

Review

THE CROSS-COUPLING REACTIONS OF ORGANIC HALIDES WITH ORGANIC DERIVATIVES OF TIN, MERCURY AND COPPER CATALYZED BY PALLADIUM

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Summary

The palladium-catalyzed cross-coupling of organic halides with organometallic compounds of tin, mercury and copper is discussed. It is shown that the "ligandless" palladium complexes $RPdXL_2$ ($L = \text{solvent}$), in which solvent molecules act as weak donating ligands, are the most active catalysts for reactions of organotin compounds. It is found that nucleophilic catalysis is an efficient method of activation of organomercury and organocopper compounds in cross-coupling reactions. In the presence of iodide ion the palladium-catalyzed reactions of these compounds proceed under mild conditions giving high yields of cross-coupling products.

Introduction

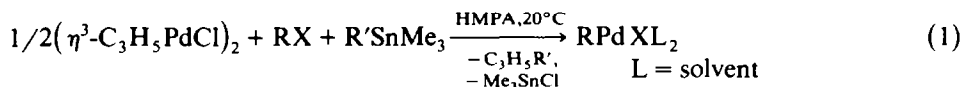
The cross-coupling reactions of organometallic reagents with organic halides, catalyzed by transition metal complexes, provide an efficient method for selective carbon-carbon bond formation. Organomagnesium compounds are most frequently employed in these reactions [1–4], although in a number of cases organozinc compounds turn out to be more suitable to retain the functional groups [5]. Organic halides with some functional groups can be used in the reaction with organoaluminium [6] and organozirconium compounds [7], obtained in situ.

The cross-coupling of organic derivatives of tin, mercury and copper, which allow the introduction of organic halides with any functional groups into the reaction, is of considerable interest for organic synthesis. However, the application of the conventionally used phosphinepalladium complexes, $Pd(PPh_3)_4$, $PhPdI(PPh_3)_2$ and $PhCH_2PdX(PPh_3)_2$, requires in the case of these organometallic compounds more stringent conditions than for compounds of magnesium, zinc, zirconium and

* This review was written jointly with Dr. N.A. Bumagin. The contribution of Dr. N.A. Bumagin in this field may be seen from the references.

aluminium, and the formation of large quantities of byproducts is observed. This situation is determined by the low nucleophilicity of organic derivatives of tin, mercury and copper during the transmetallation stage. Consequently, it is necessary to elaborate efficient methods of activation of these organometallic compounds or to use more active catalysts.

We have shown that "ligandless" palladium complexes RPdXL_2 ($\text{L} = \text{solvent}$) are the most active catalysts for cross-coupling, since they contain the weakest donating ligands. These complexes are obtained in situ from $(\eta^3\text{-C}_3\text{H}_5\text{PdCl})_2$, $(\text{MeCN})_2\text{PdCl}_2$, LiPdCl_3 , etc. in the presence of organic halides RX and organometallic compounds.

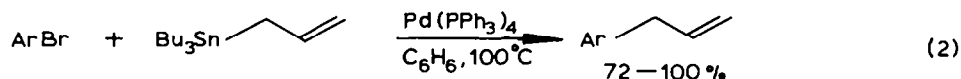


To activate the compounds of mercury and copper we used nucleophilic catalysts, which have wide application in the reactions of organometallic compounds with different electrophilic agents [8].

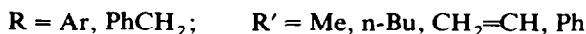
1. Reactions of RM ($\text{M} = \text{Sn, Hg, Cu}$) with $\text{R}'\text{X}$ ($\text{R}' = \text{Ar, vinyl, allyl}$)

1.1. Reactions of organotin compounds

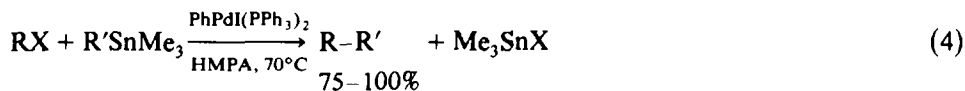
The first work on palladium-catalyzed cross-coupling of organotin compounds with aryl halides was published in 1977 [9]. It was found that allyltributyltin reacts with arylbromides in the presence of $\text{Pd}(\text{PPh}_3)_4$.



This reaction was extended to the coupling of aryl and benzyl halides with different organotin compounds $\text{R}'_4\text{Sn}$. Oxygen has a considerable accelerating effect on the reaction rate [10].



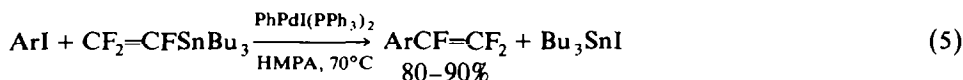
Cross-coupling reactions of the aryl derivatives of tin $p\text{-XC}_6\text{H}_4\text{SnMe}_3$ and $\text{PhC}\equiv\text{CSnMe}_3$ with nitroaryl iodides, catalyzed by $\text{PhPdI}(\text{PPh}_3)_2$, was performed in 1,2-dichloroethane at 120°C [11]. In HMPA, which increases the nucleophilicity of organotin compounds, the reactions may be carried out at lower temperatures [12]. Other organic halides such as $\text{PhC}\equiv\text{Cl}$, $\text{PhCH}=\text{CHBr}$ and 2-iodothiophene were introduced in the reaction. The cross-coupling with more active organotin compounds $\text{R}'\text{SnMe}$ ($\text{R}' = \text{CH}_2=\text{CH, PhC}\equiv\text{C}$) occurs at room temperature.



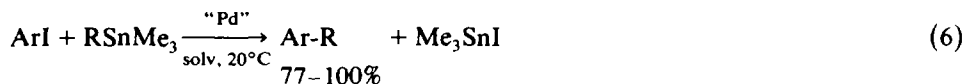
R = *p*-NO₂C₆H₄; X = I; R' = Me, CH₂=CH *, *p*-MeOC₆H₄, *p*-MeC₆H₄, Ph, *p*-ClC₆H₄,
p-NO₂C₆H₄, PhC≡C *.

R = *p*-MeCOC₆H₄, *p*-MeO₂CC₆H₄, PhC≡C, 2-C₄H₃S (2-thienyl); X = I, R' = Ph.
 R = PhCH=CH; X = Br; R' = Ph.

Coupling reactions of CF₂=CFSnBu₃ with aryl iodides, catalyzed by PhPdI(PPh₃)₂, may serve as a convenient method for the synthesis of trifluorostyrene and its derivatives [13].



We have shown that in the presence of the most active catalyst RPdXL₂ (L = solvent), in which solvent molecules act as ligands, the cross-coupling of organotin compounds with aryl iodides proceeds at room temperature. The "ligandless" palladium complex was obtained in situ from LiPdCl₃, RX and R'SnMe₃ [12].



Ar = *p*-NO₂C₆H₄;

R = CH₂=CH, Ph, PhC≡C.

Ar = Ph, *p*-CNC₆H₄, 2,4-(NO₂)₂C₆H₃;

R = Ph.

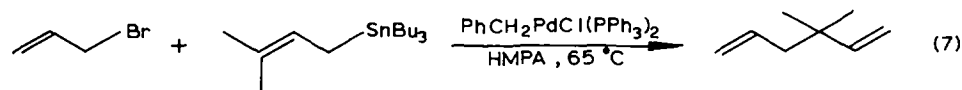
Ar = Ph;

R = *p*-MeC₆H₄.

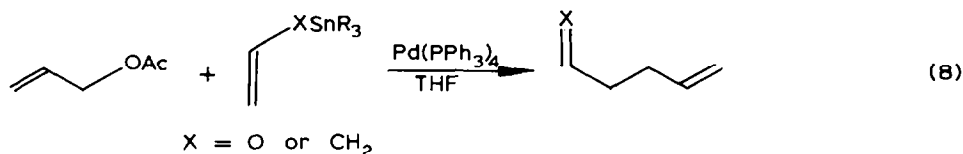
Not only HMPA or DMF but also acetone can be used as a solvent. It is interesting to note that in all these solvents the yields of coupling products are high and that the reaction rate depends on the nature of the reagents. Thus, for the combination of *p*-NO₂C₆H₄I and PhSnMe₃ the reaction rate is higher in acetone than in HMPA. In acetone 90% of the *p*-NO₂C₆H₄Ph is formed in 24 h, whereas in HMPA the conversion is only 30% after 72 h.

1.2. Reactions of organotin compounds with allylic substrates

In 1980 the cross-coupling reactions of allyl bromides and acetates with organotin compounds, catalyzed by palladium, was reported [14–16]. The reactions of allyl bromides with allylstannanes, catalyzed by PhCH₂PdCl(PPh₃)₂ or ZnCl₂, give 1,5-dienes without allylic transposition in the allylic halide but with allylic rearrangement in the allylic fragment of the tin reagent [14].

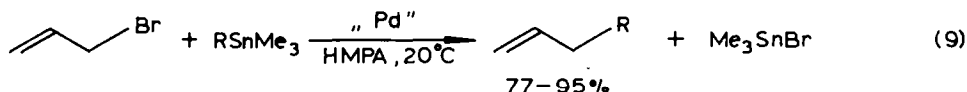


The cross-coupling reaction of organotin compounds with allyl acetates was catalyzed by Pd(PPh₃)₄ [15,16].



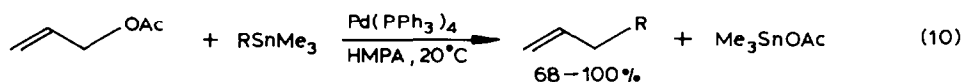
* At room temperature.

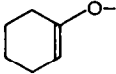
Under the conditions of "ligandless" palladium catalysis allyldemetallation of organotin compounds occurs readily in HMPA [17].



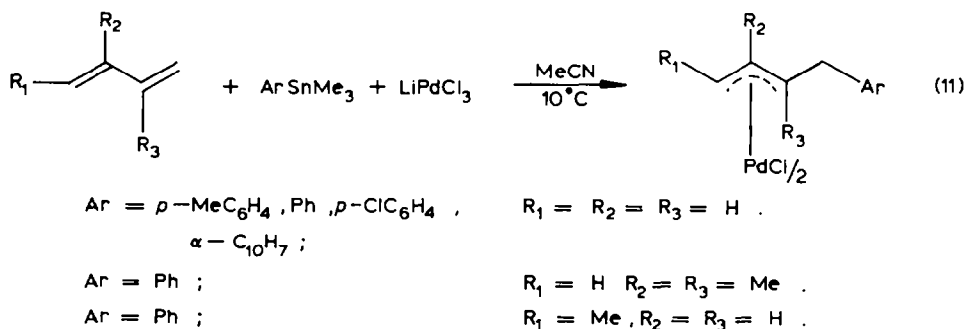
R = CH₂=CHCH₂, *p*-MeOC₆H₄, *p*-MeC₆H₄, Ph, *p*-ClC₆H₄, C₉H₉ (9-fluorenyl).

However, in the case of allyl acetates, which are less reactive than aryl iodides and allyl bromides in oxidative additions, it is again necessary to use palladium complexes with phosphine ligands. However in contrast to the reactions with aryl iodides [11-12], reactions of organotin compounds with allyl acetates take place at room temperature. Various organotin compounds were introduced into the cross-coupling reaction with allyl acetates [18].

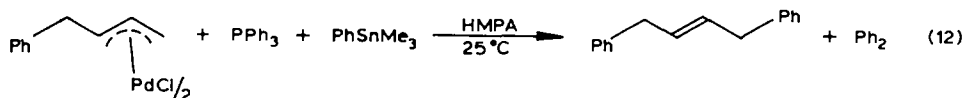


R = CH₂=CHCH₂, PhCH=CH, *p*-MeC₆H₄, Ph, 9-C₁₃H₉, C₉H₇ (indenyl), *c*-C₅H₅ (Cyclopentadienyl), Ph(CO₂Et)CH, MeCOCH₂, 

Treatment of organomercury compounds with dienes in the presence of LiPdCl₃ in MeCN leads to formation of bis(1-arylmethyl-η³-allylpalladium chlorides) with 30-60% yield [19], which undergo transformation to form substituted dienes in the presence of amines. At room temperature the first reaction is accomplished in 24 h. It was found that the use of aryltrimethylstannanes increases the yield to 70-90%, reduces the reaction time to 1 h at a decreased temperature of -30 to 10°C, which is important when using butadiene [20].

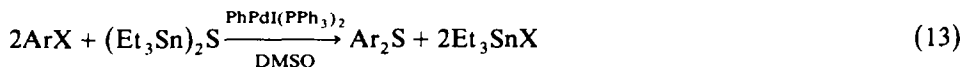


The complexes obtained react with aryltrimethylstannanes in the presence of PPh₃ in HMPA with formation of coupling products.



1.3. Reaction of $(Et_3Sn)_2S$ with aryl iodides

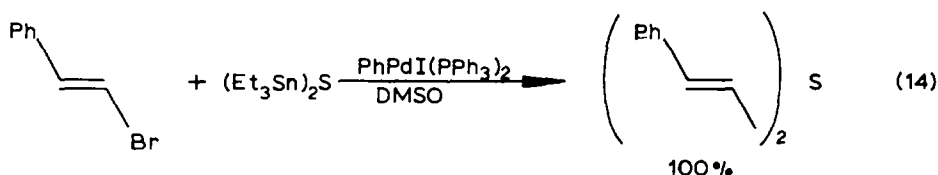
The synthesis of aryl phenyl sulfides may be carried out by reaction of sodium thiophenolate with aryl iodides or bromides, catalyzed by palladium or nickel complexes [21,22]. In phase-transfer catalysis thiophenole itself can be used [23]. Recently, Beletskaya, Lebedev and coworkers have shown that the palladium-catalyzed reaction of aryl iodides with $(Et_3Sn)_2S$ may be applied to the synthesis of diaryl sulfides.



Ar = *o*-, *m*-, *p*-MeC₆H₄, Ph, *p*-NO₂C₆H₄; X = I.

Ar = α -C₁₀H₇; X = Br.

Divinyl sulfides may be obtained from vinyl bromides. As it was shown in the case of *E*- β -bromostyrene the reaction with $(Et_3Sn)_2S$ is fully stereospecific.



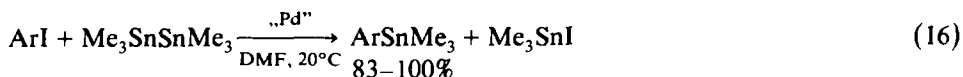
1.4. Synthesis of organotin compounds

It was shown earlier that the interaction of organic halides RX (R = allyl, benzyl, aryl) with hexamethyldisilane gave organosilanes in good yields [24–27].



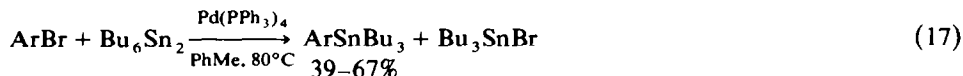
However, the preparation of $RSnMe_3$ by this way [25] could be achieved only by using aryl bromides containing electron-donating groups. In the case of aryl halides with electron-withdrawing substituents the reaction yielded only biaryl compounds.

We have shown recently that in the presence of $(\eta^3\text{-C}_3\text{H}_5\text{PdCl})_2$ as catalyst in CH_2Cl_2 it is possible to carry out the reaction between Me_6Sn_2 and aryl iodides containing electron-withdrawing functional groups, obtaining good yields of ArSnMe_3 [28]. We found later that DMF is the most effective solvent for the reaction of Me_6Sn_2 with ArI , although acetone, THF and HMPA can be used as well. The nitro, carbomethoxy, acetyl, nitrile and methoxy groups in ArI are retained [12].



Ar = *p*-MeOC₆H₄, Ph, *o*-, *m*-, *p*-NO₂C₆H₄, 2,4-(NO₂)₂C₆H₃, *o*-, *p*-MeO₂CC₆H₄, *p*-CNC₆H₄.

Catalysis of these reactions by $\text{Pd(PPh}_3)_4$ or $(\text{PPh}_3)_2\text{PdX}_2$ requires more stringent conditions and is less effective [29,30].



Ar = *o*-, *m*-, *p*-NO₂C₆H₄, *o*-, *m*-, *p*-CNC₆H₄, *o*-, *p*-MeCOC₆H₄

Together with Gulevich we have found that palladium-catalyzed dehydrogenation reaction of triorganyltin hydrides is a convenient method for the synthesis of hexaorganyldistannanes. Organotin hydrides themselves are produced in situ by reduction of R_3SnCl by $LiAlH_4$.



R = Me, Et, Bu, Ph

The distannanes obtained $(R_3Sn)_2$ can be used for the palladium-catalyzed reaction with organic halides without isolation.

1.5. Reactions of organomercury compounds

The cross-coupling reaction with aryl iodides, ArI , catalyzed by $PhPdI(PPh_3)_2$, was extended to organomercury compounds, R_2Hg and $RHgX$. However, the reaction proceeds with low selectivity, and besides the cross-coupling product $Ar-R$, the oxidative demercuration product R_2 is formed in large quantities. For example, the palladium-catalyzed reaction of Ph_2Hg with $p\text{-NO}_2C_6H_4I$ (2 eq.) in HMPA at $80^\circ C$ after 3 h leads to formation of $p\text{-NO}_2C_6H_4Ph$ (35%), Ph_2 (10%) and 65% of the $p\text{-NO}_2C_6H_4I$ remains unchanged, e.g. the ratio of cross-coupling and homo-coupling products is equal to ~ 3.5 . The demercuration products are also formed in the reactions of R_2Hg and $RHgCl$ with methyl iodide, catalyzed by $MeRhI_2(PPh_3)_2$ [31]. Thus, the easy demercuration is the main obstacle to the wide application of organomercury compounds in the cross-coupling reactions.

We have shown that in the presence of nucleophilic catalyst (iodide ion) the coupling of aryl iodides with organomercury compounds proceeds under mild conditions giving high yields of cross-coupling products. It is essential that both organic groups from R_2Hg take part in the reaction [32].



R = Me, 2,4,6- $Me_3C_6H_2$, o -, p - $MeOC_6H_4$, p - MeC_6H_4 , Ph; Ar = p - $NO_2C_6H_4$.

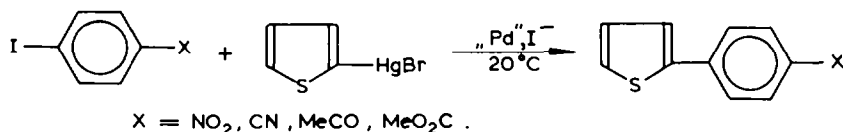
R = 2,4,6- $Me_3C_6H_2$; Ar = p - CNC_6H_4 , p - $MeCOC_6H_4$, p - $MeO_2CC_6H_4$.

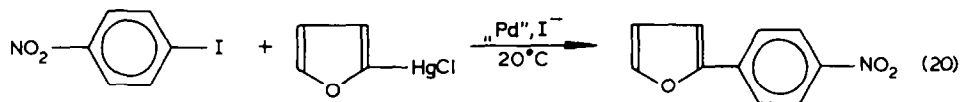
R = Ph; Ar = o -, p - $NO_2C_6H_4$, 2,4-(NO_2) $_2C_6H_3$, 2,4,6-(NO_2) $_3C_6H_2$.

In contrast to $RSnMe_3$ the cross-coupling of organomercury compounds must be carried out under inert atmosphere.

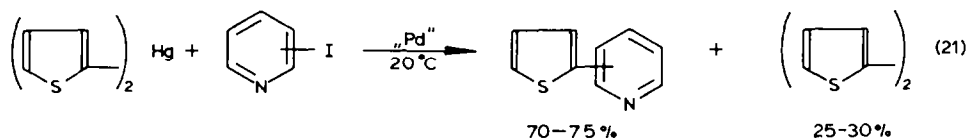
1.6. Synthesis of heterocyclic compounds

We and Kalinovskii have shown that organotin and organomercury derivatives allow one to carry out arylation of heterocyclic compounds via cross-coupling reaction. Coupling products are produced by reactions of bis-(2-thienyl)-mercury, 2-thienylmercury bromide and 2-furylmercury chloride with aryl iodides containing electron-withdrawing groups in high yields.

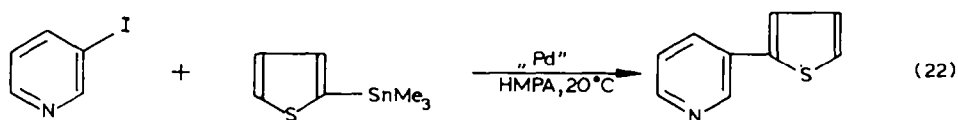




2-, 3- and 4-Iodopyridine may be used as arylating agents.



Similar reaction with 2-thienyltrimethyltin does not require an argon atmosphere and proceeds without formation of bis-2-thienyl.



However, thienyl- and furyl-mercurials may be obtained easily by direct mercuration. Moreover, in the case of R-SnMe_3 only one R radical takes part in the cross-coupling reaction.

1.7. Demercuration reactions of organomercury compounds

Rhodium-catalyzed oxidative demercuration of arylmercury derivatives leads to the formation of symmetric biaryls [33,34]. We have shown that iodide ion catalysis reduces the reaction time approximately fivefold at a decreased reaction temperature from 80 down to 25°C [35].



Ar = *p*-MeOC₆H₄, *p*-MeC₆H₄, Ph; X = Cl.

X = *p*-MeOC₆H₄, Ph, *p*-ClC₆H₄.

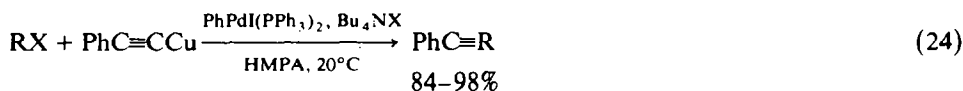
HMPA, acetone and benzene may be used as solvent. It was found that for the demercuration of Ar_2Hg , the palladium complex $\text{PhPdI}(\text{PPh}_3)_2$ is the best catalyst whereas the reaction of ArHgCl is best catalyzed by the rhodium complex $[\text{Rh}(\text{CO})_2\text{Cl}]_2$.

1.8. Reactions of organocopper compounds

Palladium catalysis may be used in cross-coupling reactions of organocopper compounds. Without palladium these reactions often require extreme conditions. For example, $\text{PhC}\equiv\text{CCu}$ reacts with aryl iodides giving substituted tolans under reflux in DMF for 8-16 h [36] or in pyridine for 6 h [37].

In the presence of 1 mol % $\text{PhPdI}(\text{PPh}_3)_2$ and 1 eq. Bu_4NX (X = Br, I) in HMPA this reaction is accomplished during 0.5-3 h at room temperature, forming tolans in high yields. Not only aryl and heteryl iodides but also vinyl and allyl bromides enter

into the reaction [38].



R = Ph, *p*-MeO₂CC₆H₄, *p*-MeCOC₆H₄, *p*-CNC₆H₄, *p*-NO₂C₆H₄, 2-C₄H₃S; X = I.
R = 2,4-(NO₂)₂C₆H₃, PhCH=CH, CH₂=CHCH₂; X = Br.

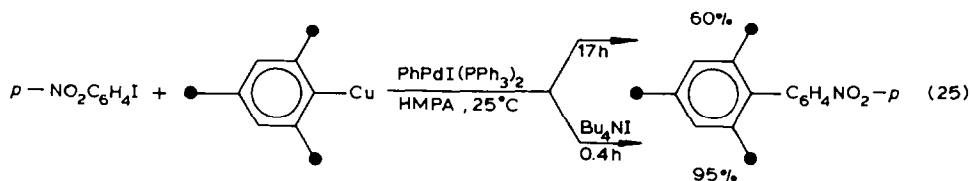
In the absence of Bu₄NX the palladium-catalyzed reaction of PhC≡CCu with RX requires higher temperatures and gives besides cross-coupling product considerable quantities of (PhC≡C)₂. In reaction with MeI, even in the presence of Bu₄NI, this process cannot be avoided, and (PhC≡C)₂ (54%) together with PhC≡CMe (46%) is formed. However, without palladium catalyst the cross-coupling reaction of PhC≡CCu with MeI could not be carried out even under extreme conditions [39]. Not only aryl iodides but also aryl bromides enter into the cross-coupling reaction with PhC≡CCu in the presence of iodide.

The reaction of PhC≡CCu with *p*-NO₂C₆H₄I was chosen as a model for the comparison of the catalytic activity of different palladium complexes. It was found that in the presence of iodide the reaction rate depends very slightly on the nature of the palladium catalyst used: PhPdI(PPh₃)₂, (AsPh₃)₂PdCl₂, (SbPh₃)₂PdCl₂, Pd(acac)₂, (MeCN)₂PdCl₂, LiPdCl₃, PdCl₂. The palladium complexes (η³-C₃H₅PdCl)₂ and (dppe)PdCl₂ are less active. So the most readily available and cheapest palladium compound PdCl₂ can be applied in the cross-coupling reaction.

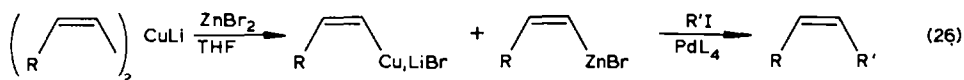
As it has been shown for the same reaction, HMPA, DMF, THF, acetone, ether, MeCN and benzene may be used as solvent. In acetone instead of Bu₄NI the more easily available NaI, LiBr or LiCl may be employed. In each case the reaction with *p*-NO₂C₆H₄I is accomplished in 15–20 min, yielding *p*-NO₂C₆H₄C≡CPh (96–98%).

Nickel complexes can also catalyze the cross-coupling reaction of PhC≡CCu with ArI, but are less efficient than palladium complexes. For example, the reaction of PhC≡CCu with *p*-NO₂C₆H₄I in acetone in the presence of NaI catalyzed by PhPdI(PPh₃)₂ yields 97% *p*-nitrotolan in 20 min; when catalyzed by (PPh₃)₂NiCl₂ 92% *p*-nitrotolan is formed after 17 h.

The role of the MX salts consists in increasing the solubility of the insoluble copper salts CuX due to formation of soluble CuX · MX complexes and as a result the surface of PhC≡CCu is cleared. However, Et₃N also forms a soluble complex with CuX, but in its presence only 20% of *p*-NO₂C₆H₄C≡CPh is obtained after 1 h. Apparently, halide ions cause nucleophilic assistance at the transmetallation stage. This conclusion is confirmed by the fact that addition of Bu₄NI, even in the homogeneous reaction of mesitylcopper with *p*-NO₂C₆H₄I, causes a sharp acceleration of the cross-coupling process. Without Bu₄NI the yield of (4-nitrophenyl)mesitylene was 60% after 17 h, and in the presence of Bu₄NI the yield of the coupling product was 95% after 0.4 h.



Palladium complex catalysis was used in the reaction of dialkenyl cuprates with vinyl and aryl iodides. Only one alkenyl group enters into cross-coupling [40,41].

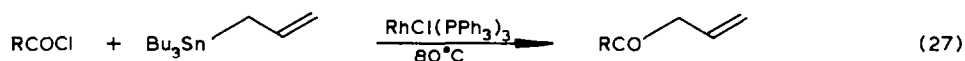


Recently it was shown that magnesium vinylcopper derivatives, in contrast to lithium dialkenyl cuprates, gave the possibility of using both alkenyl groups [42].

2. Acyldemetalation of organotin and organomercury compounds

2.1. Reactions of organotin compounds

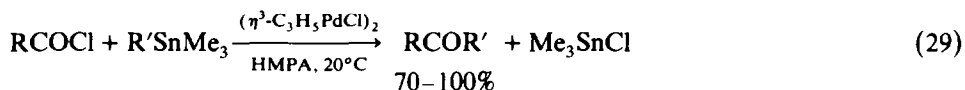
The reaction of tetraorganotin compounds with acid halides, catalyzed by transition metal complexes, has received considerable attention in recent years [43,44]. This reaction, catalyzed by $\text{RhCl}(\text{PPh}_3)_3$, was used for the synthesis of allyl ketones [43].



Later, other derivatives of tin (Me_4Sn , $\text{PhCH}_2\text{SnMe}_3$, $\text{CH}_2=\text{CHSnBu}_3$, Bu_4Sn , Ph_4Sn) were included in the scope of the acyldemetalation reaction catalyzed by $\text{PhCH}_2\text{PdCl}(\text{PPh}_3)_2$. The reactions were carried out with aliphatic, unsaturated, aromatic and heterocyclic acid chlorides [44].



The "ligandless" palladium catalysts enables synthesis of asymmetric ketones in high yields at room temperature [45].



$\text{R} = \text{Ph}$; $\text{R}' = \text{Me}$, PhCH_2 , $\text{CH}_2=\text{CH}$, Ph , $p\text{-ClC}_6\text{H}_4$, $p\text{-CNC}_6\text{H}_4$, $p\text{-NO}_2\text{C}_6\text{H}_4$, $2\text{-C}_4\text{H}_3\text{S}$.

$\text{R} = p\text{-NO}_2\text{C}_6\text{H}_4$; $\text{R}' = \text{Me}$, $\text{CH}_2=\text{CH}$, $p\text{-MeOC}_6\text{H}_4$, $p\text{-MeC}_6\text{H}_4$, Ph , C_6F_5 , $2\text{-C}_4\text{H}_3\text{S}$.

$\text{R} = \text{Me}$, $o\text{-FC}_6\text{H}_4$, PhCH_2 , $\text{PhCH}=\text{CH}$, $p\text{-ClCOC}_6\text{H}_4$; $\text{R}' = \text{Ph}$.

$\text{R} = p\text{-ClCOC}_6\text{H}_4$; $\text{R}' = \text{Me}$.

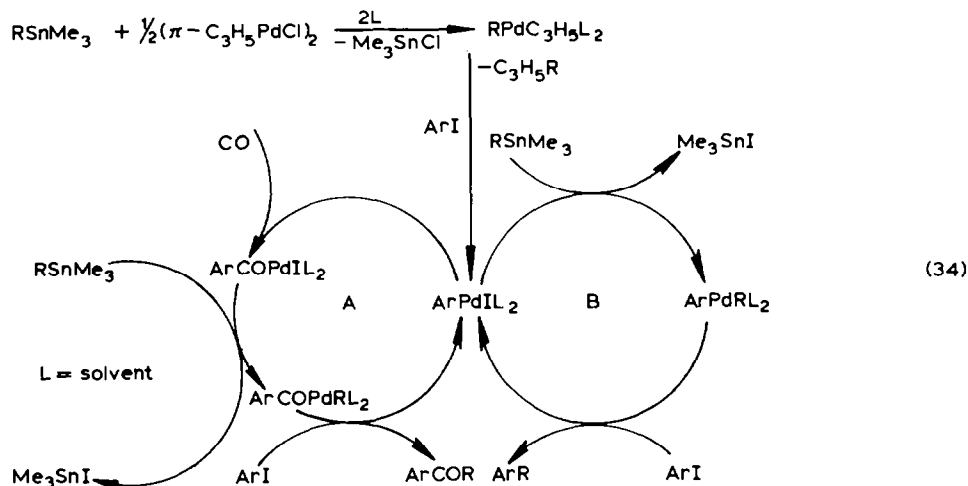
Since Me_4Sn and $\text{PhCH}_2\text{SnMe}_3$ react very slowly with $(\eta^3\text{-C}_3\text{H}_5\text{PdCl})_2$, a small quantity of Me_6Sn_2 was introduced to form the active catalyst.

The reactions with RCOCl ($\text{R} = \text{Ar}$, $\text{PhCH}=\text{CH}$), which readily enter into the oxidative addition, are fast (1 min–1 h) in HMPA. Reactions of aliphatic acid chlorides proceed at markedly lower rates (10–24 h).

The ketone yield turn out to be higher in acetone than in HMPA, although the reaction time was increased slightly. Apparently the RCOPdClL_2 ($\text{L} = \text{acetone}$) complex has a higher reactivity than the similar complex with $\text{L} = \text{HMPA}$, which to a certain extent compensates for the decreased ability of acetone to activate $\text{R}'\text{SnMe}_3$ in the transmetalation stage.

DMF and acetone can also be used as solvent in this reaction, although with increased reaction time, e.g., the carbonylation of PhSnMe_3 and $p\text{-NO}_2\text{C}_6\text{H}_4\text{I}$ takes 4 h in HMPA, 7 h in DMF and 25 h in acetone.

The carbonylation of organotin compounds RSnMe_3 ($\text{R} = \text{CH}_2=\text{CH}$, $\text{PhC}\equiv\text{C}$ and $2\text{-C}_4\text{H}_3\text{S}$), which are the most active in the transmetallation stage in HMPA, is accompanied by cross-coupling, i.e. two competitive processes are realized.

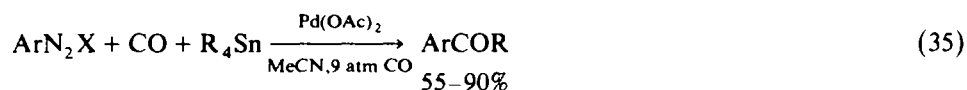


According to eq. 34 the fast reaction of RSnMe_3 with $(\eta^3\text{-C}_3\text{H}_5\text{PdCl})_2$ leads to the palladium complex $\text{RPd}(\text{C}_3\text{H}_5)\text{L}_2$ ($\text{L} = \text{solvent}$) which, on treatment with ArI , transforms into ArPdIL_2 which catalyzes both the carbonylation reaction (cycle A) and the coupling reaction (cycle B). The first stage of the catalytic cycle A is insertion of CO into the Ar-Pd bond in the ArPdIL_2 complex with formation of the acyl complex ArCOPdIL_2 . Then the transmetallation reaction between ArCOPdIL_2 and RSnMe_3 takes place. The catalytic cycle A is concluded by reductive elimination of ArCOR from the intermediate ArCOPdRL_2 , which is facilitated by ArI . The process of CO insertion is probably the rate-determining step of the catalytic cycle A due to low solubility of CO in HMPA under atmospheric pressure. This is why the stationary concentration of the acyl complex ArCOPdIL_2 is considerably lower than that of the aryl complex ArPdIL_2 . The catalytic cycle A involves participation of two palladium complexes able to take part in the transmetallation reaction: ArPdIL_2 and ArCOPdIL_2 , but the reactivity of the first complex is greater than that of the latter. However, due to the relatively low ArCOPdIL_2 concentration, the rate of the transmetallation reaction of the aryl complex for the interaction with RSnMe_3 ($\text{R} = \text{CH}_2=\text{CH}$, $2\text{-C}_4\text{H}_3\text{S}$, $\text{PhC}\equiv\text{C}$) becomes comparable with the transmetallation rate for the acyl complex (in the case of vinyl and 2-thienyltrimethyltin even surpasses it).

The selectivity of the reaction in this case could be enhanced by either increasing the CO concentration in the solution by applying higher pressure, or by using a solvent in which the rate difference between acylation and coupling reactions is greater than in HMPA. We found that acetone suits these conditions. Using acetone as a solvent we could achieve quantitative yield of the carbonylation product in the

reactions of $\text{CH}_2=\text{CHSnMe}_3$ and $2\text{-C}_4\text{H}_3\text{SSnMe}_3$. In the reaction of $\text{PhC}\equiv\text{CSnMe}_3$, the relative yield of the carbonylation product also increases.

Recently a direct transformation of ArN_2X to acyl arenes using metathesis between the in situ-formed aroyl palladium species and R_4Sn in the presence of CO was reported [51].



$\text{Ar} = \text{Ph}, o\text{-}, m\text{-}, p\text{-MeC}_6\text{H}_4, o\text{-}, p\text{-ClC}_6\text{H}_4, p\text{-BrC}_6\text{H}_4, p\text{-IC}_6\text{H}_4, m, p\text{-NO}_2\text{C}_6\text{H}_4;$

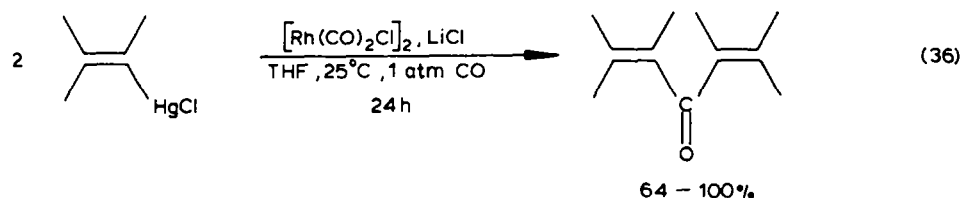
$\text{R} = \text{Me}.$

$\text{Ar} = \text{Ph}; \text{R} = \text{Et}.$

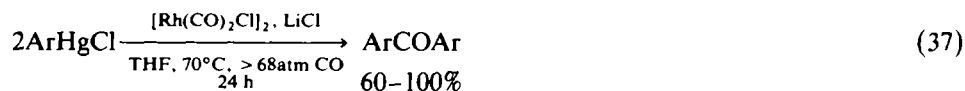
$\text{Ar} = p\text{-MeC}_6\text{H}_4, p\text{-Br C}_6\text{H}_4; \text{R} = \text{Ph}$

3.2. Carbonylation of organomercury compounds

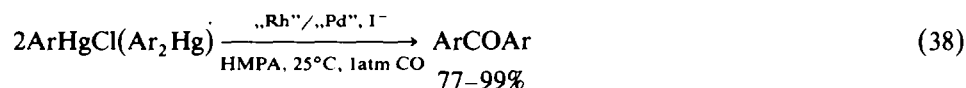
As it was shown earlier, vinylmercuric chlorides readily react with carbon monoxide in the presence of rhodium(I) and rhodium(III) catalysts to give excellent yield of divinyl ketones [52].



The best reaction conditions are 0.5 mol% $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and 2 eq. of LiCl under 1 atm of carbon monoxide at room temperature. However, more stringent reaction conditions are required for carbonylation of arylmercuric chlorides. An increase of the reaction temperature to 70°C and carbon monoxide pressure to 68–104 atm allows formation in THF of a high yield of diaryl ketones [52].



We found that in the presence of Bu_4NI the carbonylation of Ar_2Hg and ArHgCl , catalyzed by $\text{PhPdI}(\text{PPh}_3)_2$ or $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, may be carried out under extremely mild conditions: 25°C and 1 atm of CO [53].



$\text{Ar} = p\text{-MeOC}_6\text{H}_4, p\text{-MeC}_6\text{H}_4, \text{Ph}, p\text{-ClC}_6\text{H}_4.$

Small quantities of biaryls are also formed as a by-product due to oxidative demercuration of the organomercury compounds. This process can be avoided by use of the rhodium catalyst $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ for Ar_2Hg and the palladium catalyst $\text{PhPdI}(\text{PPh}_3)_2$ for ArHgCl .

4. Conclusion

In contrast to Grignard reagents organotin and organomercury compounds are comparatively rarely used in organic chemistry due to their low reactivity. However, since organic compounds of tin and mercury are readily available, do not react with oxygen and atmospheric moisture, are thermally stable and inert towards many functional groups, it is of considerable interest to employ them in organic synthesis. Their low reactivity is easily overcome with transition metal complex catalysis. One could say that metal complex catalysis "revitalized" these compounds and the purpose of the present article was to illustrate some aspects of this phenomenon.

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