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Historical note

Palladium-catalyzed cross-coupling reaction of organic halides with Grignard reagents, organolithium compounds and heteroatom nucleophiles

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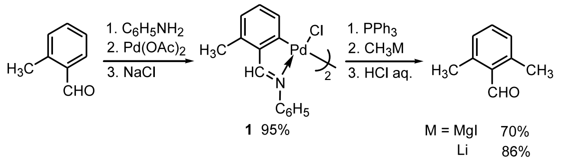
Abstract

Since palladium-catalyzed cross-coupling reaction of vinyl and aryl halides with Grignard reagents and organolithium compounds has been found, great progress on the related palladium-catalyzed reaction, which includes the reaction with heteroatom nucleophiles, has been made. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Palladium catalyst; Cross-coupling; Grignard reagents; Organolithium compounds; Heteroatom nucleophiles

1. Introduction

The difficulty of nucleophilic substituiton at a sp^2 carbon atom by conventional organic techniques is overcome by using transition metals. In the 1970s C–C bond formation by the transition metal catalyzed cross-coupling reaction of vinyl halides with either Grignard reagents or organolithium compounds is one of the attractive and important pathways for the synthesis of alkenes. The stoichiometric process for synthesis of alkenes was established by the reaction of vinyl halides with organocopper compounds [1]. This stoichiometric reaction has been replaced by the catalytic reaction. Stereoselective synthesis of alkenes by cross-coupling reaction of vinyl halides with Grignard reagents was shown using iron catalysts by Kochi et al. in 1970 [2]. Then, the nickel-catalyzed cross-coupling reactions of vinyl halides with Grignard reagents were found to proceed highly efficiently by Corriu et al. [3], and Kumada and Tamao et al. [4] in 1972. However, the nickel catalysts are unfortunately not applicable to the reaction with organolithium compounds, which are highly versatile reagents. Therefore, we aimed at using palladium catalysts for cross-coupling reaction of vinyl halides, because at that time we had demonstrated that palladium-catalyzed reactions which include, alkylation of allyl acetates [5], alkyl exchange reactions of amines (C–H bond activation) [6], oxypalladation [7], and *ortho*-alkylation of benzaldehydes [8] can be performed efficiently. We were interested in the reactivity of Pd–C bonds towards carbon nucleophiles. In order to have a compound which has suitable Pd–C bonds, we prepared Schiff base palladium complex **1** by ortho-metallation. Treatment of the complex **1** with Grignard reagents or organolithium compounds gave ortho-alkylated benzaldehydes (Eq (1)). Higher yields were obtained with alkyllithium in comparison with alkylmagnesium iodide. If one repeats the process twice, 2,6-dialkylated benzaldehydes can be prepared selectively [8].



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In relation to this chemistry, we aimed at stereoselective synthesis of alkenes from vinyl halides using palladium catalysts rather than the cross-coupling reaction of aryl halides, because control of the reaction of vinyl halides is much more difficult than that of aryl halides, and the reactions are easily applied to cross-coupling reaction of aryl halides. We will discuss the palladium-

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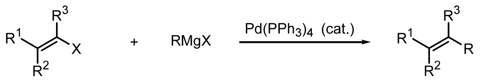
catalyzed cross-coupling reaction of vinyl halides with Grignard reagents, organolithium compounds, and heteroatom nucleophiles in the 1970's and their development.

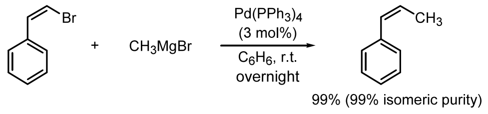
2. Palladium-catalyzed cross-coupling reaction of vinyl and aryl halides with Grignard reagents

The first two reports on the palladium-catalyzed cross-coupling reaction appeared in 1975 [9,10]. We found that tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ is an effective catalyst for stereoselective cross-coupling reaction of vinyl halides with Grignard reagents (Eqs. (2)) [9,11].



(2)

Cassar reported the palladium-catalyzed cross-coupling reaction of aryl halides with sodium acetylides [10]. The palladium-catalyzed cross-coupling reaction with Grignard reagents proceed stereoselectively in excellent yields (Eqs. (3)–(5)). The stereochemistry of the products must be checked in each reaction, because we were not sure of the stereochemistry of these reactions at that time.



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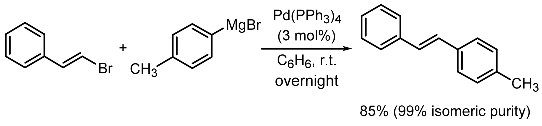

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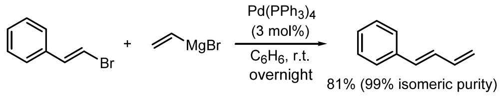
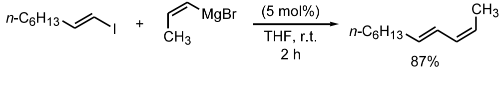


(5)

Actually, the corresponding silver-catalyzed [2b,12] and ruthenium-catalyzed [11] cross-coupling reactions proceed highly efficiently, but the stereochemistry was not satisfactory. After we reported the palladium-catalyzed cross-coupling reaction, the method was developed quite rapidly. The palladium-catalyzed cross-coupling reaction of vinyl halides with vinyl magnesium bromide (Eq. (6)) [13], and that of aryl halides with Grignard reagents (Eqs.(7) and (8)) [14–16] were reported.



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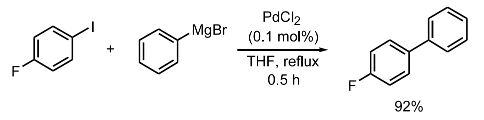

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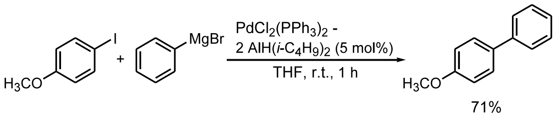
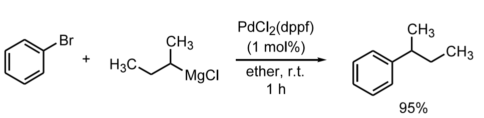


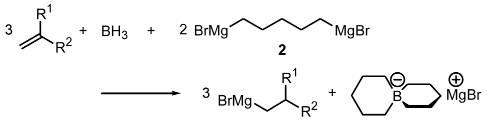
(8)

The important finding is that the isomerization of secondary alkyl group to the primary one is retarded by using 1,1′-bis(diphenylphosphino)ferrocene (DPPF) as a ligand (Eq. (9)). It can be said that DPPF on palladium hinders the β-hydride elimination and accelerates the reductive elimination from the diorganopalladium intermediate [17].



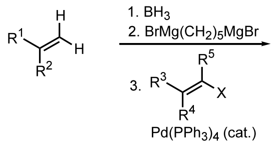
(9)

At that time, the palladium-catalyzed cross-coupling reaction of vinyl halides with Grignard reagents had no particular advantage over the corresponding nickel-catalyzed reaction except for higher stereoselectivity. Therefore, in order to raise the value of our palladium-catalyzed reaction, we aimed at combining the palladium-catalyzed cross-coupling reaction with boron chemistry, which has anti-Markovnikov addition to alkenes. Transmetallation of organoboron compounds to Grignard reagents is very attractive. However, it is a rather difficult task, because the transmetallation of organoboron compounds to Grignard reagents is in equilibrium, and the product is a mixture of organoboron compounds and Grignard reagents. We discovered that selective transformation of trialkylboranes to alkylmagnesium compounds occurs selectively upon treatment with pentane-1,5-di(magnesium bromide) (**2**) (Eq. (10)) [18]. The efficiency of the transformation is enhanced by the selective hydroboration in an anti-Markovnikov fashion and its tolerance for various common functional groups such as halogens and alkenes.



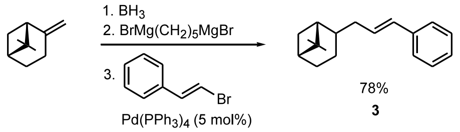
(10)

Actually, we succeeded in preparation of Grignard reagents directly from alkenes in an anti-Markovnikov fashion selectively [18]. Stereospecific one-pot synthesis of alkenes from vinyl halides and the Grignard reagents thus formed is accomplished conveniently by the palladium-catalyzed cross-coupling reaction (Eq. (11)).



(11)

The efficiency of this method is augmented by the ease with which it is performed as typified in the following procedure for the one-pot preparation of compound **3** from (−)-β-pinene and (*E*)-β-bromostyrene (Eq. (12)) [18].



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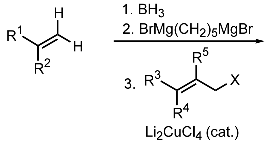
(12)

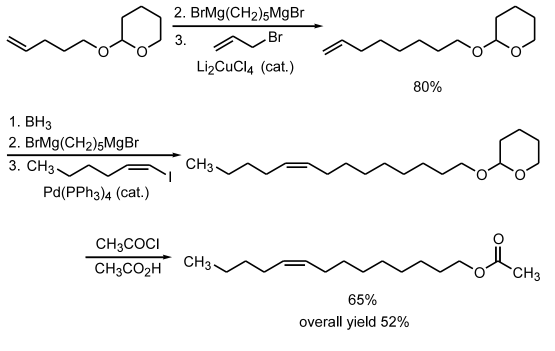
Three carbon homologation of alkenes can be performed efficiently, when allyl halides are allowed to react with the Grignard regents, thus formed from alkenes (Eq. (13)).



(13)

These methods can be utilized for the three-step synthesis of the sex pheromone of the southern armyworm moth. The synthetic procedure based on the $C_5 + C_3 + C_6$ is shown in the following Scheme 1.

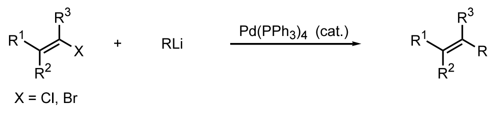
The transformation of organoboron compounds, which are derived from alkenes in an anti-Markovnikov fashion, to the other organometallic compounds such as organocopper [19] and organozinc compounds [20–22] are particularly useful. Knochel et al. reported highly efficient methods for transformation of organoboron compounds to organozinc compounds, which can be used for the transition metal-catalyzed cross-coupling reaction [22].



Scheme 1. Synthesis of the sex pheromone of the southern army moth.

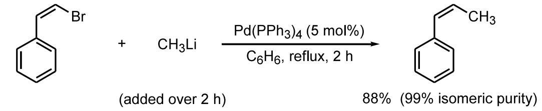
3. Palladium-catalyzed cross-coupling reaction of vinyl and aryl halides with organolithium compounds

One of the main reasons we started to study the palladium-catalyzed cross-coupling reaction was that the nickel-catalyzed cross-coupling reaction with organolithium compounds did not work well. Since organolithium compounds are versatile reagents and have advantages, which include the ready formation by direct lithiation of hydrocarbons [8], the palladium-catalyzed cross-coupling reaction with organolithium compounds will open a wide range of synthetic procedures (Eq. (14)).



(14)

We reported the palladium-promoted reaction of vinyl halides with organolithium compounds in 1975 [9]. And then the catalytic reaction of organolithium compounds was reported in a full paper in 1979 (Eqs. (15) and (16)) [11].



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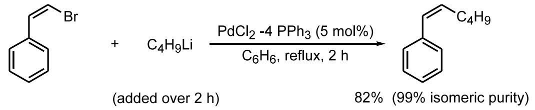
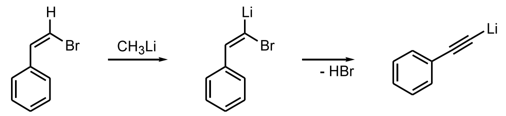


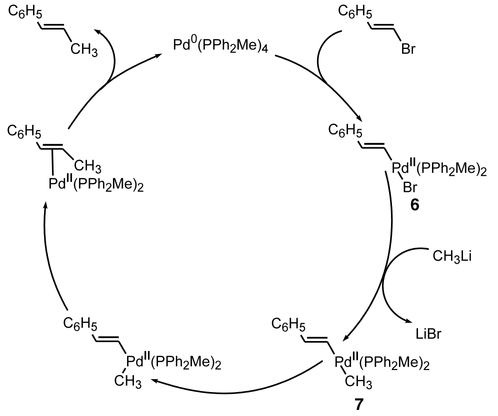
(16)

Importantly, when using palladium catalysts, vinyl halides undergo the cross-coupling reaction with organolithium compounds stereoselectively to give alkenes, whose isomeric purity is higher than those obtained from the nickel-catalyzed cross-coupling reaction of vinyl halides with Grignard reagents. To accomplish the catalytic reaction cleanly, the rate of addition of organolithium compounds is crucial, because fast addition of organolithium compounds produces α-bromoalkenyllithium, which undergoes Fritsh–Butlenberg–Wiechell type rearrangement to give the corresponding lithium acetylide (Eq. (17)), giving lower yield of the desired product.



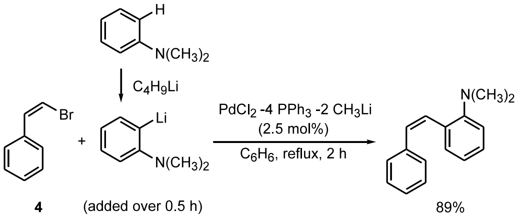
(17)

After we published this full paper, we received an invitation letter from Organic Synthesis, and we submitted the procedure [23]. The strongest merit of organolithium compounds is direct lithiation of hydrocarbons because of chelation effect of heteroatoms [24].



Scheme 2. Mechanism of the palladium-catalyzed cross-coupling reaction of (*E*)-β-bromostyrene with methyllithium.

Typical examples are shown as follows. Direct lithiation of *N*,*N*-dimethylaniline gave the *ortho*-lithiated compound, which undergoes the palladium-catalyzed cross-coupling reaction with either (*Z*)-β-bromostyrene (**4**) or tolyl iodide (**5**) in very good yields (Eq. (18) and (19)).



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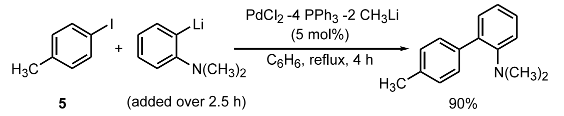
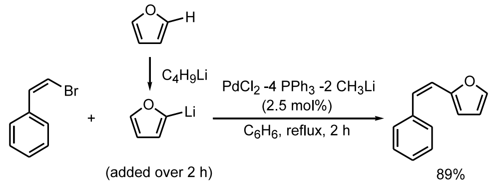


(19)

Similarly, stereoselective synthesis of (*Z*)-(2-furyl)-styrene can be performed highly efficiently (Eq. (20)).



(20)

The crucial point of these reactions is to design highly reactive palladium(0) catalysts. Therefore, we wanted to make such highly reactive palladium(0) catalysts as follows [11,23]. Treatment of dichloropalladium(II) $PdCl_2$ with two molar equivalents of methyllithium in the presence of triphenylphosphine PPh_3 in benzene at reflux for 2 h gave a clear solution of palladium(0) catalyst, which is extremely reactive. The idea is that treatment of $PdCl_2$ with methyllithium in the presence of PPh_3 would give dimethylbis(triphenylphosphine)palladium(II) lithium chloride $Pd(CH_3)_2(PPh_3)_2LiCl$, which undergoes reductive elimination to give palladium(0) species $Pd(PPh_3)_2LiCl$ and ethane (Eq. (21)) [23].

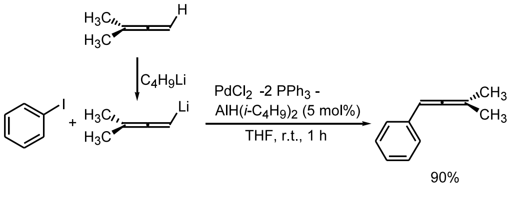
$$PdCl_2 + 2\,CH_3Li + PPh_3 \longrightarrow Pd(PPh_3)_2LiCl + CH_3CH_3 \qquad (21)$$

The complex $Pd(CH_3)_2(PPh_3)_2LiCl$ obtained from dichlorotris(triphenylphosphine)palladium $PdCl_2(PPh_3)_3$ and methyllithium undergoes decomposition at 40 °C to give a black solution [25]; however, our catalytic system is a clear solution, which produces $Pd(PPh_3)_2LiCl$. Actually, the palladium-catalyzed cross-coupling reactions can be performed highly efficiently by using this palladium(0) catalyst. The reactivity of our catalyst is much higher than $Pd(PPh_3)_4$. The important and strong points are that a clean catalyst can be prepared, and the scale-up of the reaction is performed readily. The high reactivity of this catalyst may be due to the coordination of chloride ion to bis(triphenylphosphine)palladium(0) $Pd(PPh_3)_2$. Thus, we refined the catalytic system and published the procedure in Organic Synthesis in 1984 [23]. Our catalytic system was analyzed by Negishi et al. in 1986, and the presence of $Pd(PPh_3)_2LiCl$ was confirmed [26]. Furthermore, the role and effects of chloride ion to $Pd(PPh_3)_2$ was proved by Amatore et al. [27]. The other methods for synthesis of highly reactive palladium(0) species are treatment of $PdCl_2$ with potassium in the presence of two molar equivalents of PPh_3 in THF, giving palladium slurry [11], or treatment of $PdCl_2(PPh_3)_2$ with $AlH(i\text{-}C_4H_9)_2$ [16].

The palladium-catalyzed cross-coupling reaction of (*E*)-β-bromostyrene and methyllithium can be rationalized by assuming the mechanism as shown in Scheme 2, which includes oxidative addition of (*E*)-β-bromostyrene to yield (*E*)-bromo(styryl)bis(methyldiphenylphosphine)palladium(II) (**6**), transmetallation to give (*E*)-methyl(styryl)bis(methyldiphenylphosphine)palladium(II) (**7**) and reductive elimination to produce (*E*)-propenylbenzene [11].

Stille et al. confirmed this mechanism by isolation of the unstable species **7** and the spectroscopic observation of styryl and methyl coupling [28]. Furthermore, the mechanism of the palladium-catalyzed cross-coupling reaction was deeply investigated, and the steps of transmetallation and reductive elimination have been disclosed [27,29,30].

After we published our full paper, the palladium-catalyzed cross-coupling reaction with organolithium compounds have been widely used. The preparations of arylallene (Eq. (22)) [31] and 5-substituted 2(3H)-butenolide (Eq. (23)) [32] are such examples.



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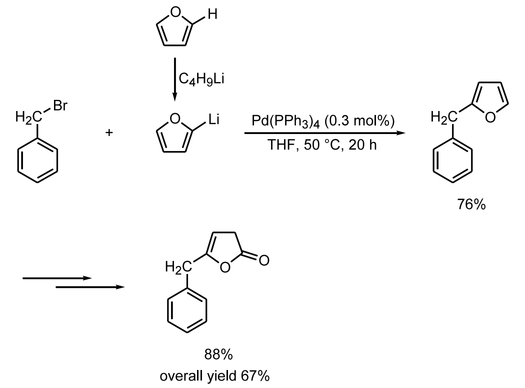


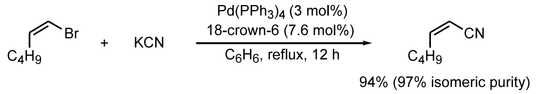
(23)

The palladium-catalyzed cross-coupling reaction with the Grignard reagents and oraganolithium compounds was criticized for the occurrence of transmetallation of vinyl halides or aryl halides with Grignard reagents and oraganolithium compounds, which give homocoupling products and reduced products [33]. However, the palladium-catalyzed cross-coupling reaction will occur without any problem, when one keeps in mind the following points: (i) careful treatment with exactly necessary amount of reagents, such as oraganolithium compounds [33], (ii) use of highly active clean palladium(0) catalysts, and (iii) control of the rate of addition of a reagent to keep going the catalytic cycle.

The palladium-catalyzed cross-coupling reaction appears to be more chemo- and stereoselective and of broader scope with carbon nucleophiles than the corresponding nickel-catalyzed reaction; therefore, various carbon nucleophiles were found to be used for the palladium-catalyzed cross-coupling reaction in the 1970s. Organosodium [10], organocopper [34,35], organoaluminum [36], organozinc [16,37], organotin [38,39], organozirconium [40], and organoboron [41] compounds have been used in addition to Grignard reagents [9] and organolithium compounds [11,22]. It is important that each metal has its unique property, which can be combined with the palladium-catalyzed cross-coupling reaction. Organoaluminum and organoboron compounds are highly useful, because direct carbometallation and hydrometallation of alkynes gives the corresponding alkenyl metal compounds selectively. Recently, organozinc, organotin, and organoboron compounds are often used for these cross-coupling reactions, because these orgnaometal compounds are relatively unreactive towards common nucleophiles, making the cross-coupling reaction chemoselectively. The transition metal-catalyzed cross-coupling reaction of each metal will be described in the separated sections in this issue. Organotin and organoboron compounds show thermal and hydrolytic stability to make their subsequent handling easier. However, these stable organotin and organoboron compounds are often prepared by transmetallation of the corresponding organolithium compounds; therefore, direct use of organolithium compounds with the active palladium(0) catalyst [23] for the cross-coupling reaction should be considered, because of relatively high toxicity associated with these compounds and also atom economy. Direct ortho-lithiation is a highly useful property of organolithium compounds for synthesis of organic compounds [23,42].

4. Palladium-catalyzed cyanation of vinyl and aryl halides

Palladium-catalyzed synthesis of vinyl nitriles from vinyl halides can be performed highly effectively [11]. Treatment of a variety of vinyl halides with two molar equivalents of potassium cyanide in benzene in the presence of palladium(0) catalyst and 18-crown-6 results in the formation of vinyl nitriles, which are hardly accessible, in an excellent yield and in a stereospecific manner (Eqs. (24) and (25)) [43]. In the absence of crown ether, vinyl halides do not undergo cyanation under even more forcing conditions.



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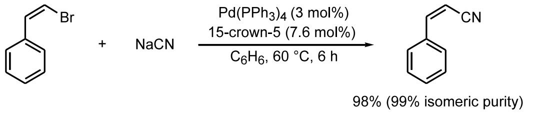
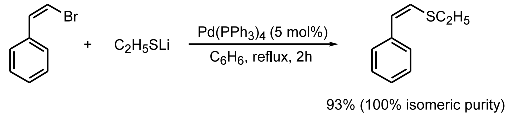


(25)

Palladium-catalyzed cyanation of aryl halides proceeds without difficulty [44].

5. Palladium-catalyzed coupling reaction of vinyl and aryl halides with heteroatom nucleophiles

This class of the palladium-catalyzed cross-coupling reaction has been extended to heteroatom nucleophiles, because palladium(0) catalysts tolerate various nucleophiles. The palladium-catalyzed sulfenylation of sp^2 carbon halides is highly useful, particularly for the stereospecific synthesis of (*Z*)- and (*E*)-vinyl sulfides (Eqs. (26) and (27)) [11]. At that time, the method for synthesis of vinyl sulfides is limited to Corey's method [45]. The palladium-catalyzed sulfenylation of aryl halides proceeds to give aryl sulfides [46].



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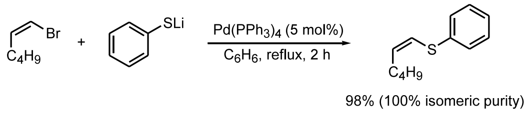

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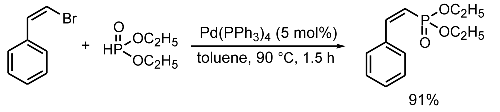
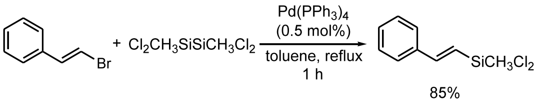
The palladium-catalyzed phosphonation of sp^2 carbon halides with dialkyl phosphites gives dialkyl vinylphosphonates stereoselectively (Eq. (28)) [47].



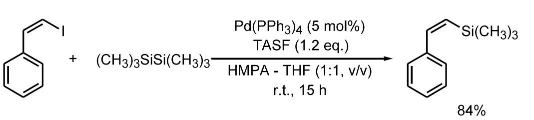
(28)

Vinylsilanes can be prepared conveniently by the palladium-catalyzed reaction of vinyl halides with 1,1,2,2,-tetrachloro-1,2-dimethyldisilane (Eq. (29)) [48].



(29)

The palladium-catalyzed trimethylsilylation of vinyl halides with hexamethyldisilane takes place in the presence of tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF) (Eq. (30)) [49].



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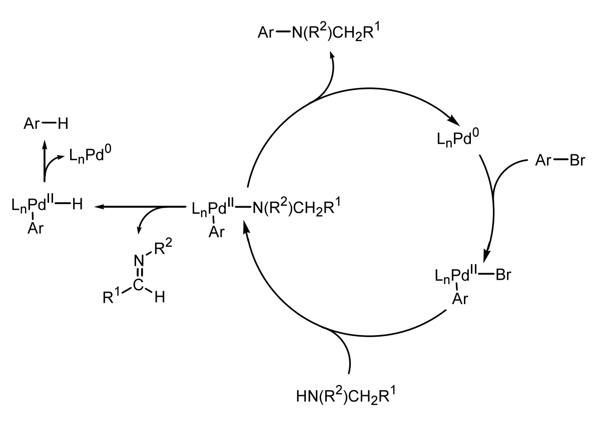
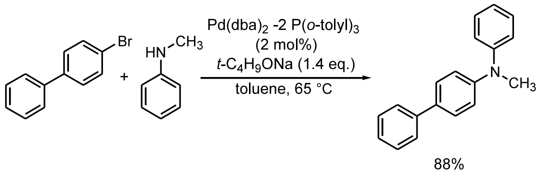
One of the most attractive palladium-catalyzed reaction with heteroatom nucleophiles is amination of aryl halides. This method had not been accomplished for a long time, because the Ar–$Pd^{II}NHR^1R^2$ intermediate can undergo β-hydride elimination to produce $ArPd^{II}$–H species which can reductively eliminate to afford the arene side-product and regenerate the palladium(0) catalyst (Scheme 3) [50,51].

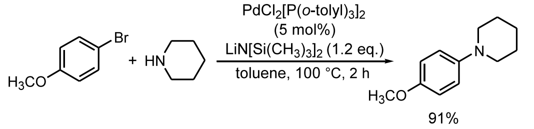
Using tributyl(diethylamino)tin and tri-*o*-tolylphosphine P(*o*-tolyl)$_3$, Kosugi and Migita et al. succeeded in amination reaction in 1983 [51]. Mechanistic study of this reaction led to the discovery of the tin free catalytic process in 1995 by Buchwald et al. [52] and Hartwig et al. [53]. The difficulty was overcome by the use of P(*o*-tolyl)$_3$ and a base bearing no β-hydrogen such as sodium *tert*-butoxide (Eq. (31)) [52] and lithium bis(trimethylsilyl)amide (Eq. (32)) [53]. The key intermediate is that the *tert*-butoxy palladium species, which does not undergo β-elimination to give the corresponding ketones. The palladium-catalyzed amination of aryl halides provides a general route to a variety of arylamines, which are particulary useful for the synthesis of precursors of material science and medicines.



Scheme 3. Mechanism of the palladium-catalyzed amination of aryl bromides [51].

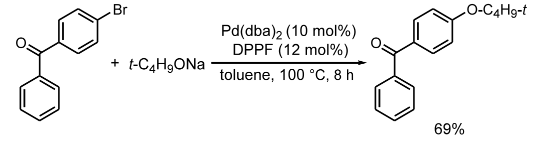


(31)

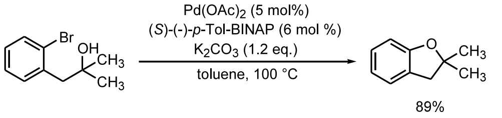


(32)

The critical point is to use a bulky and electron-rich phosphine ligand. Furthermore, these catalytic system can be applied to the synthesis of aryl ethers and heterocycles via palladium-catalyzed C–O bond formation (Eqs. (33) and (34)) [54,55].



(33)



(34)

With these findings it was recognized that the nature of phosphine ligands influences the reactivity dramatically. Also, bulky and electron-rich phosphine ligands, such as tricyclohexylphosphine [56], tri-*tert*-butylphosphine [57], 2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl (*p*-Tol-BINAP) [55], and imidazolium salt [58] have been explored, and the palladium-catalyzed cross-coupling reactions and the other reactions, which include the reaction of aryl chlorides, have improved enormously.

Since the first report on the palladium-catalyzed cross-coupling reaction was reported in 1975, this kind of reaction has developed quite rapidly and has given highly useful methods for organic synthesis and industrial use. However, the fundamental and theoretical understandings, such as why palladium catalysts can accept other nucleophiles than nickel catalysts, are not revealed yet. By deep understandings of chemistry, the transition metal-catalyzed cross-coupling reactions will make a more important contribution and be utilized in many aspects.

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