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Highlight Review

Cross-coupling Reactions of Organoboranes: An Easy Method for C–C Bonding

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Abstract

The palladium-catalyzed cross-coupling reaction between different types of organoboron compounds and various organic halides or triflates in the presence of base provides a powerful and general methodology for the formation of carbon–carbon bonds. The Csp^2–B compounds (such as aryl- and 1-alkenylboron derivatives) and Csp^3–B compounds (alkylboron compounds) readily cross-couple with organic electrophiles to give coupled products selectively in high yields. Recently, the Csp–B compounds (1-alkynylboron derivatives) have been also observed to react with organic electrophiles to produce expected cross-coupled products. The overview of some of such coupling reactions is discussed here in this article.

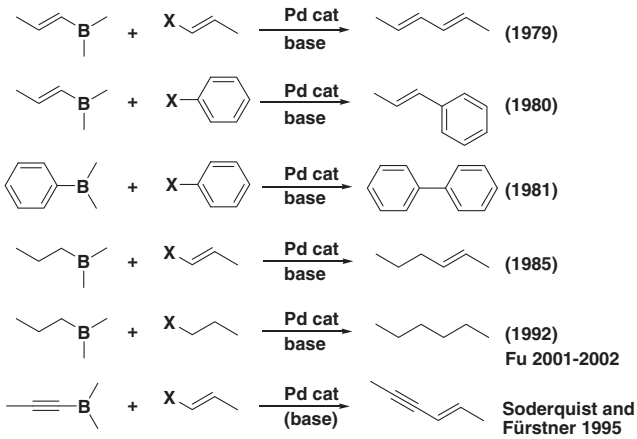
♦ Introduction

Carbon–carbon bond formation reactions are important processes in chemistry, because they provide key steps in building complex, bioactive molecules developed as pharmaceuticals and agrochemicals. They are also vital in developing a new generation of ingeniously designed organic materials with novel electronic, optical, or mechanical properties, likely to play a significant role in the burgeoning area of nanotechnology.

During the past 40 years, most important carbon–carbon bond-forming methodologies have involved using transition metals to mediate the reactions in a controlled and selective manner. The palladium-catalyzed cross-coupling reaction between different types of organoboron compounds and various organic electrophiles including halides or triflates in the presence of base provides a powerful and general methodology for the formation of carbon–carbon bonds. Here, some representatives of such reactions are shown in Scheme 1. Numbers in parentheses indicate the years first reported by our group.

As one defect of the reaction, one would point out the use of bases. However, the difficulty could be overcome by using suitable solvent systems and adequate bases. Consequently, these coupling reactions have been actively utilized not only in academic laboratories but also in industrial processes. In this paper, three topics, routes to conjugated alkadienes, application to biaryls, and B-alkyl-borane coupling will be discussed. In addition, recent topics will be introduced.

Such coupling reactions offer several advantages:
(1) Ready availability of reactants.
(2) Mild reaction conditions and high product yields.
(3) Water stability.



Scheme 1.

(4) Easy use of the reaction both in aqueous and heterogeneous conditions.
(5) Toleration of a broad range of functional groups.
(6) High regio- and stereoselectivity of the reaction.
(7) Insignificant effect of steric hindrance.
(8) Use of a small amount of catalysts.
(9) Application in one-pot synthesis.
(10) Nontoxic reaction.
(11) Easy separation of inorganic boron compound.
(12) Environmentally friendly process.

♦ Reaction of Vinylic Boranes with Vinylic Halides. A Route to Conjugated Alkadienes

Cross-coupling reactions between vinylic boranes and vinylic halides were not reported to proceed smoothly in the presence of only palladium catalysts. During the initial stage of our exploration, we postulated that a drawback of the coupling is caused by the following aspects of the mechanism. The common mechanism of transition-metal-catalyzed coupling reactions of organometallic compounds with organic halides involves sequential (a) oxidative addition, (b) transmetalation, and (c) reductive elimination.[1] It appeared that one of the major reasons that 1-alkenylboranes cannot react with 1-alkenyl halides is step (b). The transmetalation process between R–M–X (M = transition metal, X = halogen) and organoboranes does not occur readily because of the weak carbanion character of the organic

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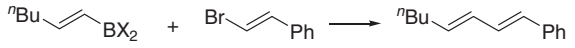
Table 1. Cross-coupling reaction of **1** with **2**



1 **2** **3**

1[a]	Catalyst[b] (mol %)	Base (equiv/**2**)	Solvent	Reac. time/h	Yield of **3**/%
1b	PdL_4 (3)	None	THF	6	0
1b	PdL_4 (3)	None	Benzene	6	0
1a	PdL_4 (3)	2 M NaOEt(2)–EtOH	THF	2	73
1b	PdL_4 (1)	2 M NaOEt(2)–EtOH	Benzene	2	86

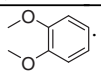
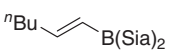
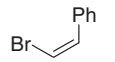
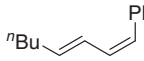
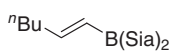
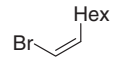
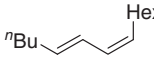
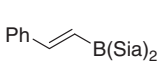
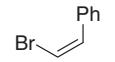
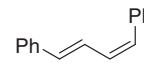
[a]**1a**, $X_2 = (Sia)_2$; **1b**, X_2 =  . [b]$L = PPh_3$.

Table 2. Cross-coupling reaction of (*E*)-1-vinyldisiamylboranes[a]

1-Alkenylborane	1-Alkenyl bromide	Product	Yield/% (Purity/%)
			86 (98)
			88 (99)
			89 (98)

[a]Reaction conditions: $[Pd(PPh_3)_4]$/NaOEt/benzene/reflux/2 h.

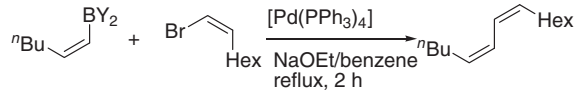
groups in the organoboranes. To overcome this difficulty, we anticipated the use of tetracoordinate organoboron compounds, instead of tricoordinate organoboron derivatives. According to a study by Gropen and Haaland,[2] the methyl group in tetramethylborate was observed to be 5.5 times more electronegative than the methyl group in trimethylborane. Such behavior was also expected for the reaction of triorganoboranes in the presence of base. Thus, we found that the reaction of vinylic boron compounds with vinylic halides proceeds smoothly in the presence of a base and a catalytic amount of a palladium complex to provide the expected conjugated alkadienes and alkenynes stereo- and regioselectively in excellent yields (Table 1).

Although the coupling reaction of (*E*)-1-alkenylboranes readily obtained via the hydroboration of appropriate alkynes with disiamylborane (bis(1,2-dimethylpropyl)borane) or dicyclohexylborane proceeds readily with (*E*)- and (*Z*)-1-alkenyl bromides and iodides to give the corresponding dienes readily (Table 2), (*Z*)-1-alkenylboranes, prepared by hydroboration of 1-haloalkynes followed by the reaction with *t*-butyllithium, gave low product yields, near 50% (Table 3). It turned out that high yield and high stereoselectivity could be achieved by coupling (*Z*)-alkenyl halides with (*Z*)-1-alkenyldialkoxyboranes.

♦ Mechanism of the Vinylic–Vinylic Cross-coupling

The principal features of the cross-coupling reaction are as follows: (a) Small catalytic amounts of palladium complexes (1–3 mol %) are required to obtain the coupled products. (b) The

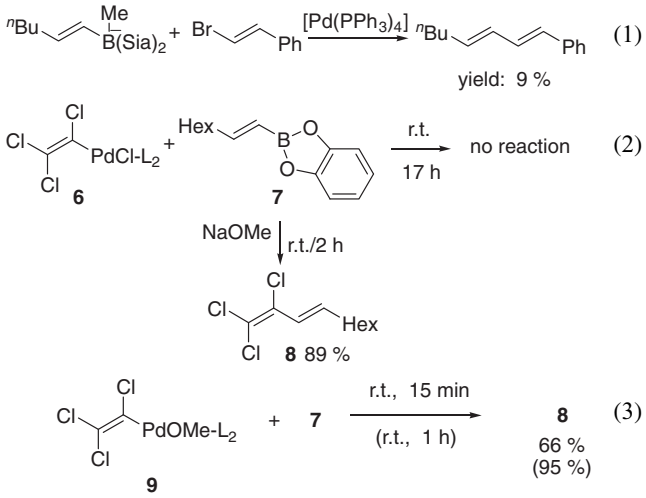
Table 3. Cross-coupling of (*Z*)-1-hexenyldisiamyl- or (*Z*)-1-hexenyldiisopropoxyborane



4 **5**

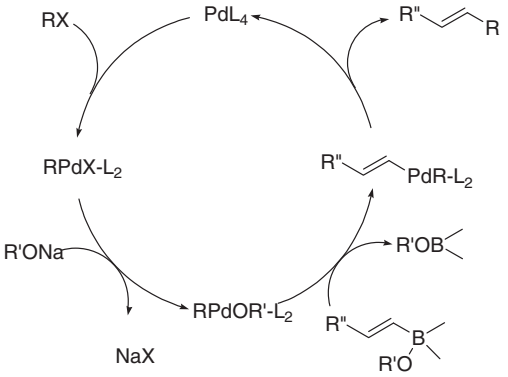
BY_2 in **4**	Yield of **5**/%	Purity of **5**/%
$B(Sia)_2$	49	>98
$B(O^iPr)_2$	87	>99

coupling reactions are highly regio- and stereoselective and take place while retaining the original configurations of both the starting alkenylboranes and the haloalkenes. The isomeric purity of the products generally exceeds 98%. (c) A base is required to carry out a successful coupling. In the initial stage of the study, as mentioned previously, we considered that tetracoordinate organoboron compounds facilitate the transfer of organic groups from the boron to the palladium complex in the transmetalation step. In order to check this possibility, the reaction of lithium (1-hexenyl)methyldisiamylborate was examined as shown in eq 1. The coupled product, however, was obtained only in 9%. On the other hand, it was found that (trichlorovinyl)palladium(II) complexes **6** and **9** both prepared as pure solids, reacted with vinylborane **7** to give diene **8**, as depicted in eq 2 and eq 3. In the case of **6**, no reaction occurs without a base, whereas the coupling reaction proceeds smoothly in the presence of a base to give the coupled product in 89% yield. The intermediate **9** readily reacts with **7** without a base to provide the same product **8** in almost quantitative yield after 1 h. Consequently, such evidence suggests that vinylic alkoxypalladium(II) compounds such as **9** were necessary intermediates in these cross-coupling reactions. Accordingly it is thought that the reaction proceeds through the catalytic cycle as shown in Scheme 2.[3]



♦ Reaction with Aromatic Boronic Acid Derivatives with Aromatic Halides. Synthesis of Biaryls

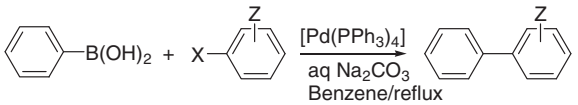
The synthesis of biaryls is of particular interest to industry. These motifs increasingly turn up in materials important to



Scheme 2. Catalytic cycle for the coupling reaction of alkenylboranes with haloalkenes.

society such as pharmaceuticals and biocides. Biaryls are also often the construction blocks of new generations of specialized engineering materials such as high-strength, rigid-rod polymers, molecular wires, liquid crystals, and nonlinear optical materials. The coupling of aryl halides with copper at a high temperature is called the Ullmann reaction, which is of broad scope and has been used to prepare many symmetric biaryls. However, when a mixture of two different aryl halides is used, three possible biaryl products are prepared. Consequently, the development of a selective and general synthesis of all kinds of biaryls has been desired.

The first method to prepare biaryls by the cross-coupling of arylboranes with haloarenes was reported in 1981 (eq 4).[4] The reaction proceeds even under heterogeneous conditions to give the corresponding coupled products selectively in high yields. After this discovery, various modifications have been made to the reaction conditions. As the bases, Na_2CO_3, $NaHCO_3$, Tl_2CO_3, K_3PO_4, etc. are employed. In some cases, CsF or Bu_4NF can be used instead of usual bases (eq 5).[5] The Suzuki aromatic–aromatic coupling reaction provides all kinds of biaryls selectively in high product yields.



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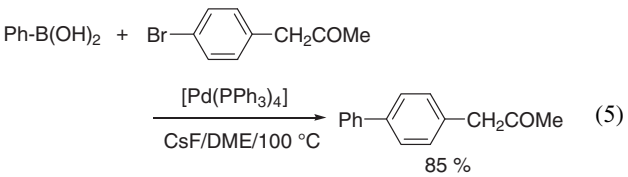


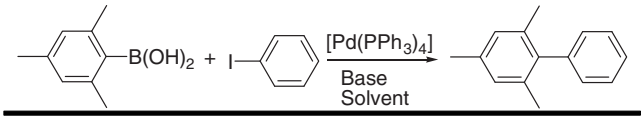
(5)

Carbon–carbon bond formation reactions employing organoboron compounds and organic electrophiles have been recently recognized as powerful tools for the construction of new organic compounds. Among such reactions, aromatic–aromatic (or heteroaromatic) couplings between aromatic boronic acids or esters and aromatic electrophiles providing symmetric and unsymmetrical biaryls selectively in high yields have been used most frequently. The importance of biaryl units as components in many kinds of compounds, pharmaceuticals, herbicides, and natural products, as well as engineering materials, such as conducting polymers, molecular wires, and liquid crystals has attracted enormous interest from the chemical community. Such aromatic–aromatic, aromatic–heteroaromatic, and heteroaromatic–heteroaromatic coupling reaction have been recently reviewed in detail.[6]

♦ *Coupling of Arylboronic Acid Derivatives Having High Steric Hindrance or Electron-withdrawing Functionalities*

Although steric hindrance of aryl halides is not a major factor for the formation of substituted biaryls, low yields result when *ortho*-disubstituted arylboronic acids are used. For example, the reaction with mesitylboronic acid proceeds only slowly because of steric hindrance during the transmetalation to palladium(II) complex. The reaction of mesitylboronic acids with iodobenzene at 80 °C in the presence of $[Pd(PPh_3)_4]$ and various bases has been reported.[7] The results are summarized in Table 4.

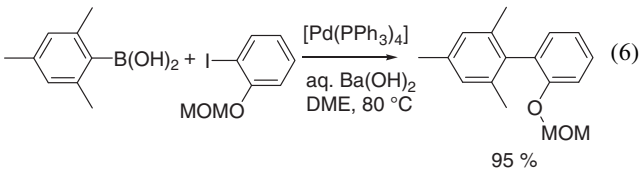
Table 4. Reaction of mesitylboronic acid with iodobenzene under different conditions



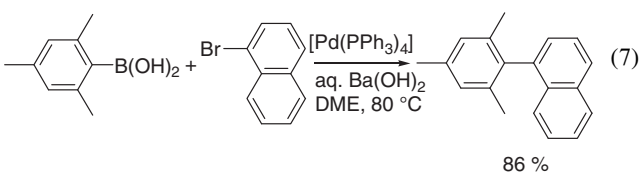
Base	Solvent	Temp /°C	Yield/%[a] Time: 8 h	24 h	48 h
Na_2CO_3	Benzene/H_2O	80	25 (6)	77 (12)	84 (25)
Na_2CO_3	DME/H_2O	80	50 (1)	66 (2)	83 (7)
K_3PO_4	DME/H_2O	80	70 (0)		
NaOH	DME/H_2O	80	95 (2)		
$Ba(OH)_2$	DME/H_2O	80	99 (2)		

[a]GLC yields of the coupling product based on iodobenzene and the yields of mesitylene are shown in the parentheses.

Aqueous Na_2CO_3 in benzene or DME (dimethoxyethane) is not effective as a base for the coupling of mesitylboronic acid and the reaction is not completed even after 2 days. Although the side reactions such as homocoupling are negligibly small, the formation of mesitylene was observed by hydrolytic deboronation increasing with the reaction time. It is noteworthy that such hydrolytic deboronation is faster in benzene/H_2O than the modified conditions using aqueous DME. On the other hand, the addition of stronger bases, e.g., aqueous NaOH or $Ba(OH)_2$, both in benzene and DME exerts remarkable effect on acceleration of the rate of coupling. By using aqueous $Ba(OH)_2$ in DME at 80 °C, mesitylboronic acid couples with iodobenzene within 4 h to give the corresponding biaryl in a quantitative yield. Some of such coupling reactions are depicted in eq 6 and eq 7.



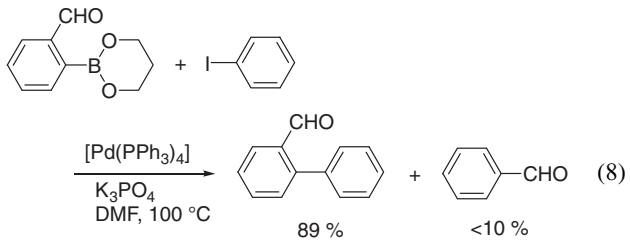
(6)



(7)

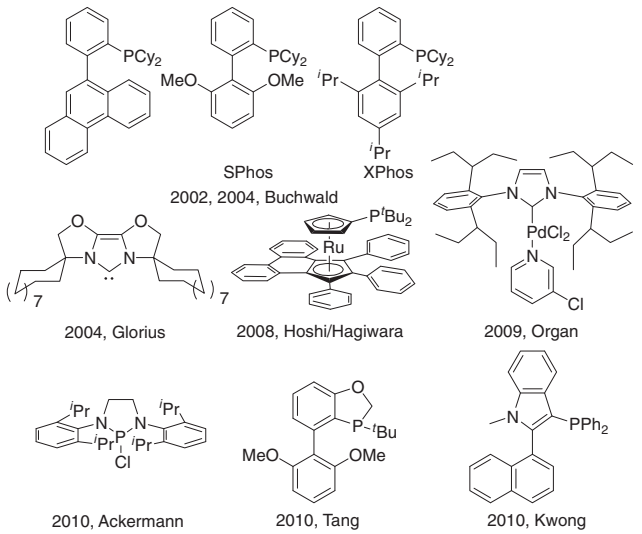
Even without sterically hindered substrates, the reaction under aqueous conditions is often undesirable because of competitive hydrolytic deboronation. Kinetic study[8] into the reaction of substituted arylboronic acids showed that electron-withdrawing substituents accelerate the deboronation. Although there is no large effect between *meta*- and *para*-substituted phenylboronic acids, substituents at the *ortho*-position may greatly increase the rate of deboronation. For example, the 2-formyl group on arylboronic acids is known to accelerate the rate of hydrolytic deboronation.

Indeed, the coupling of 2-formylphenylboronic acid with 2-iodotoluene at 80 °C using Na_2CO_3 in DME/H_2O gives only a 54% yield of the corresponding biaryl, with accompanying benzaldehyde (39%). Anhydrous conditions are desirable for such boronic acids sensitive to aqueous base. Thus, the trimethylene glycol ester of 2-formylphenylboronic acid readily couples with iodobenzene at 100 °C in DMF to give the coupled product in a yield of 89%, with less than 10% of benzaldehyde formation (eq 8).[7]



(8)

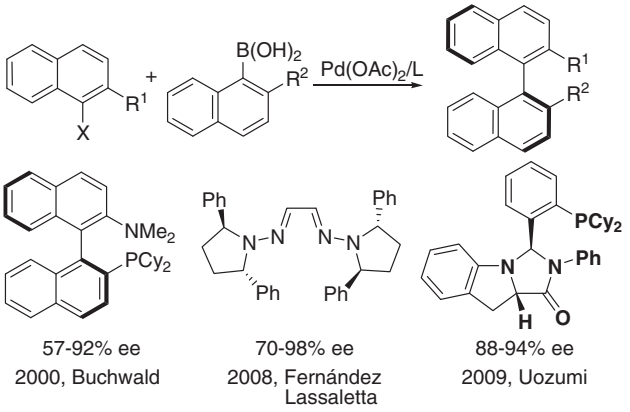
Recently, Buchwald et al. and other groups have reported interesting catalysts and ligands to prepare tetra-*ortho*-substituted unsymmetrical biaryls (Scheme 3).[9–15] Furthermore, asymmetric coupling for the axially chiral biaryls were reported by Buchwald,[16] Fernández,[17] and Uozumi[18] independently (Scheme 4).



Scheme 3.

♦ Coupling with Aromatic Chlorides

In aromatic–aromatic cross-coupling reactions, cheap and readily accessible aryl chlorides are particularly important as starting materials from an industrial viewpoint. Recently some research groups, especially Fu's group[19] and Buchwald's group[9,20] have reported very efficient methods for aryl chloride reaction. For example, Fu and his co-workers[19] have observed that the use of $[Pd_2(dba)_3]/P(^tBu)_3$ (dba: dibenzylideneacetone) as a catalyst and ligand for a wide range of aryl and vinyl halides, including chlorides, undergo the Suzuki cross-coupling with arylboronic acids in very good yield, typically at room temperature. Furthermore, these catalysts display novel reactivity patterns, such as the selective coupling by $[Pd_2(dba)_3]/PCy_3$/KF of a sterically hindered aromatic chloride.



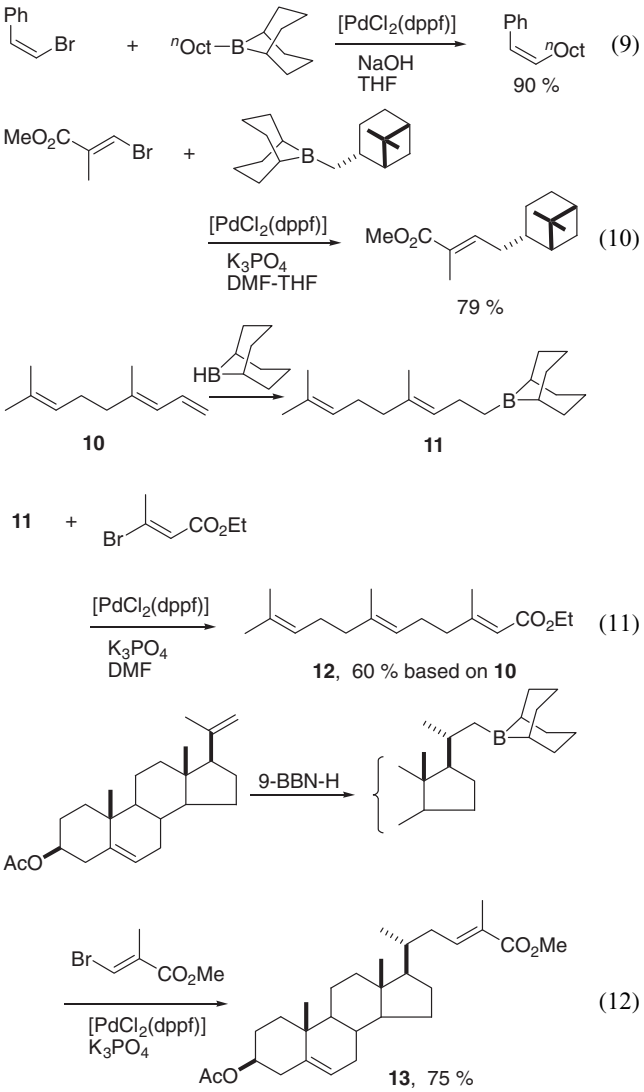
Scheme 4. Asymmetric cross-coupling reaction.

Despite the good yields in many Suzuki reactions of chloroarenes, generally, comparatively large amounts of catalyst are required. Beller et al. reported a new catalyst system, with which they achieved the coupling of nonactivated and deactivated aryl chlorides highly efficiently in good yields with generally only 0.005 mol % palladium and thus industrially useful.[21] For instance, as a new efficient catalyst system, they used diadamantyl-*n*-butylphosphane ($P(Bu)(Ad)_2$) as a ligand and found that it proved to be extremely reactive. In addition, the new ligands described in Scheme 3, work effectively in the coupling reaction of aromatic chlorides again.[9–15]

♦ Coupling of B-alkyl-boranes with Alkenyl or Aryl Halides

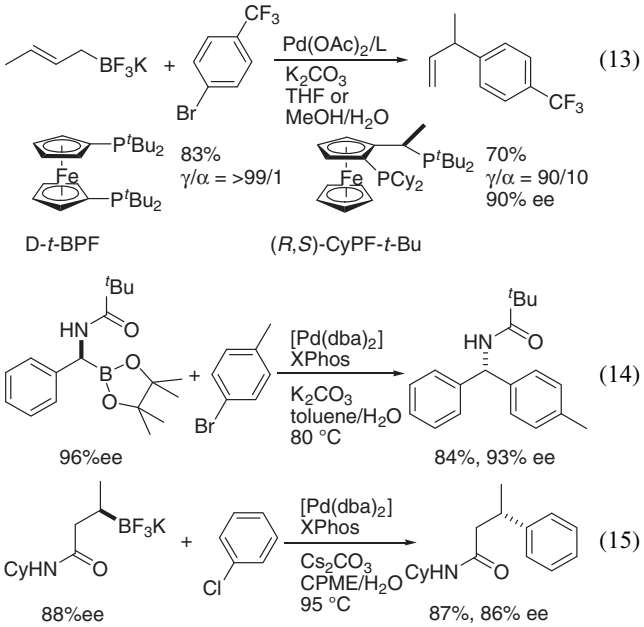
Although organometallic reagents with 1-alkenyl, 1-alkynyl, and aryl groups were successfully used for the coupling reactions, those with alkyl groups having sp^3 carbons containing β-hydrogens were severely limited due to the competitive side reactions. In 1971–1972 Kochi, Kumada, and Corriu reported independently that the reaction of alkyl Grignard reagents with alkenyl or aryl halides are markedly catalyzed by Fe(III) or Ni(II) complexes, and then Negishi demonstrated the synthetic utility of alkylzinc compounds by use of palladium catalyst. Thereafter, alkyllithium, -tin, and -aluminum reagents were also employed for such cross-coupling reactions. The reaction of alkylborane derivatives is particularly useful when one wishes to start from alkenes via hydroboration. Consequently, we intended to examine the coupling reactions between alkylboron compounds and various organic halides in the presence of base and palladium complex, and found that no cross-coupling reactions of B-alkyl-9-borabicyclo[3.3.1]nonanes (B-R-9-BBN), readily

obtainable from alkenes by hydroboration, with 1-halo-1-alkenes or haloarenes occurred under the standard coupling conditions using [Pd(PPh$_3$)$_4$] as a catalyst, but the coupling proceeds smoothly by using a catalytic amount of [PdCl$_2$(dppf)] (dppf: 1,1′-bis(diphenylphosphino)ferrocene) and bases, such as NaOH, K_2CO_3, and K_3PO_4 to give the corresponding substituted alkenes or arenes in excellent yields (eq 9).[22] Because the reaction is tolerant of a variety of functionalities on either coupling partner, stereochemically pure functionalized alkenes and arenes can be obtained under mild conditions (eq 10). The utility of the reaction was demonstrated by the stereoselective synthesis of 1,5-alkadienes **12** (eq 11) and the extension of a side-chain in a steroid **13** (eq 12).[22]



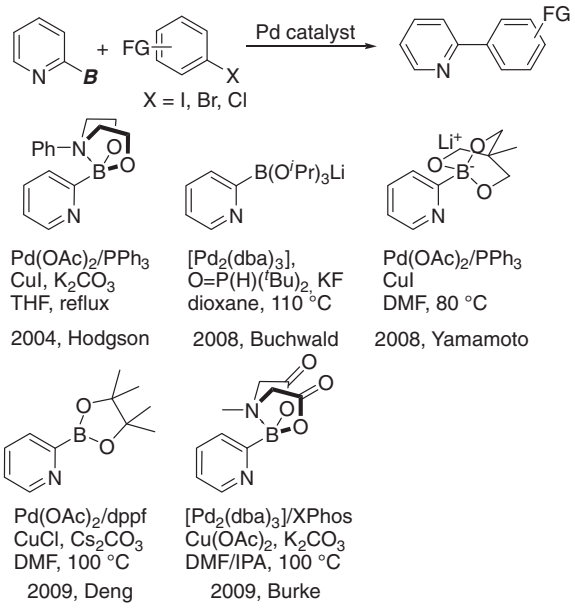
Many chemists applied such a Suzuki coupling reaction using B-saturated alkylboron compounds. For instance, Danishefsky et al. reported a total synthesis of the promising anticancer agent (−)-epothilone B using this coupling method,[23,24] and a sister compound, epothilone A was also synthesized by a similar procedure.[25] A full paper reporting the total synthesis of epothilones A and B appeared later.[26]

More recently, other attempts at cross-coupling using various alkylboron derivatives have been reported. We reported the efficiency of D-*t*-BPF for γ-selective coupling of potassium allyltrifluoroborates with bromoarenes and asymmetric reaction using (*R*,*S*)-CyPF-*t*-Bu as the chiral auxiliary (eq 13).[27] Molander and co-workers reported the use of functional potassium alkyltrifluoroborates, which are stable to air and moisture.[28,29] Moreover, Crudden,[30] Suginome,[31] and Molander[32] independently reported stereospecific cross-coupling of secondary alkylboron reagents (eqs 14 and 15).



♦ *Various Organoboron Reagents for Cross-coupling Reactions*

As mentioned above, the C–B bond of organoboronic acids is totally covalent which is inert to ionic reactions, but nucleophilicity of organic groups on a boronic atom are significantly enhanced by quaternerization by an anionic ligand. Thus, tetracoordinated ate-complexes are a key species that has been successfully used for coupling reactions of organoboron compounds. Air- and water-stable trifluoroborates [RBF$_3$]K are typical ate-complexes that are advantageous over boronic acids in preparation and handling of pure and water-stable crystalline materials.[28,29] Sodium trihydroxyborates [RB(OH)$_3$]Na were synthesized recently as isolated discrete species for cross-coupling in anhydrous solvent without the aid of an additional base.[33] Other isolable ate complexes are 1-alkynylborates [RC≡CBR$_2$(OR′)]Li,[34] tetraarylborates [Ar$_4$B]Na[35] and ArB(OR)$_3$Li.[36] Recently, we have developed cyclic triolborates that have high levels of stability in air and water. High performance of triolborates for transmetalation is demonstrated in C–C bond forming reactions.[37] The cross-coupling reactions of arylboronic acids in aqueous solvents often suffer from low yields due to hydrolytic B–C bond cleavage. Especially such cleavage is accelerated by *ortho*-substituents, and significantly accelerated by adjacent heteroatoms in the boronic acids. 2-Pyridylboronic acid is a typical boron compound that undergoes very rapid cleavage with water during coupling reaction. A recent advance in this approach is the use of pinacol ester,[38] *N*-phenyldiethanolamine ester,[39] triisopropoxyborate,[36] or *N*-methyliminodiacetic



Scheme 5. Cross-coupling of 2-pyridylboron compounds.

acid (MIDA) boronate.[40] It is remarkable that 2-pyridylboronate affords a high yield of the coupling product (Scheme 5).

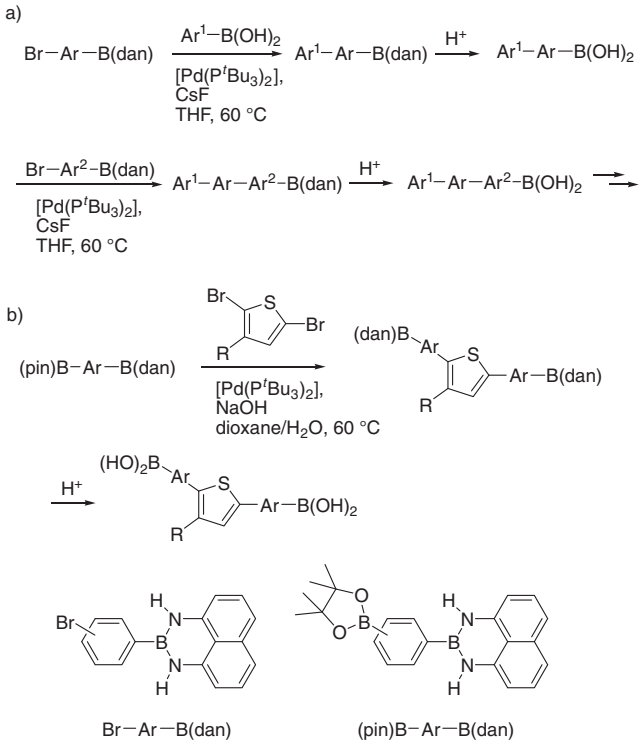
Iterative cross-coupling reactions were achieved by the use of efficient B-masked groups such as 1,8-diaminonaphthalene or *N*-methyliminodiacetic acid. The 1,8-diaminonaphthalene group can be deprotected by treatment with aqueous acid to generate the corresponding boronic acids. The use of haloarylboronamide or monoprotected benzenediboron compounds makes possible synthesis of boron-substituted oligoarenes (Scheme 6).[41]

On the other hand, Burke and co-workers reported *N*-methyliminodiacetic acid (MIDA) boronate as masked boron reagent.[42] The MIDA boronates are inert toward cross-coupling under anhydrous conditions. MIDA can be readily hydrolyzed with aqueous base to generate a boronic acid. Recently, demonstrating the simplicity of the iterative cross-coupling approach, a highly complex polyene framework was formed using a single reaction (Scheme 7).

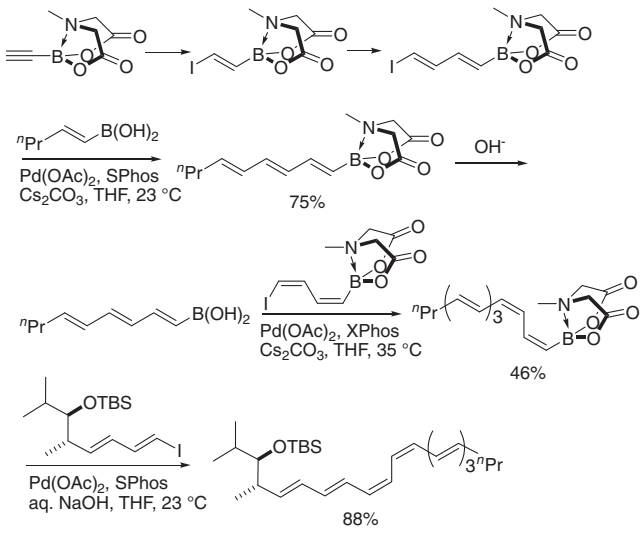
♦ The Future

Today, the Suzuki reaction continues to evolve, with many new possibilities reported during the past decade. For example, a nickel-catalyzed stereoconvergent enantioselective Suzuki coupling of racemic secondary alkyl electrophiles was reported.[43] In addition, the coupling reactions via nickel-catalyzed selective C–O bond cleavage have been studied.[44] Solid-phase Suzuki coupling has been developed using either resin-bound aryl halides with solution-phase boronic acids[6] or vice versa.[45] Such approaches, of course, play an important role in the combinatorial and parallel methodologies now used to explore chemical reactivity, especially well-suited in medicinal chemistry.

Increasingly, industry is seeking to use more environmentally friendly processes. These often require ingenious solutions to which the Suzuki coupling is well-suited. Research groups around the world are investigating modifications of the reaction that work in aqueous media or with trace amounts of



Scheme 6. Iterative cross-coupling reactions using masked boronic acids.



Scheme 7. Synthesis of polyene framework via iterative cross-coupling.

catalysts. For example, Leadbeater and his team carry out the Suzuki coupling using ultra-low (ppb) palladium concentration in water,[46] while Kabalka and colleagues have combined a solvent-free, solid-state approach with the application of microwave radiation to achieve coupling in just a few minutes.[47] Ionic liquids, which are excellent solvents for transition-metal catalysts, are also being investigated.[48]

We can expect to see more interesting versions of the Suzuki coupling in the future.

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Yasunori Yamamoto was born in Hokkaido, Japan in 1968. He received his B.Eng. (1991) and M.Eng. (1993) from Hokkaido University under the direction of Professor Akira Suzuki. He worked at Mitsubishi Chemical Corporation as Researcher in 1993–1995. In 1995, he then moved to Hokkaido University as an assistant professor of N. Miyaura research group and received his Ph.D. degree in 2003 from Hokkaido University. His research interests are in the organic syntheses via metal-catalyzed reactions of organoboron compounds.

