution with α-(tributylstannyl)acrylate showed that nonpolar solvents favor cine substitution, whereas ligands of different donicity have remarkably little effect on the product distribution.[245] Other authors have independently observed similar cine substitutions,[374–376] and high-yielding Stille coupling can be restored, once again, by using cocatalytic Cu(I).[246]

Cine substitution is a rare event in the coupling of organostannanes and is so far limited to 1-substituted 1-stannylethylenes, but it is a mechanistically intriguing process. From the mechanistic point of view, use of Cu(I) salts presumably yields intermediate organocopper species,[33] which undergo transmetallation with the "correct" regiochemistry. Silver carbonate has been used in one reaction to avoid cine substitution.[375] The generality of these observations remains to be verified.

Phosphorus-to-Palladium Aryl Migration

Arylpalladium(II) complexes like **32** (Eq. 107) undergo exchange of substituents between phosphorus and palladium at temperatures as low as 50° to yield **33**-**35**.[377] Thus, it is remarkable that this scrambling has not been detected



(Eq. 107)

in most of the classical Stille couplings. Recently, however, some examples of side products originating from aryl transfer by the phosphine were reported.[375,378] Triphenylarsine and tri(2-furyl)phosphine also lead to this side reaction. An obvious way to limit this unwanted process is to run the coupling at as low a temperature as possible.

Electrophile Reduction

Electrophile reduction is often a side reaction in Stille couplings, especially at high temperatures. It has been observed in the coupling of aryl triflates,[189,379] heteroaryl iodides,[126,128] alkenyl halides,[380] and allylic electrophiles.[163] The origin of this side process is uncertain. Alkyl transfer with β elimination prior to reductive elimination may be involved, although a radical mechanism is also possible.

Product Isomerization

In the coupling of acyl chlorides with alkenylstannanes, *E/Z* isomerization is observed under the coupling conditions.[146] Allylic stannanes, on the other hand, may yield mixtures of α,β- and β,γ-unsaturated ketones.[146] Geometric isomerization of olefins has often been reported as a side reaction.[46,51,153,157,269,289,381,382] Double bond migration has also been observed quite frequently.[56,135,383] It is likely that isomerization occurs at the product stage, but it is not clear whether it is catalyzed by palladium. Mild thermal conditions are believed to prevent or reduce

isomerization. In addition, tri(2-furyl)phosphine-based catalysts prevent *E*/*Z* isomerization in the coupling of acyl chlorides and (*Z*)-alkenylstannanes.[11] The generality of this observation must be verified.

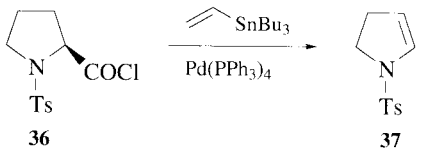
Miscellaneous Side Reactions

When using aryl triflates, hydrolytic cleavage to the corresponding phenols is a side reaction, especially at high temperatures.[55] Replacement of triflate with chloride owing to the presence of LiCl is a rare event, but it must be kept in mind as a possibility, especially for activated substrates.[40,173,195]

When carrying out Stille reactions on substrates containing isolated double bonds, the intermediate organopalladium species may undergo insertion across the double bond (Heck reaction), as discussed in the section on complex strategies.[336]

Reduction of enones has also been observed. The reducing agent is the tributyltin halide produced in the coupling.[148]

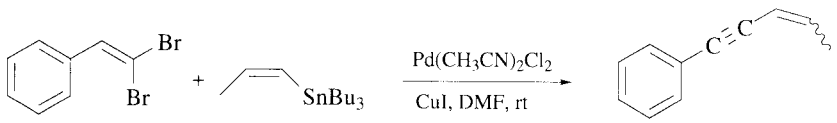
In one example, attempted coupling of an acyl chloride with vinyltributylstannane has led to dehydrodecarbonylation. Thus, proline derivative **36** gives **37** in unreported yield (Eq. 108). Use of the catalyst $Pd(dppf)Cl_2$ obviates the problem.[381]



36 **37** (Eq. 108)

In reactions where the electrophile contains a quinone system, reduction to a dihydroquinone is a serious side reaction.[58,384]

1,1-Dibromoolefins couple with stannanes only once, whereas the second bromine moiety is eliminated (Eq. 109).[385] This side reaction may not be palladium catalyzed.



Z:*E* = 74:26, (39%)

(Eq. 109)

The large variety of side reactions described for the Stille coupling does not reflect serious weaknesses in this cross-coupling method, but rather the careful scrutiny given to this important synthetic method in recent years. The side reactions can often be minimized or eliminated by using simple modifications of the traditional conditions, such as the use of appropriate ligands, solvents, additives, and temperatures, as described in this section.

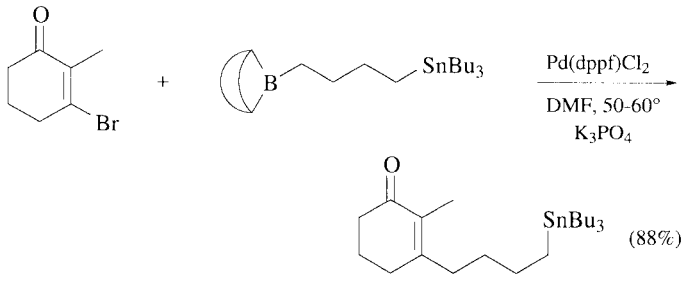
COMPARISON WITH OTHER METHODS

A direct comparison between the Stille reaction and other cross-coupling protocols has been made in only a few cases, and these studies must be regarded with skepticism, since often each particular coupling was not separately optimized, as it should for the comparison to be legitimate. Thus, in a study of several alkenyl-alkenyl couplings in an approach to vitamin A,[386] it was concluded that the Stille coupling was unsatisfactory because of extensive homocoupling and that the reaction of alkenyl iodides with organozinc reagents gave better results. However, a limited set of conditions was explored.

Similarly, it has been concluded that zinc acetylides are better partners than alkynylstannanes in the coupling with certain alkenyl iodides.[387] In the coupling of an iodoglucal with arylmetals, the yields using arylzinc and arylboron compounds were quite superior to the ones obtained with the corresponding stannanes, but only under one set of conditions.[388] Similar conclusions were reached in a related system.[389] The synthesis of polyphenylenes by the Suzuki coupling appears to be superior to the corresponding Stille approach.[390]

Conversely, in other reactions, the Stille protocol outperforms the competition. In the 2-arylation of benzofuran derivatives, the use of organostannanes gives better results than the corresponding zinc derivatives.[391,392] In the synthesis of tamoxifen analogs, coupling of an alkenyl bromide with organotin, organozinc, and organoboron derivatives gives excellent results in each case.[50] Coupling of tetraalkylstannanes is reported to be superior to alkylaluminum and alkylzinc derivatives.[43] The Stille coupling is also the preferred route to substituted nucleosides.[132,374] A commonly given reason for preferring the use of organozinc and organoboron reagents over organostannanes is the toxicity of the latter. Conversely, the stannanes are often preferred because of the unusually mild and absolutely neutral conditions their coupling involves.

Bifunctional derivatives bearing a 9-BBN moiety and a tributylstannane residue couple selectively at the boron end under basic conditions (Eq. 110).[393]



(Eq. 110)

In general, the Stille reaction will continue to be a favorite method for carbon-carbon bond formation, owing to the lack of cross-reactivity displayed by the organostannanes with most functional groups. Its general utility is demonstrated by the many diverse applications reported in the tables.

EXPERIMENTAL CONDITIONS

The Stannane: Preparation and Handling

Caution! Many organotin compounds are toxic, especially the lower alkyl derivatives. Their acute toxicity decreases dramatically with increasing alkyl group length.[394,395] As a precaution, the preparation and use of all stannanes should only be carried out in a well-ventilated hood. After use, all glassware should be thoroughly washed, preferably after soaking in a KOH/alcohol bath to remove surface-bound tin alkoxides and/or halides.

Organostannanes are typically synthesized by reaction of organolithium or organomagnesium derivatives with trialkyltin halides. Another important method is the radical-induced or Pd-promoted addition of tin hydrides to unsaturated systems (e.g., alkynes, alkenes). Very important also is the transition metal-catalyzed cross-coupling of hexaalkyldistannanes with organic electrophiles, as discussed in the section on scope and limitations. Tin acetylides are best formed by the reaction of trialkyltin diethylamide with an alkyne.[396] A thorough treatment of the synthesis of organostannanes is outside the scope of this review, and the reader is referred to reviews on organostannanes.[6,395]

Most organostannanes are stable to air and moisture and can therefore be distilled and/or chromatographed. Stannanes are often too nonpolar to be efficiently purified on silica gel, but C-18 flash chromatography appears to be useful.[397] Given their ease of purification, for best results stannanes should not be used as crude preparations in Stille couplings.

Alkenyl and Aryl Triflates

Alkenyl triflates are typically synthesized by the reaction of triflic anhydride with a ketone or aldehyde in the presence of a hindered base, such as 2,6-di-*tert*-butylpyridine.[398,399] Enolates can be trapped with *N*-aryltriflimides, such as *N*-phenyltriflimide.[400,401] Vinyl triflates are also available from the addition of triflic acid to alkynes, though regio- and stereochemical considerations may be a problem.[402,403]

Aryl triflates are readily prepared by the reaction of triflic anhydride with a phenol in the presence of a base such as triethylamine or pyridine.[189] *N*-Phenyltriflimide can also be used for this transformation.[404] A thorough treatment of the synthesis of vinyl and aryl triflates is beyond the scope of this review, and the reader is referred to reviews on the formation and reactions of triflates.[405,406]

Choice of Nontransferable Ligands

Using nontransferable ligands is an area of the Stille reaction that needs further improvement. As discussed above, tributylstannane derivatives are usually preferred because of the low cost and low toxicity of tributyltin chloride, as well as the fact that competitive transfer of the butyl groups is a rare event. On the other hand, removal of traces of tributylstannane derivatives from the product can be problematic. Trimethylstannane derivatives have the disadvantage that

methyl group transfer can often compete with the desired transfer of the unsaturated group, but the trimethylstannane derivatives produced in the coupling can usually be removed from the product by simple aqueous wash. Nontransferable ligands that speed up the transmetallation have been described in recent years, but have not yet found general acceptance.[41] Trichlorostannates have recently been used and can be employed to carry out Stille reactions in aqueous systems.[282,283]

Choice of Catalyst and Ligands

As discussed earlier, both Pd(0) and Pd(II) catalysts may be used to promote the cross-coupling reaction. Pd(II) catalysts have the advantage of being air stable, but must be reduced before entering the catalytic cycle. Typically, reduction is achieved in situ through the homocoupling of two equivalents of stannane, or with some reductant such as carbon monoxide. In rare instances, Pd(II) catalysts are pre-reduced by the addition of a Grignard or hydride reagent (often L-Selectride or DIBAL).[43] Pd(0) catalysts can enter the catalytic cycle directly, but can suffer from air and/or light stability problems.

Most catalysts are commercially available. Some of the most commonly used are: tetrakis(triphenylphosphine)palladium(0),[407] bis(dibenzylideneacetone)-palladium(0),[408] bis(acetonitrile)palladium(II) dichloride,[409] bis(triphenylphosphine)palladium(II) chloride,[410,411] benzyl[bis(triphenylphosphine)]palladium(II) chloride,[21,412] 1,1′-bis(diphenylphosphino)ferrocenepalladium(II) dichloride,[413] and allylpalladium(II) chloride dimer.[414] Catalysts that do not incorporate strong ligands are often used in conjunction with added phosphines. Particularly useful among them are the Pd-dibenzylideneacetone complexes, which are commercially available and air stable. They can be used in conjunction with a variety of ligands. In addition to the traditional triphenylphosphine, ligands of reduced donicity, such as tri(2-furyl)phosphine and triphenylarsine, or increased steric bulk, such as tri(*o*-tolyl)phosphine, usually lead to much faster coupling.[11] These ligands are all commercially available. Nitrogen-based ligands have been used in a few cases, but their scope and utility have not been well established.[169,171,415] In some instances, it is advantageous to completely omit the ligand from the Stille reaction.[5] Ligandless catalysts usually afford high coupling rates but also premature interruption of the catalytic cycle.

Choice of Solvent

Solvents used include benzene, toluene, xylene, mesitylene, chloroform, 1,2-dichloroethane, THF, DME, dioxane, DMF, DMA, NMP, DMSO, HMPA, and water. Given the stable nature of the stannane organometallic species, it is fair to say that almost any conceivable solvent is likely to be compatible with the Stille protocol. Most couplings are carried out either in an ethereal solvent like THF or dioxane, or in highly dipolar solvents, such as DMF or NMP. Any of these four solvents represents a reasonable first choice when studying a new Stille coupling. The solvents are typically of anhydrous quality, but there does not seem to be a compelling reason to avoid traces of moisture. In many cases the literature spe-

cifically mentions that moisture accelerates the reaction. The same can be said about air: Whereas many Pd(0) complexes are air sensitive, during the Stille coupling the active catalyst is normally in the air-stable Pd(II) oxidation state (owing to rapid oxidative addition), and oxygen has no deleterious effect on the reaction. Many Stille reactions have been run in the presence of oxygen: Under these conditions a black precipitate of Pd metal signals the end of the reaction, where air-sensitive Pd(0) species accumulate. However, atmospheric oxygen can sometimes induce efficient homocoupling of the stannane (as discussed in the section on side reactions). In this event, careful deoxygenation by multiple freeze-thaw cycles is recommended.

Additives

The use of copper salts to facilitate the Stille cross-coupling is one the more significant recent developments in this area; the "copper effect" was discussed in the mechanistic section. The use of silver salts was also mentioned. Zinc chloride has often been used as additive. Yields are often better in the presence of stoichiometric amounts of Zn(II) salts, although the origin and the generality of the effect are not understood. The use of a stabilizing halide source, such as LiCl, and its complex effect on reaction rates in conjunction with the coupling of triflates have been discussed in the mechanistic section. When coupling triflates in ethereal solvents, LiCl appears to be necessary to induce coupling; in DMF or NMP (and presumably other dipolar solvents), LiCl is often unnecessary when coupling alkenyl triflates, whereas it sometimes appears to be necessary when coupling the less reactive aryl triflates. The experimentalist is urged to try the reaction both with and without LiCl. Bases such as triethylamine,[54,416] diisopropylethylamine,[80] lithium carbonate,[417] sodium carbonate,[298,418] pyridine,[419] and 2,6-di-*tert*-butyl-4-methylpyridine,[417] have also been employed as additives, presumably to minimize degradation of stannanes by adventitious acid.

Antioxidants, such as BHT, di-*tert*-butylphenol, or *tert*-butylcatechol are sometimes added to minimize side product formation via radical pathways.

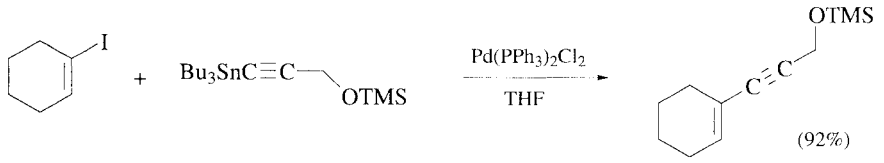
Some reactions proceed more rapidly or in higher yield when run under dry air.[19] Palladium compounds catalyze the oxidation of triphenylphosphine to triphenylphosphine oxide by atmospheric oxygen. The rate enhancement found when running reactions under air may simply be due to the depletion of excess phosphine (see the "Mechanistic Considerations" section).

Workup: Removal of Tin Halides

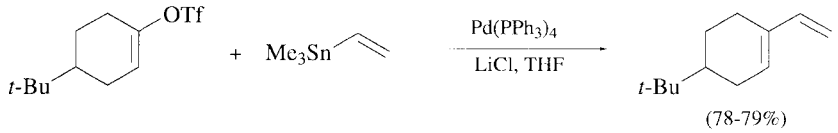
A major consideration in working up reaction mixtures from the Stille cross-coupling is the removal of tin byproducts. Trimethyltin chloride is water soluble and rather volatile and is therefore readily removed on normal aqueous workup. Tributyltin chloride has low volatility (bp 171–173° at 25 mm Hg) and is soluble in most common organic solvents. Separation by chromatography on silica gel is made difficult by the tendency for tributyltin chloride to elute under relatively nonpolar conditions and to streak. A variety of methods have been devised to remove bulk tributyltin chloride prior to final purification. Aqueous KF solutions react with tributyltin halides under biphasic conditions to form polymeric tri-

butyltin fluoride, which may be removed by filtration. Ammonia complexes with tributyltin halides, making them somewhat water soluble. Thus, washing of organic solutions with dilute ammonium hydroxide can remove the stannane.[88] Tributyltin chloride is insoluble in acetonitrile. Thus, dissolving crude or partially purified reaction mixtures in acetonitrile followed by washing with hexanes (in which tributyltin chloride is soluble) will remove most of the tin.[420] DBU in wet diethyl ether, followed by filtration through silica, has also been used to remove tributyltin residues.[420a] Scott and Stille proposed that CsF as a coupling additive might cause the formation of tributyltin fluoride in situ, thus facilitating workup.[28]

EXPERIMENTAL PROCEDURES

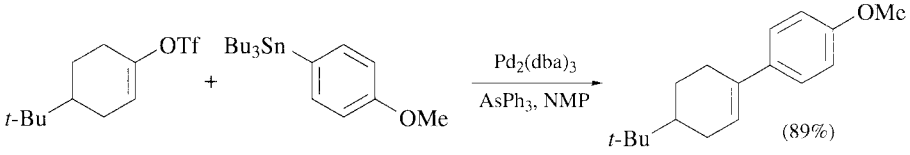


Trimethyl([3-(cyclohexen-1-yl)-2-propynyl]oxy)silane [Cross-Coupling of a Vinyl Halide with an Alkynylstannane Using $Pd(PPh_3)_2Cl_2$].[47] To a solution of 1-iodocyclohexene (0.424 g, 2.04 mmol), and trimethyl[3-(trimethylstannyl)-2-propynyl)oxy]silane (0.592 g, 2.04 mmol) in dry THF (25 mL) was added $Pd(PPh_3)_2Cl_2$ (0.0215 g, 0.031 mmol). The resulting mixture was stirred at 22–25° for 2 hours. The progress of the reaction was followed by TLC. The reaction mixture was diluted with CH_2Cl_2, coated onto alumina (10 g), and eluted with pentane. The resulting pentane solution was washed with water (3 × 25 mL) and a saturated NaCl solution (25 mL), dried (K_2CO_3), and concentrated under reduced pressure to give a pale yellow liquid (0.388 g, 92%): ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 1.48–1.68 (m, 4 H), 2.00–2.15 (m, 4 H), 4.36 (s, 2 H), 6.04–6.12 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ -0.3, 21.5, 22.3., 25.6, 29.1, 51.5, 84.9, 86.8, 120.5, 134.5; IR (neat) 3040, 2218, 1442, 1322, 1258 cm^{-1}; Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 68.93; H, 9.70.

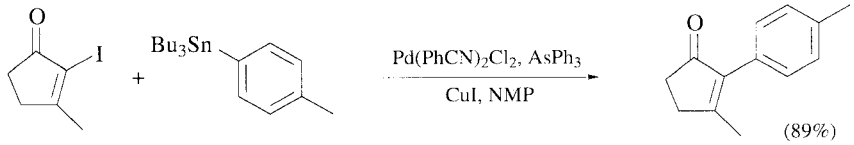


4-*tert*-Butyl-1-vinylcyclohexene [Cross-Coupling of a Vinyl Triflate with a Vinylstannane Using $Pd(PPh_3)_4$ and LiCl)][421] A slurry of $Pd(PPh_3)_4$ (1.18 g, 1.02 mmol) and LiCl (12.9 g, 0.305 mol) in dry THF (500 mL) was stirred for 15 minutes under a static Ar atmosphere, then a solution of 4-*tert*-butylcyclohexenyl triflate (28.0 g, 0.0979 mol) and trimethylvinylstannane (19.0 g, 0.0997 mol) in dry THF (250 mL) was added, followed by an additional 250 mL of THF. The resulting solution was heated under gentle reflux for 48 hours, then

was cooled to room temperature and partitioned between water (500 mL) and pentane (250 mL). The aqueous layer was back-extracted with pentane (2 × 250 mL), and the combined organics were washed with a saturated $NaHCO_3$ solution (2 × 250 mL), water (2 × 250 mL), and a saturated NaCl solution (2 × 250 mL). The organic extracts were dried ($MgSO_4$), filtered through a pad of silica gel (4 cm × 4 cm), and concentrated by distillation using a 10-cm Vigreux column. Bulb-to-bulb distillation (Kugelrohr; oven temperature 65–68° at 0.55 mm Hg) gave the desired product (12.6–12.8 g, 78–79%): bp 45° (0.1 mm Hg); ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9 H), 1.08–1.34 (m, 3 H), 1.84–2.36 (m, 4 H), 4.88 (d, J = 10.7 Hz, 1 H), 5.04 (d, J = 17.5 Hz, 1 H), 5.73–5.75 (m, 1 H), 6.35 (dd, J = 17.5, 10.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.8, 25.3, 27.2 (3C), 27.4, 32.2, 44.4, 109.7, 129.8, 136.0, 139.7; IR (neat) 3100, 3020, 1650, 1610, 1395, 1365, 985, 890 cm^{-1}.

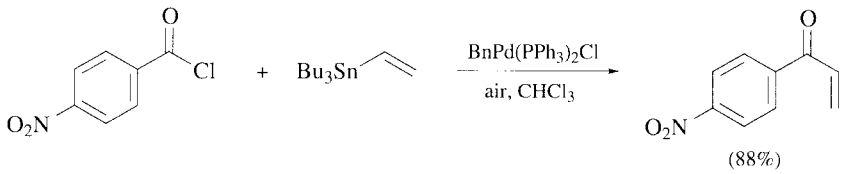


1-(4-Methoxyphenyl)-4-*tert*-butylcyclohexene [Cross-Coupling of a Vinyl Triflate with an Arylstannane Using $Pd_2(dba)_3$ and $AsPh_3$].[30] A solution of $Pd_2(dba)_3$ (0.0083 g, 0.0184 mmol), $AsPh_3$ (0.023 g, 0.0734 mmol), and 4-*tert*-butylcyclohexenyl triflate (0.263 g, 0.918 mmol) in anhydrous degassed NMP (5 mL) was allowed to stand until the purple color was discharged (5 minutes), and (4-methoxyphenyl)tributylstannane (0.430 g, 1.083 mmol) in dry NMP (2 mL) was added. The resulting solution was stirred at room temperature for 16 hours, then stirred with a 1 M aqueous KF solution (1 mL) for 30 minutes, diluted with EtOAc, and filtered. The filtrate was washed extensively with water, dried, and concentrated to give a crude oil. The oil was purified by reverse phase flash chromatography (C-18, 10% CH_2Cl_2, 90% CH_3CN) to give a white solid which was recrystallized (MeOH), (0.201 g, 89%): mp 78–79°; ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 9 H), 1.22–1.39 (m, 2 H), 1.89–2.02 (m, 2 H), 2.19–2.54 (m, 3 H), 3.80 (s, 3 H), 6.04 (m, 1 H), 6.84 (d, J = 9.0 Hz, 2 H), 7.32 (d, J = 9.0 Hz, 2 H); Anal. Calcd. for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.58; H, 9.85.

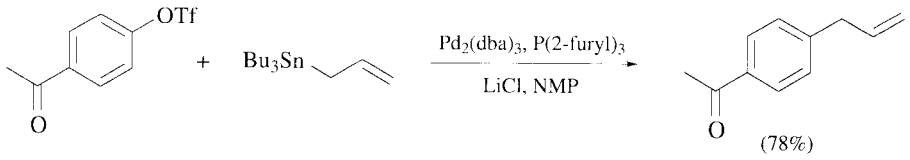


3-Methyl-2-(4-tolyl)-2-cyclopentenone [Cross-Coupling of an Unreactive Alkenyl Halide Under "Modified" Conditions Using $Pd(PhCN)_2Cl_2$, $AsPh_3$, and CuI as Cocatalyst].[61] A solution of 2-iodo-3-methyl-2-cyclopentenone (0.222 g, 1.00 mmol), CuI (0.019 g, 0.10 mmol), $AsPh_3$ (0.031 g, 0.10 mmol), and $Pd(PhCN)_2Cl_2$ (0.019 g, 0.05 mmol) in NMP (1 mL) was treated under Ar with

p-tolyltributylstannane (0.37 mL, 1.20 mmol), and the mixture was heated in an oil bath at 100° for 30 minutes. After cooling, the solution was diluted with EtOAc (100 mL) and washed with aqueous KF (0.67 satd., 3 × 30 mL) and water (2 × 20 mL). The combined aqueous layers were back-extracted with EtOAc (60 mL). The combined organics were dried ($MgSO_4$), filtered, and evaporated to dryness. The resulting oil was purified by silica gel chromatography (gradient 2–10% EtOAc in pet. ether) to yield a white solid (0.165 g, 89%): mp 102–103° (EtOAc/pet. ether); ^{1}H NMR ($CDCl_3$) δ 7.20 (m, 4 H), 2.61 (m, 2 H), 2.51 (m, 2 H), 2.35 (s, 3 H), 2.15 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 207.6, 171.2, 140.1, 137.2, 128.9, 34.7, 31.7, 21.2, 18.2. IR ($CHCl_3$) 1685 cm^{-1}; Anal. Calcd for $C_{13}H_{14}O$: C, 83.87; H, 7.54. Found: C, 84.06; H, 7.42.

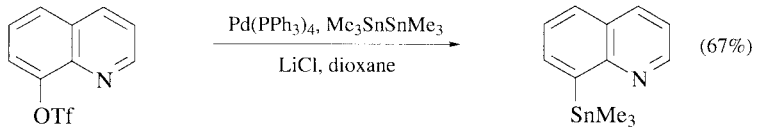


1-(4-Nitrophenyl)-2-propenone (Cross-Coupling of an Acid Chloride with an Arylstannane).[146] To a solution of 4-nitrobenzoyl chloride (5.00 mmol) and $BnPd(PPh_3)_2Cl$ (0.015–0.020 g, 0.020–0.026 mmol) in chloroform (1 mL) was added a solution of tributylvinylstannane (5.20 mmol) in chloroform (4 mL). The resulting yellow solution was heated at 65° under dry air until palladium metal precipitated (20 minutes). The reaction mixture was diluted with Et_2O (30 mL) and washed with water (30 mL). The organic phase was shaken with an aqueous KF solution (15 mL of saturated KF solution/15 mL of water) and allowed to stand for 15–30 minutes. The resulting white precipitate (Bu_3SnF) was removed by filtration. The organic layer was separated and again treated with an aqueous KF solution. After decantation from the resulting white precipitate, the organic phase was washed with concentrated NaCl solution, dried ($MgSO_4$), and concentrated under reduced pressure. Treatment of the residue with EtOAc afforded an additional crop of white precipitate, which was removed by filtration through a Celite pad. Following concentration under reduced pressure, recrystallization from chloroform/hexanes gave the product as a yellow solid (0.780 g 88%): mp 87–89°; ^{1}H NMR ($CDCl_3$) δ 6.0 (dd, J = 10.2 Hz, 1 H), 6.4 (dd, J = 18.2 Hz, 1 H), 7.1 (dd, J = 18.1 Hz, 1 H), 8.0 (d, J = 9 Hz, 2 H), 8.3 (d, J = 9 Hz, 2 H); IR (KBr) 1670 cm^{-1}; Anal. Calcd. for $C_9H_7NO_3$: C, 61.02; H, 3.93. Found: C, 61.23; H, 4.11.

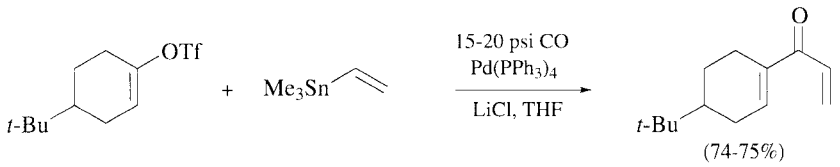


4-Allylacetophenone [Cross-Coupling of an Aryl Triflate Under Mild Conditions Using Tri(2-furyl)phosphine as Ligand].[11] A solution of 4-

(triflyloxy)acetophenone (0.566 g, 2.11 mmol) in NMP (3 mL) was treated with anhydrous LiCl (0.268 g, 6.30 mmol), tri(2-furyl)phosphine (0.0392 g, 0.168 mmol), and $Pd_2(dba)_3$ (0.0193 g, 0.042 mmol Pd). After 10 minutes at room temperature, the solution was treated with allyltributylstannane (0.72 mL, 2.464 mmol) and the mixture was stirred at room temperature for 24 hours. The solution was stirred with a saturated aqueous KF solution, diluted with EtOAc, and filtered. Washing the organics with water, drying (anhydrous Na_2SO_4), and evaporation of the solvent gave a crude oil which was purified by flash chromatography (silica gel, 5% EtOAc in hexanes) to yield a colorless liquid (0.264 g, 78.5%); bp (Kugelrohr) 90–95° (0.2 mmHg); ^{1}H NMR ($CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 2 H), 7.27 (d, J = 8.2 Hz, 2 H), 5.94 (m, 1 H), 5.13–5.06 (m, 2 H), 3.43 (d, J = 6.7 Hz, 2 H), 2.57 (s, 3 H); Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.11; H, 7.56.

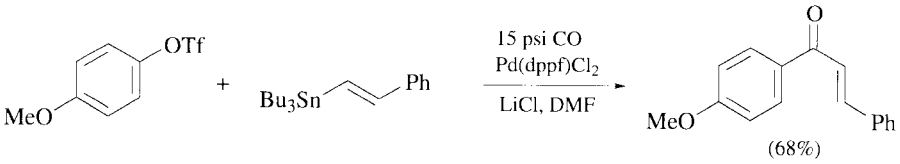


8-(Trimethylstannyl)quinoline (Preparation of an Arylstannane by Cross-Coupling of an Aryl Triflate with Hexamethyldistannane).[189] To a solution of 8-(triflyloxy)quinoline (1.98 mmol) in dioxane (9 mL) were added hexamethyldistannane (2.05 mmol), LiCl (0.252 g, 5.94 mmol) $Pd(PPh_3)_4$ (0.046 g, 0.040 mmol), and a few crystals of BHT. The mixture was heated to reflux for 75 hours, cooled, and treated with pyridine (1 mL) and pyridinium fluoride (1.4 M in THF, 2 mL) for 16 hours at room temperature. The mixture was diluted with Et_2O, filtered through Celite, and washed with water, 10% HCl, water, and brine. Drying ($MgSO_4$) and concentration afforded an oil. Silica gel chromatography and bulb-to-bulb distillation (bp: 103–104° at 0.4 mm Hg) gave a colorless oil in 67% yield; ^{1}H NMR ($CDCl_3$) δ 8.86 (dd, J = 4.2, 1.7 Hz, 1 H), 8.07 (dd, J = 8.2, 1.8 Hz, 1 H), 7.88 (d, J = 6.5, 1.3 Hz, 1 H), 7.75 (dd, J = 8.1, 1.3 Hz, 1 H), 7.49 (dd, J = 8.1, 6.6 Hz, 1 H), 7.31 (dd, J = 8.2, 4.2 Hz, 1 H), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 153.17, 153.06, 149.35, 147.56, 136.94, 127.97, 126.21, 125.83, -8.32; IR (neat) 3050, 2970, 2905, 1485, 810, 785 cm^{-1}; Anal. Calcd. for $C_{12}H_{15}NSn$: C, 49.37; H, 5.18. Found: C, 49.50; H, 5.25.



4-(*tert*-Butyl-1-vinylcyclohexen-1-yl)-2-propenone [Carbonylative Cross-coupling of an Alkenyl Triflate with an Alkenylstannane Using $Pd(PPh_3)_4$ and LiCl].[421] A slurry of $Pd(PPh_3)_4$ (1.12 g, 0.968 mmol) and LiCl (13.2 g,

0.312 mol) in dry THF (500 mL) was stirred for 15 minutes under a static Ar atmosphere, then a solution of 4-*tert*-butylcyclohexenyl triflate (28.6 g, 0.100 mol) and trimethylvinylstannane (19.1 g, 0.100 mol) in dry THF (250 mL) was added, followed by an additional 250 mL of THF. The reaction mixture was flushed with carbon monoxide and maintained under a carbon monoxide atmosphere (15–20 psi) while heating to 55°. After 40 hours the reaction mixture darkened and was cooled to room temperature. The resulting solution was diluted with pentane (500 mL), washed with water (2 × 200 mL), saturated $NaHCO_3$ solution (2 × 200 mL), and brine (2 × 200 mL), then was dried ($MgSO_4$), filtered through a 4-cm × 4-cm pad of silica gel, and concentrated under reduced pressure. Bulb-to-bulb distillation (Kugelrohr) at 85–95° (0.35 mm Hg) gave the desired product (14.3–14.5 g, 74–75%): bp 75° (0.1 mm Hg); ^{1}H NMR ($CDCl_3$) δ 0.81 (s, 9 H), 1.21–2.65 (m, 7 H), 5.58 (d, J = 9.0 Hz, 1 H), 6.14 (d, J = 17.2 Hz, 1 H), 6.75–7.00 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.3, 24.6, 26.9 (3C), 27.8, 32.0, 43.4, 127.1, 131.5, 141.1, 190.8; IR (neat) 1665, 1645, 1612 cm^{-1}.



(*E*)-1-(4-Methoxyphenyl)-3-phenyl-2-propenone [Carbonylative Cross-Coupling of an Aryl Triflate With an Alkenylstannane Using Pd(dppf)Cl_2 and LiCl].[336] To a solution of 4-methoxyphenyl triflate (0.390 g, 1.52 mmol) in DMF (7 mL) was added (*E*)-(β-tributylstannyl)styrene (0.645 g, 1.64 mmol), LiCl (0.200 g, 4.72 mmol), Pd(dppf)Cl_2 (0.045 g, 0.060 mmol), a few crystals of BHT, and 4 Å molecular sieves (0.10 g). The resulting mixture was heated at 70° under 15 psi of CO. After 23 hours the reaction was cooled to room temperature, diluted with Et_2O, and filtered. The filtrate was washed with water (3 times) and saturated NaCl solution, dried ($MgSO_4$), and concentrated. The resulting material was purified by chromatography (silica gel, 10:1 hexanes/EtOAc) to give the product as a white solid (0.250 g, 68%), which was recrystallized from 20:1 hexanes/EtOAc: mp 105–106°; ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3 H); 6.94, (d, J = 8.8 Hz, 2 H), 7.36–7.39 (m, 3 H), 7.53 (d, J = 15.7 Hz, 1 H), 7.59–7.63 (m, 2 H), 7.79 (d, J = 15.7 Hz, 1 H), 8.03 (d, J = 8.9 Hz, 1 H).

TABULAR SURVEY

The literature was searched to the end of 1994 by Chemical Abstracts, extensive citation searches and browsing. A few of the papers which describe Stille couplings but are missing a vital piece of information (i.e., clear structure of substrates and/or products) were not abstracted. No attempts were made to cover the patent literature. A dash indicates lack of reported yield. When only GLC, NMR,

or HPLC yields were reported, these were simply incorporated in the tables without specific notation. When both isolated and "estimated" yields were given, the isolated yields are shown in the tables. If experimental conditions were not given, the appropriate column usually contains the generic statement "Pd(0)". Reactions that appear well documented but afford none of the anticipated product are still reported, and 0% yield is shown next to the structure of the expected product. We think failed reactions may stimulate further research and new thinking. In some papers, the attempt to optimize a reaction led to many experiments done on the same substrate under slightly different catalytic conditions. In most cases, for the sake of simplicity, we report only the highest yielding of all these experiments. However, in some cases the comparison of two or more sets of conditions on the same substrate proves a point which, in our opinion, was important enough to warrant a separate entry.

Some of the 1995 papers were incorporated in the tables as they appeared in the literature, but only those which, in our opinion, reported new catalytic systems or new classes of substrates.

The substrates are broken down into specific classes according to electrophile type, to reflect the classification made in the "Scope and Limitations" section. Some classes (heterocyclic or acyl electrophiles) are further broken down into subclasses to facilitate target finding. The electrophiles are listed in order of increasing carbon count for the moiety that is being transferred (the leaving group is not included in the carbon or heteroatom count). Within a given C count, they are listed in order of increasing numbers of heteroatoms, the priority being assigned alphabetically except for H, which has *the lowest* priority. For example C_6H_5ClO has priority over C_6H_5O and/or C_6H_6ClO. This ranking was the simplest and visually the most pleasing of a number of alternatives that we examined.

Electrophiles where the halide moiety is attached to a heterocyclic system or an aryl ring fused to a heterocyclic system (be it aromatic or partially saturated) are considered heterocyclic electrophiles. If the heterocyclic portion is *isolated* from the electrophilic moiety, then it is not considered.

The stannanes are similarly arranged according to the moiety that is being transferred. Tin hydrides are listed first, then all the C-based nucleophiles in the order explained above (in addition, trimethylstannanes have priority over tributylstannanes and bis[stannanes] are listed after all the monostannanes within a given electrophile), then the heterostannanes are listed (priority is assigned based on the alphabetical rank of the atom whose bond to tin is being broken). Intramolecular Stille couplings are listed in separate tables. A special case is the coupling of bis(stannanes) with bis(electrophiles), ultimately yielding a cyclic product. These reactions are listed twice: once in the appropriate table for the Stille coupling which our mechanistic knowledge tells us is taking place first, the second time in the intramolecular table. We realize this is cumbersome and causes duplication, but it seems the only logical way of dealing with the problem in an informative way. Other, more complex strategies in which the Stille reaction is coupled to other reactions are listed separately in Tables XXXII (no CO

involved) and XXXIII (CO involved). The structures of stannanes that were formed in situ are enclosed in brackets.

The following abbreviations are used in the tables:

BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
Bn	benzyl
Boc	*tert*-butoxycarbonyl
BOM	benzyloxymethyl
Bz	benzoyl
Cbz	benzyloxycarbonyl
d	day(s)
dba	dibenzylideneacetonyl
DIOP	2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane
DME	1,2-dimethoxyethane, glyme
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
dppb	1,3-bis(diphenylphosphino)butane
dppf	1,1′-bis(diphenylphosphino)ferrocene
dppp	1,3-bis(diphenylphosphino)propane
EE	(1-ethoxy)ethyl
FMOC	fluorenylmethyloxycarbonyl
HMPA	hexamethylphosphoric triamide
MEM	methoxyethoxymethyl
MOP	2-(diphenylphosphino)-2′-methoxy-1,1-binaphthyl
MOM	methoxymethyl
Ms	methanesulfonyl
NMP	*N*-methylpyrrolidinone
Ph-BIAN	bis(phenylimino)acenaphthene
PMB	*p*-methoxybenzyl
PNB	*p*-nitrobenzyl
rt	room temperature
SEM	(2-trimethylsilylethoxy)methyl
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
Tf	trifluoromethanesulfonyl
Thexyl	1-(1,1,2-trimethyl)propyl
TIPS	tri(isopropyl)silyl
THF	tetrahydrofuran
THP	tetrahydropyranyl
TMS	trimethylsilyl
p-Tol	*p*-tolyl
Ts	*p*-toluenesulfonyl

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