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Review

TRANSITION-METAL CATALYSIS IN ORGANOTIN CHEMISTRY

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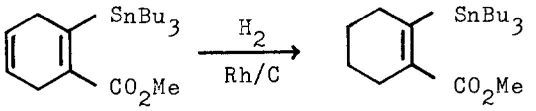
1. INTRODUCTION

Although the use of transition-metal catalysts in organosilicon chemistry has been common for many years, commencing with platinum catalysis of hydrosilylation, their first application in organotin chemistry was only reported in 1976 (ref.1), and only from 1980 onwards has the number of papers published yearly in this area exceeded 3. The reason for the slow acceptance of such catalysts in tin chemistry may lie in the fact that transition-metal catalysed hydrogenation of vinyl- and alkynyltins does not occur, as clearly shown in a recent example:

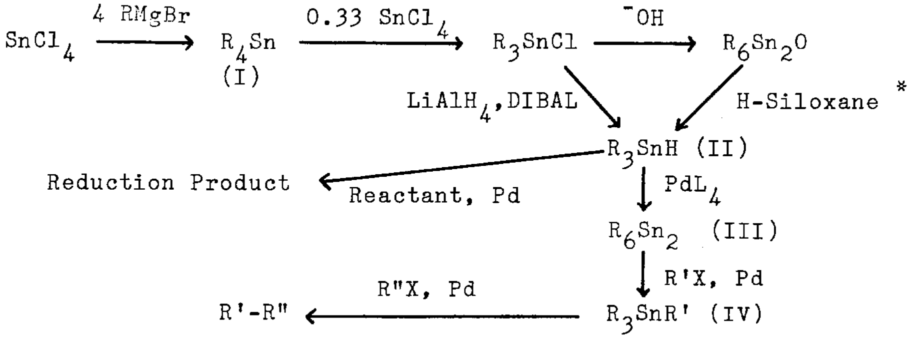


(ref.2)

Since 1980, however, transition-metal catalysis has become increasingly widespread in syntheses involving organotin compounds, with over 65 papers published up to mid-1985. The metal of choice has been palladium, other metals appearing rarely: the most commonly used catalyst has been tetrakis(triphenylphosphine)-palladium(0) (this will be referred to below as PdL_4, L also denoting PPh_3 when other catalysts are referred to). This catalyst has the advantage of ready commercial availability (though in our experience commercial samples, even from one supplier, may differ greatly in their reactivity). PdL_4 may however well not be the best catalyst in any particular situation, as has been shown in several cases.

Themain application of palladium catalysts has been in the area of carbon-carbon bond formation, using symmetrical or mixed tin tetraorganyls; in 1983 Beletskaya (ref.3) reviewed cross-coupling reactions of organic halides with organic derivatives of tin, mercury and copper catalysed by palladium, and cited more than 20 publications (literature coverage probably up to autumn 1982). Further advances in this and other areas have been made by her group and by others in the past three years, and it thus appears useful to survey the presently known applications of transition-metal catalysis in organotin chemistry.

For those not familiar with this type of chemistry but wishing to enter the field without relying on commercial suppliers for their starting materials, the following "flow chart" may be useful (the literature shows that R in R_3Sn is almost without exception Me or n-Bu, the latter obviously being preferred because of its lower toxicity but having disadvantages in some cases).



* only for R=n-Bu; cost of Bu_6Sn_2O ca. \$0.04/g.

The chemistry to be discussed below is basically that of compounds I-IV; while these can be prepared in other ways, syntheses starting from $SnCl_4$ (R=Me) or Bu_6Sn_2O are simply carried out (ref.4).

The following discussion will not be ordered in terms of reactions of I-IV but in terms of the bond formed in the reaction product of synthetic interest.

2. CARBON-HYDROGEN BOND FORMATION: USE OF Bu_3SnH

As shown above, in the absence of a reaction partner, triorganotin hydrides are converted by PdL_4 (and by other palladium catalysts) to ditins (ref.5): this is the simplest and most convenient method for making symmetrical ditins. However, PdL_4 also catalyses the selective reduction of acyl chlorides by Bu_3SnH to aldehydes (ref.6):

$$RCOCl + Bu_3SnH \xrightarrow{PdL_4} RCHO \quad (75\text{-}97\%) \qquad (1)$$

The same authors later showed that palladium(II) complexes and also $PdCl_2$ in the presence of triphenylphosphine catalyse this reaction and that PdL_4 catalyses both the reduction of α,β-unsaturated to saturated carbonyl compounds and (in poorer yields) the selective reduction of α,β-unsaturated acyl chlorides to the corresponding aldehydes (ref. 7)

$$RCH{=}CH\text{-}COCl + Bu_3SnH/PdL_4 \longrightarrow RCH{=}CH\text{-}CHO \qquad (2)$$

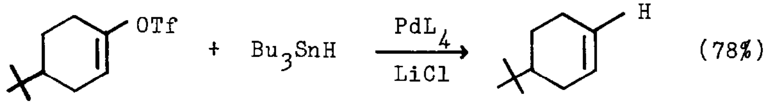
$$RCH{=}CH\text{-}CHO + Bu_3SnH/PdL_4 \longrightarrow RCH_2CH_2CHO \qquad (3)$$

The presence of a number of other functional groups can be tolerated. It was shown that the yields of saturated carbonyl compounds in this reaction can be greatly increased by addition of a radical scavenger and by aqueous workup (ref.8). The same group has reported the reductive cleavage of allylic substituents using Bu_3SnH (ref.9)

$$4\text{-}RC_6H_4CH{=}CH\text{-}CH(Y)R' + Bu_3SnH/PdL_4 \longrightarrow 4\text{-}RC_6H_4CH{=}CH\text{-}CH_2R' \qquad (4)$$

$(Y{=}OAc,\ NH_2;\ R{=}H,\ Hal,\ Me;\ R'{=}H,\ CN,\ Ph,\ 4\text{-}C_6H_4CHO)$

A recent paper (ref.10) concerned with carbon-carbon coupling contains a report of a PdL_4-catalysed reduction by Bu_3SnH of a vinyl triflate to the corresponding alkene:

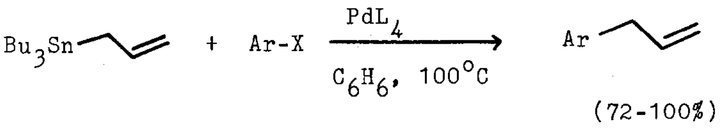


(5)

3. CARBON-CARBON BOND FORMATION

Since this area has been reviewed in detail by Beletskaya (ref.3), we shall emphasise further developments published in the last 3 years after outlining the initial results.

Kosugi et al. (ref.11) originally showed that the reaction of tributylallyltin with aryl bromides in the presence of PdL_4 yields coupling products in good yield:



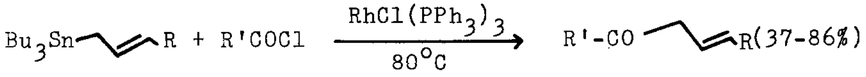
(6)

(X=Cl, Br, I; Ar=Ph, p-YC_6H_4 with Y=Me, Cl, NO_2)

Shortly afterwards, the same group reported reactions of acyl chlorides with tetraorganotins and showed that in the case of tributylvinyltin the vinyl group was preferentially transferred (tributyltin chloride transferred a butyl group) (ref.12).

$$R_4Sn \;+\; R'COCl \xrightarrow{PdL_4} RCOR' \quad (40\text{-}90\%) \qquad (7)$$

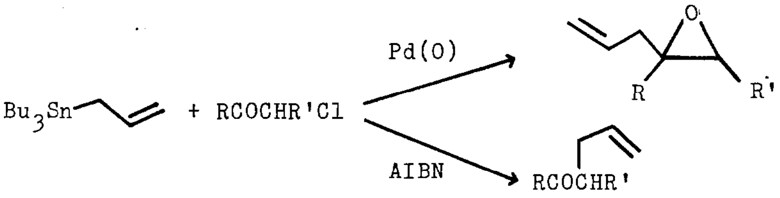
They further showed (ref.13) that rhodium catalysed the formation of allyl ketones from tributylallyltins and acyl chlorides:



(8)

(R=H, Me; R'=Me, Et, i-Pr, t-Bu, Ph)

Tributylbenzyltin also reacts and transfers the benzyl group. It was also shown (ref.14) that α-chloroketones react to give epoxides rather than the simple substitution products obtained in the presence of AIBN:



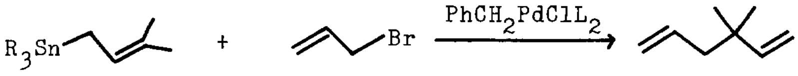
(9)

(R=Me, Et; R'=H, Me)

The next group of papers was published by Stille and co-workers (ref.15-18); they used $PhCH_2Pd(Cl)L_2$ rather than PdL_4. Apart from studying the reaction of acyl chlorides with tetraorganotins (ref. 15,17), they concerned themselves with those of tetraorganotins with benzyl and aryl halides (ref.16) and of trialkylallyltins with allyl bromides, the latter reaction proceeding with allylic rearrangement in the allylic fragment of the organotin (ref.18):

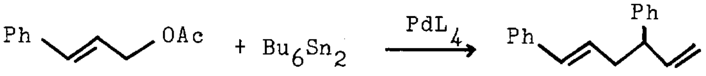
$$R_3SnR' \;+\; R''Br \xrightarrow[\text{HMPA, } 65^{\circ}C]{PhCH_2PdClL_2} R' - R'' \quad (62\text{-}100\%) \qquad (10)$$

(R=Me, Bu, Ph, $CH=CH_2$, $PhCH_2$; R"=$PhCH_2$, Aryl)

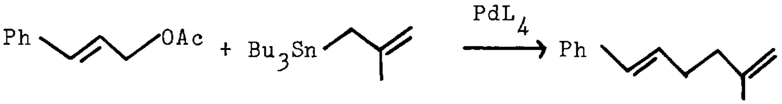


(11)

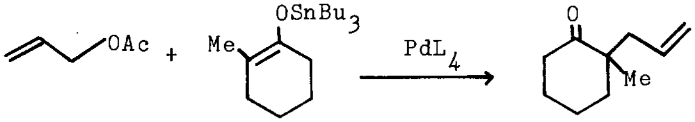
Trost and Keinan carried out similar reactions using allyl acetates; homocoupling was observed when hexabutylditin was used (ref.19), cross-coupling when allylstannanes (ref.19) or stannyl enolates (ref.20) were taken:



(51%) (12)



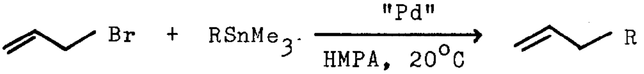
(65%) (13)



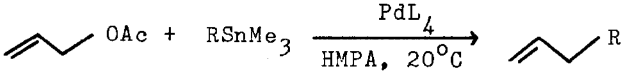
(90-95%) (14)

Beletskaya's group first concerned itself with the use of other palladium catalysts: they used $PhPdIL_2$ for the cross-coupling of a wide variety of organotins and organic halides (ref.21) and π-allyl palladium chloride dimer for ketone formation from tetraorganotins and acyl chlorides (ref.22).

They used so-called "ligandless" palladium in HMPA at room temperature for reactions between allyl bromides and tetraorganotins (ref.23), but found it necessary to resort to PdL_4 to carry out similar reactions with the less reactive allyl acetates (ref. 24):

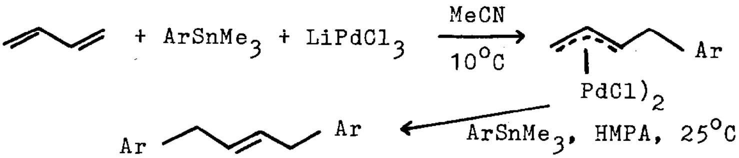


(77-95%) (15)



(68-100%) (16)

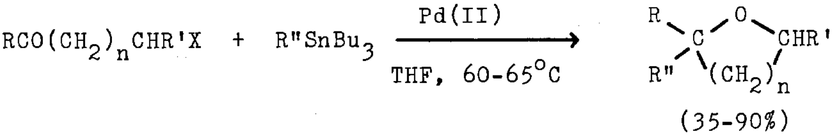
A stoichiometric reaction between butadienes, $LiPdCl_3$ and trimethylaryltins to form π-allylpalladium complexes was also reported (ref.25); these in turn react further under appropriate reaction conditions (ref.26):



(17)

Literature on C-C bond formation referred to below has appeared since Beletskaya's review was written.

Stille and co-workers have shown that the ketone synthesis reported by them earlier (ref.15, 17) can be more advantageously carried out at 65°C in chloroform instead of HMPA (ref.27). They have also reacted acetonyl- and allyltins with α-haloketones and α-haloaldehydes to form substituted cyclic ethers using various palladium(II) catalysts (ref.28): this reaction was originally reported by Kosugi et al. (ref.14) for epoxide formation.

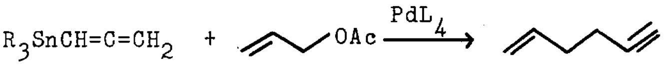


(18)

(n=0-2;X=Cl, Br; $R''=CH_2COCH_3$, $CH_2=CH-CH_2$)

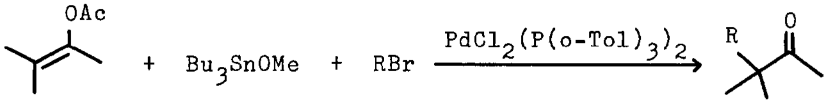
$PhCH_2PdClL_2$ was generally the best catalyst; catalysts containing optically active phosphines gave low asymmetric induction.

PdL_4 has been used as a catalyst for transferring the propargyl group from an allenyltin to an allylic moiety (ref.29):



(19)

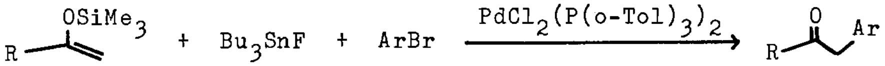
Tributyltin methoxide has been used as an intermediary in the palladium(II)-catalysed α-phenylation (ref.30) and α-1-alkenylation (ref.31) of ketones; both processes occur via intermediate tin enolates, which have been used previously as discrete starting materials (ref.20):



(20)

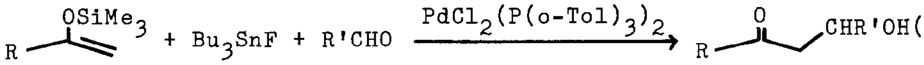
(R=Ph, 1-Alkenyl)

Another method of forming tin enolates in situ involves the use of silyl enol ethers and tributyltin fluoride: a "one-pot" reaction leads to arylation of methyl ketones (ref.32):



(21)

The above is the best catalyst; Bu_3SnCl or Bu_3SnOMe are ineffective in this reaction. The same methodology has also been applied to the aldol reaction (ref.33):

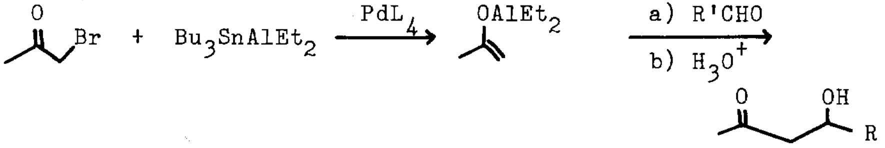


(22)

Two other reactions should be mentioned in this context, since they involve the use of organotin reagents. An alternative route to silyl enol ethers is provided by the reaction of tin-silicon bonds with α-haloketones (ref.34):

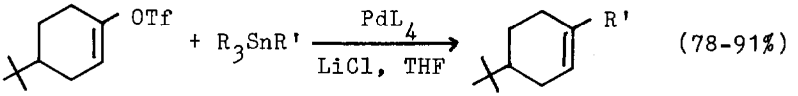
$$\text{BrCRR'COR''} + \text{Me}_3\text{Sn-SiMe}_3 \xrightarrow{\text{PdCl}_2/\text{P(OMe)}_3} \text{RR'C=C(R'')OSiMe}_3 \quad (23)$$

Similarly, tin-aluminium reagents can be used to form aluminium enolates which then give a Reformatsky-type reaction: the addition of PdL_4 improves the yield by up to 20% (ref.35).



(24)

The related vinyl triflates undergo coupling with tetraorganotins in the presence of a palladium catalyst: lithium chloride must be added to ensure a clean reaction (ref.10)



(25)

($R' = CH{=}CH_2$, Bu, $CH_2CH{=}CH_2$, $C{\equiv}CSiMe_3$)

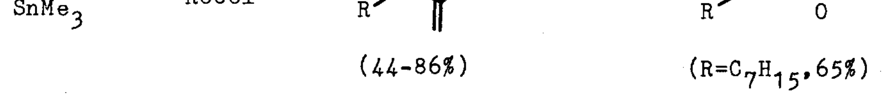
An alternative source of aryl groups for coupling reactions has been suggested: instead of aryl halides, aryl diazonium salts (ref. 36) react in the presence of palladium(0) or palladium(II) :

$$\text{ArN}_2\text{X} + \text{R}_4\text{Sn} \xrightarrow{\text{Pd}} \text{Ar-R} \quad (26)$$

($R_4Sn = Me_4Sn$, Ph_4Sn, $Bu_3SnCH{=}CH_2$, $PhSnBu_3$)

In the latter two cases, only vinyl or phenyl groups are transferred.

The synthetic scope of the coupling reactions of vinyltin compounds has been increased by introducing an α-oxygen function, providing a route to α-oxygenated enones which can in turn undergo further conversions (ref.37):

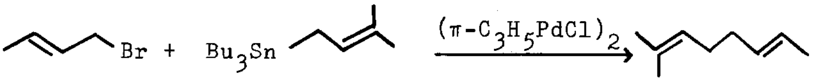


Beletskaya's group has published several papers (ref.38-43) dealing with cross-coupling basically as described previously, but also extended the methodology by reacting acyl chlorides with hexaethylditin (ref. 42, 43): this reaction probably proceeds via the virtually unknown stannyl ketones (acyltins). However if this is the case these apparently decarbonylate at some stage, since the main product is the diarylketone:

$$ArCOCl + Et_6Sn_2 \xrightarrow[PhCH_3]{PhPdIL_2} \underset{(47\text{-}68\%)}{Ar_2CO} + \underset{(3\text{-}25\%)}{(ArCO)_2} + \underset{(3\text{-}30\%)}{Ar_2} \qquad (28)$$

At a carbon monoxide pressure of 8atm, the yield of the α-diketone was raised to 50-76% for comparable acid chlorides.

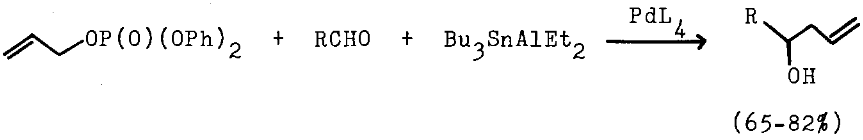
Schwartz (ref.44) has noted that the reaction of allyltins with π-allylpalladium chlorides yield bis(allyl)palladium species which only couple by reductive elimination on adding maleic anhydride, and used this information to develop a catalytic synthesis:



(40%)

However, the amounts of homocoupled products formed are usually comparable to those of the cross-coupled product.

The synthesis of homoallylic alcohols starting from allylic phosphates and aldehydes and using a tin-aluminium reagent has also been described (ref.45):

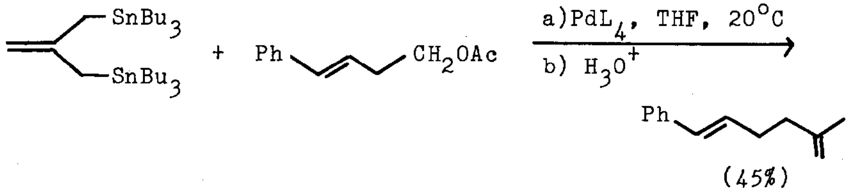


(29)

(R=Ph, C_5H_{11})

Other tin-aluminium reagents such as $Me_3SnAlEt_2$ or $Et_2AlSnClF_2$ give comparable yields. The stereochemistry of the formation of the intermediate allyltins has been determined.

One reaction of a compound containing two allylic stannyl residues has been reported (ref. 46): only one stannyl group is substituted.



(30)

4. CARBON-CARBON BOND FORMATION UTILISING CO

It was noted in 1979 that the cross-coupling between an organic iodide and a tetraalkyltin could be readily modified by introducing carbon monoxide to give an alternative method for ketone synthesis (ref. 47):

$$RX + CO + R'_4Sn \xrightarrow[HMPA]{PhPdIL_2} RCOR' \quad (62\text{-}86\%) \tag{31}$$

($R=Ph$, $PhCH_2$, $PhCH=CH$, EtO_2CCH_2; $X=Cl$, Br, I; $R'=Me$, Bu, Ph)

Organic halides with β-hydrogens could also be used (ref.48), and comparative studies showed that in the systems studied (Me_4Sn plus $PhCH(Br)Me$, $PhCH(Br)Et$, $MeCH(Br)CO_2Et$) the best catalyst was $PdCl_2(AsPh_3)_2$. Nickel catalysts were also found to be suitable (ref. 49), that of choice being the air-stable $Ni(CO)_2(PPh_3)_2$: however, though this reacts with Me_4Sn, no reaction is observed using Ph_4Sn.

The carbonylation reaction was extended to include mixed tetraorganotins by Beletskaya and co-workers (ref.50) using π-allyl palladium chloride as catalyst. They also carried out the reaction between hexaethylditin, CO and an aryl iodide to produce an α-diketone (ref. 42, 43)

$$Et_6Sn_2 + 4\text{-}MeOC_6H_4I + 2\ CO \xrightarrow{Pd(II)} (4\text{-}MeOC_6H_4CO)_2 \quad (71\%) \tag{32}$$

In a recent publication (ref.51) they have described the use of trialkylstannyl nucleophiles to form carboxylic acid derivatives:

$$ArI + Alk_3SnNu + CO \xrightarrow[20^{o}C,\ 1\ atm\ CO]{PhPdIL_2} ArCONu \tag{33}$$

($Nu=MeO$, RS, Et_2N)

Stille (ref.52) has used tributyltin hydride as a precursor for aldehyde formation:

$$RX + Bu_3SnH + CO \xrightarrow[toluene,\ 50^{o}]{PdL_4} RCHO \quad (38\text{-}100\%) \tag{34}$$

($R=Ar$, $PhCH_2$, $CH=CH_2$, $CH_2\text{-}CH=CH_2$; $X=Cl$, Br, I)

and has also described a route to unsymmetrical divinyl ketones (ref.53):

$$\mathrm{R_3SnCH{=}CHR' + R''CH{=}CHI + CO \xrightarrow{Pd(II)} R'CH{=}CH\text{-}CO\text{-}CH{=}CHR''} \qquad (34)$$

(40-93%)

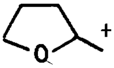
(R=Me, Bu; R'=H, Me, Ph, $\mathrm{CO_2CH_2Ph}$)

The catalysts used were $\mathrm{PhCH_2PdClL_2}$ or $\mathrm{Cl_2PdL_2}$; the geometries of both vinyl constituents are retained in the ketone, though Z/E isomerisation (slowed in the dark) is observed under the reaction conditions.

5. FORMATION OF BONDS BETWEEN CARBON AND OTHER ELEMENTS

In view of the plethora of publications which have been concerned with carbon-carbon bond formation, it might have been expected that the formation of other carbon-element bonds would also have been looked at in some detail. In fact this is only the case for carbon-tin bonds, as will be seen below.

Stille (ref.54) has reported that the cleavage of certain ethers (cyclic, allylic and benzylic) by acyl halides is catalysed by palladium(II) complexes and trialkyltin halides. Cyclic esters yield ω-haloesters:



$$\mathrm{+\ PhCOCl \xrightarrow{Pd(II),\ Bu_3SnCl} PhCO_2(CH_2)_3CH(CH_3)Cl} \qquad (35)$$

(81%)

In the case of benzyl or allyl ethers, the benzyl- or allyl-oxygen bond is cleaved:

$$\mathrm{PhCH_2OR + R'COCl \xrightarrow{Pd(II),\ Bu_3SnCl} PhCH_2Cl + RCO_2R'}$$

However, the reaction of allyl ethers is stoichiometric with regard to the tin halide:

$$\mathrm{Bu_3SnCl + CH_3COCl + PhOCH_2CH{=}CH_2 \xrightarrow{Pd(II)} Bu_2SnCl_2 + CH_3CO_2Ph + C_4H_8 + CH_2{=}CHCH_3} \qquad (36)$$

These cleavage reactions appear to have some advantages as deprotection reactions.

Migita et al. have shown (ref.55) that stannyl amines can be used in palladium-catalysed amination of aryl bromides:

$$\mathrm{Bu_3SnNEt_2 + RC_6H_4Br \xrightarrow{PdCl_2(P(o\text{-}Tol)_3)_2} RC_6H_4NEt_2} \qquad (37)$$

(16-81%)

The first report of palladium-catalysed tin-carbon bond formation was published by Eaborn et al. (ref.1) in 1976. In this preliminary work it was shown that hexamethyl- and hexabutylditin react with aryl bromides to give trialkylaryltins, but that biaryls are formed in substantial amounts in several cases. $Me_3SnSiMe_3$ was converted to the tin halide with formation of trimethylarylsilane.

Biaryl formation was particularly high when electron-withdrawing substituents were present in the aryl ring. Beletskaya's group showed (ref.56) that this problem can be solved by the use of π-allyl palladium chloride:

$$ArI + Me_6Sn_2 \xrightarrow[\text{DMF, } 20^{\circ}C]{(\pi\text{-}C_3H_5PdCl)_2} ArSnMe_3 \quad (83\text{-}100\%) \qquad (40)$$

While PdL_4 or X_2PdL_2 can also be used (ref.57, 58), yields are poorer (39-67%) and reaction conditions more extreme (toluene, $80^{\circ}C$). Benzyl and allyl halides were also shown to react.

A further note on work similar to that presented in ref.57 has since appeared (ref.59):PdL_4 was used as the catalyst.

$$RC_6H_4X + Bu_6Sn_2 \xrightarrow{PdL_4} XC_6H_4SnBu_3 \quad (21\text{-}98\%) \qquad (41)$$

($R = p\text{-}NO_2$, $m\text{-}NO_2$, $o\text{-}NO_2$, $p\text{-}MeCO$, $p\text{-}CN$; $X = Br$, I)

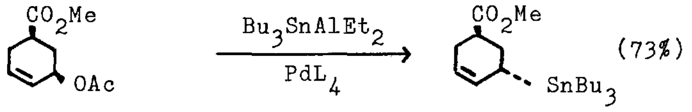
Iodide was clearly much superior to bromide as the leaving group.

Beletskaya's group has concerned itself recently not only with aryl iodides (ref.60) but also with allyl acetates and halides, for reactions of which they used PdL_4 as the catalyst (ref.61).

$$Me_6Sn_2 + \text{Allyl-X} \xrightarrow{PdL_4} Me_3Sn\text{- Allyl} \quad (73\text{-}96\%) \qquad (42)$$

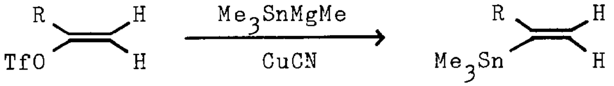
(X=OAc, catalyst PdL_4; X=halogen, catalyst $(\pi\text{-}C_3H_5PdCl)_2$)

Trost (ref.62) has also worked with allyl acetates, but instead of ditins has used a tin-aluminium reagent to form the tin-carbon bond. An example is shown below.



(43)

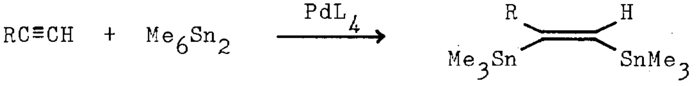
The tin-aluminium reagent shows a high degree of regio- and chemoselectivity and appears to react with inversion at the centre of substitution. Enol triflates or vinyl iodide also react with $Me_3SnMgMe$ in the presence of CuCN. to give vinyl stannanes in good yield:



(44)

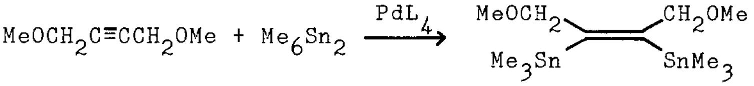
However, the corresponding stannyllithium reagent (with CuCN) or stannylaluminium compound (with PdL_4) did not react satisfactorily (yields 0 or 10% respectively).

The present author's group has recently concerned itself with addition reactions of ditins to unsaturated species. The first observation (ref.63) was that hexamethylditin adds in a cis-fashion to 1-alkynes



(10-90%) (45)

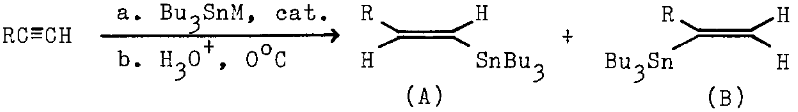
Partial or complete photochemical isomerisation to give the E-compounds is possible. A more complete account of this chemistry is in preparation: one interesting observation is that the presence of oxygen in the group R favours the reaction sufficiently that certain non-terminal alkynes can be used:



(46)

Hexabutylditin is less suitable than the hexamethyl compound as it is generally not consumed quantitatively, leading to difficult separation problems (ref.64).

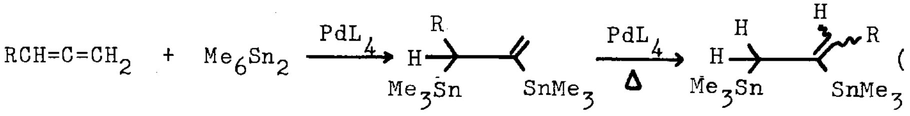
It has since been shown (ref.65) that tin-magnesium, tin-zinc or tin-aluminium reagents also add to 1-alkynes.



(47)

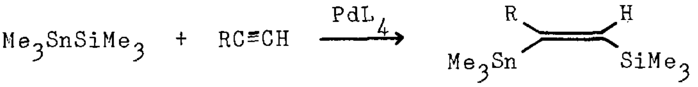
PdL_4 (or in one case Cl_2PdL_2) was used as the catalyst when M=Zn, while for the remaining reactions CuCN (in one case $CuBr.SMe_2$) was taken. The regiospecificity of the reaction varies widely and unpredictably (between A:B=100:0 and 5:95 in the cases studied), though the yields are good and the addition appears to be strictly cis.

Hexamethylditin also adds to allenes (ref.66); in the case of unsymmetrically substituted allenes kinetic and thermodynamic products are formed according to the reaction conditions:

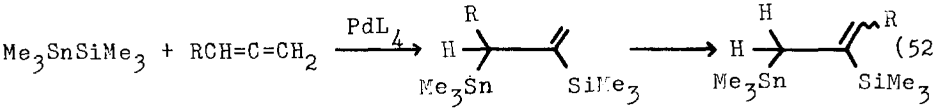


(50)

The tin-silicon bond also reacts with both 1-alkynes and allenes (ref.67): while the former is a regiospecific cis-addition the latter is regiospecific with respect to silicon, though again kinetic and thermodynamic products are observed:

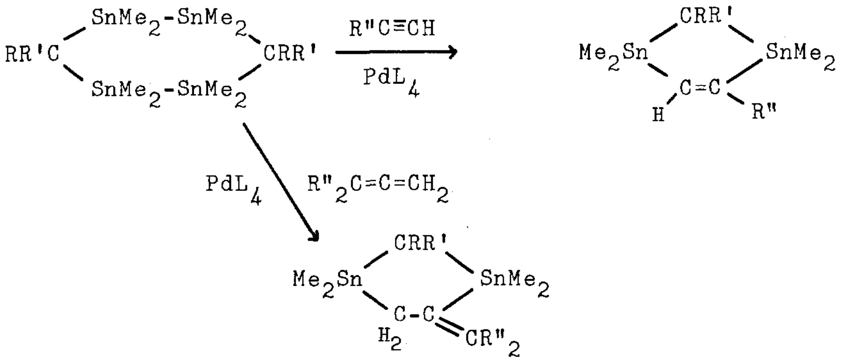


(28-65%) (51)



(52)

The tin-tin bond in tetrastannacyclohexanes also reacts with 1-alkynes and allenes (ref.68); in this case the products are five-membered heterocycles and not the ten-membered rings originally expected (though the formation of eight-membered rings has been observed).



(53)

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