Award Accounts

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Metal-Catalyzed Reactions of Organoboronic Acids and Esters

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Metal-catalyzed B–C and C–C bond-forming reactions of organoboronic acids that have been pursued in the past three decades by our group are summarized in this article. B–C bond-forming reactions for the synthesis of organoboronic acid derivatives include metal-catalyzed addition reactions of pinacolborane or catecholborane (hydroboration), bis(pinacolato)diboron (diboration), and alkylthioboranes (thioboration) to alkenes, alkynes, 1,3-alkadienes, or 1,2-alkadienes (allenes). Other B–C bond-forming reactions include coupling reactions of pinacolborane or bis(pinacolato)diboron for borylation of C–halogen bonds with palladium catalysts and C–H bonds of arenes and alkenes with iridium catalysts. These reactions have provided a convenient new access to aryl-, 1-alkenyl-, allyl-, or benzylboronates. Metal-catalyzed C–C and C–N bond-forming reactions using boronic acid derivatives include synthesis of novel cyclic triolborate salts for palladium- or copper-catalyzed cross-coupling reactions with organic halides or amines, rhodium- or palladium-catalyzed 1,4-addition reactions of arylboronic acids to α,β-unsaturated carbonyl compounds and rhodium-catalyzed addition of aryl- and 1-alkenylboronic acids to aldehydes and imines.

1. Introduction

Until recently, organoboronic acids had limited use in organic synthesis due to their inertness to ionic and radical reactions. Over the past three decades, however, it has become increasingly clear that they are valuable reagents capable of undergoing many catalytic C–C bond formations in organic syntheses.[1–4] Boronic acids were positioned as a mainstay of modern synthetic chemistry by two discoveries in 1979. A diastereoselective addition of allylboronates to aldehydes by Hoffmann and Zeiss[5] and a metal-catalyzed C–C bond-forming reaction (Suzuki coupling)[6] by our group have been widely embraced by synthetic chemists in academia and industry worldwide because boronic acids are convenient reagents that are generally thermally stable and are inert to water and oxygen, and because it is easy to remove the inorganic by-products from the reaction mixture, making the reactions suitable for industrial processes. These were followed by discoveries of various C–C, C–N, and C–B bond-forming reactions over the past two decades including Petasis Mannich reaction (1993),[7] metal-catalyzed reactions of diborons (1993),[8] rhodium-catalyzed conjugate addition to electron-deficient alkenes (1997),[9] copper-promoted arylation of N–H bonds (1998),[10] and iridium-catalyzed C–H borylation of alkanes, alkenes, and arenes (2000).[11] There have also been extensive studies on biological and medicinal applications of boronic acids for ^{10}B carriers of neutron capture therapy and proteasome inhibitor for cancer therapy. Such chemistry of boronic acids is summarized in this review,[12] but this review is mainly restricted to our own efforts in metal-catalyzed reactions.

2. B–C Bond-Forming Reactions for Synthesis of Organoboronic Acid Derivatives

A traditional method for the synthesis of organoboron compounds is addition of B–H compounds to unsaturated hydrocarbons (hydroboration).[13] Although this method is now common for large-scale preparations, catalyzed reactions are an interesting strategy for obtaining chemo-, regio-, and stereoselectivities that are different to those achieved by uncatalyzed hydroboration.[8d,14] Such a catalytic protocol that involves oxidative addition of an H–B bond to a low-valent transition metal has been extended to analogous metal-catalyzed addition reactions of B–B,[8] B–S,[15] B–Si,[16] and B–Sn[17] compounds. On the other hand, coupling reactions of B–B[8,18] or B–H[19] compounds with aryl, vinyl, allyl, and benzyl halides or triflates have provided a simple method for borylation of organic electrophiles without using lithium or magnesium intermediates. Because of the availability of various electrophiles and mild reaction conditions, this method has allowed convenient access to organoboron compounds that have a variety of functional groups. An extension of this methodology to aliphatic or aromatic C–H borylation is of significant value for direct preparation of organoboron compounds from economical hydrocarbons. Some key steps in putative catalytic cycles have been established by Hartwig via stoichiometric C–H borylation of alkanes and arenes with (boryl)metal complexes. Those discoveries were followed by the rapid development of catalytic processes for C–H borylation of hydrocarbons with bis(pinacolato)diboron (B_2pin_2) or pinacolborane (HBpin).[11] In most reactions, it is widely recognized that the catalytic cycle involves

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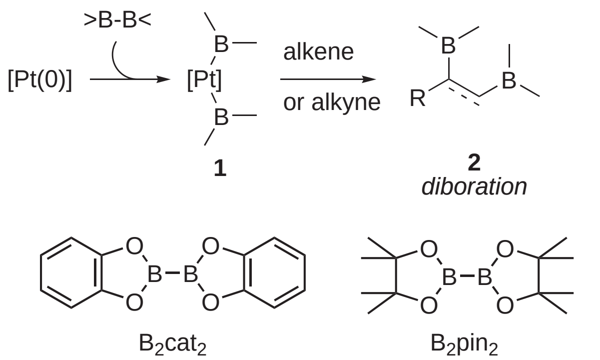


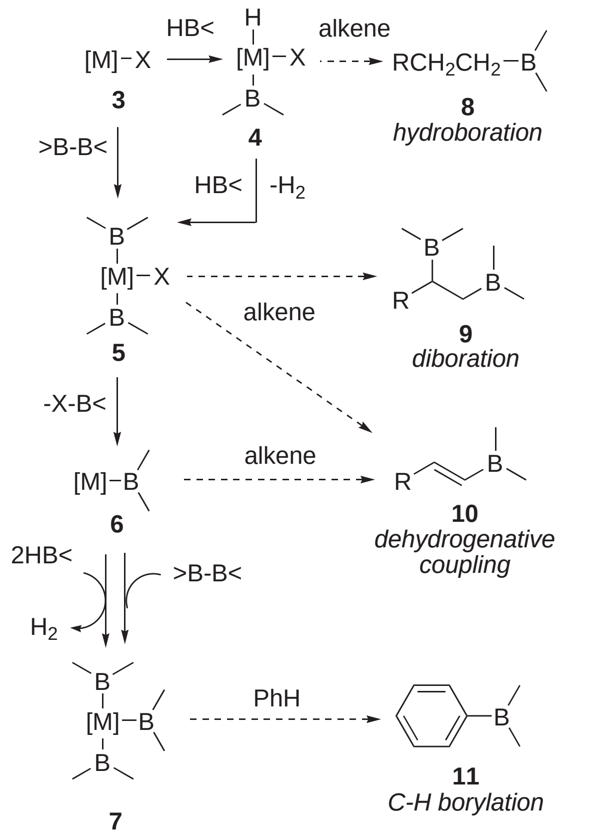
Scheme 1.

a (boryl)metal species generated by transmetalation or oxidative addition.[8b–8d,11g–11j] The synthesis, characterization, bonding, and reactivity of these catalytically important species have recently been reviewed.[8b]

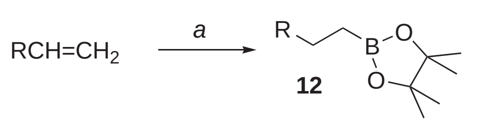
2.1 Oxidative Addition of Boranes or Diborons to Low-Valent Transition-Metal Complexes. The reaction between $Pt(PPh_3)_4$ or $Pt(C_2H_4)(PPh_3)_2$ and B_2pin_2 or B_2cat_2 provides a single crystal of **1** consisting of a distorted square-planar coordination geometry for the Pt atom containing two *cis*-boryl and phosphine ligands, which allows insertion of alkenes and alkynes into the Pt–B bond (Scheme 1).[20–22] This process has been used for catalyzed additions of B–B, B–Si, and B–Sn compounds to alkenes and alkynes with Pd^0, Pt^0, or Rh^I complexes.[8,16,17]

Reaction between rhodium(I) or iridium(I) complexes ([M]–X, X = halogen, OAc, and OR) with HBcat, HBpin, or B_2pin_2 yields species effective for catalyzed hydroboration of alkenes and alkynes **4**, diboration and dehydrogenative coupling of alkenes **5** and **6** and C–H borylation of alkanes, arenes, and alkenes **7** (Scheme 2). The oxidative addition of HBcat to $RhCl(PPh_3)_3$ affords a coordinatively unsaturated **4**,[23] which is believed to be an active species of the catalyzed hydroboration. Further oxidative addition of a borane to **4** generates H_2 and a diborylrhodium(III) complex **5**,[24] which undergoes diboration **9** or dehydrogenative borylation of alkenes **10**.[25] H_2 thus generated will hydrogenate a part of the alkenes. Thus, catalyzed hydroboration of alkenes with HBcat often provides a mixture of $RCH(Bcat)CH_2(Bcat)$ (**9**), $RC(Bcat)=CH_2$, $RCH=CH(Bcat)$ (**10**), and RCH_2CH_3, along with the desired hydroboration product **8**. Interaction between a rhodium(I) or iridium(I) complex of **6** with HBpin,[26] HBcat,[27] B_2pin_2, or B_2cat_2 yields a tris(boryl) complex **7**.[26–28] $Ir(Bpin)(PMe_3)_4$ (**6**) and $Ir(Bpin)_3(PMe)_3$ (**7**) react cleanly with the C–H bond of benzene to produce PhBpin and $[Ir(H)(PMe_3)_4]$ or *fac*-$[Ir(Bpin)_2(H)(PMe_3)_3]$ at room temperature, thus indicating that both iridium(I) and iridium(III) species are viable for aromatic C–H borylation.[26] However, mechanistic studies by Hartwig and Smith have shown that an Ir^{III} complex **7** is a component involved in the C–H borylation.[11e,26]

2.2 Additions of Boranes to Alkenes and Alkynes (Hydroboration). Catalyzed hydroboration did not attract much attention until a report by Männig and Nöth in 1985[29] that a Wilkinson complex ($RhCl(PPh_3)_3$) accelerates the addition of catecholborane (HBcat) to alkenes or alkynes.[8d,14] Most studies have employed HBcat, but pinacolborane (HBpin) is an excellent alternative because it is a more stable, easily prepared and stored hydroboration reagent that is convenient for organic syntheses. Hydroboration of terminal and internal alkenes with HBpin proceeds at room temperature in the presence of an iridium(I) catalyst (eqs 1 and 2).[30] All internal alkenes yield single products coupled at the terminal carbons **13** via isomerization before reductive elimination.

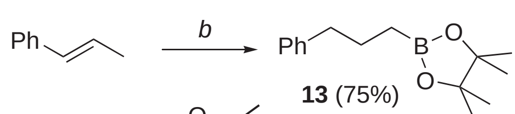


Scheme 2.

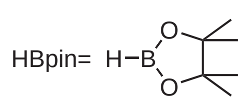


(1)

R= n-C_6H_{13} (89%), Ph (93%), C_6F_5 (82%)

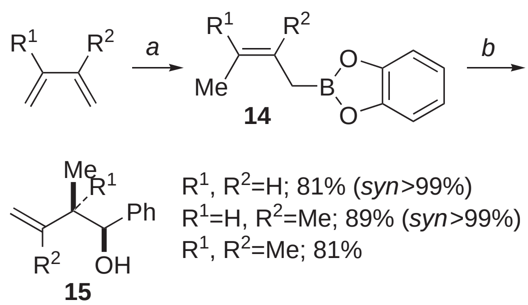


(2)

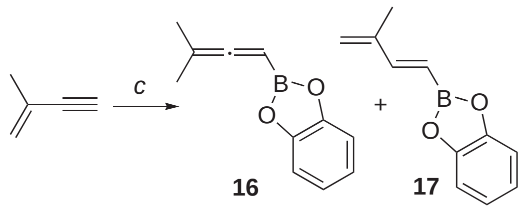


a) HBpin, $[IrCl(cod)]_2$/2dppe, CH_2Cl_2, rt
b) HBpin, $[IrCl(cod)]_2$/2dppm, CH_2Cl_2, rt

The palladium-catalyzed hydroboration of conjugate 1,3-dienes with a Pd, Ni, or Rh catalyst yields allylboronates via an oxidative addition–insertion–reductive elimination process (eq 3).[31,32] The cis addition of the H–B bond to dienes affords *cis*-allylboronates (Z > 99%) with selective addition of hydrogen to the unsubstituted double bond to give single regioisomers **14** for asymmetric dienes. The hydroboration of enynes yields either 1,4-addition **16** or 1,2-addition products **17**, the ratio of which dramatically changes with the phosphine ligand as well as the molar ratio of the ligand to palladium metal (eq 4).[31,33]



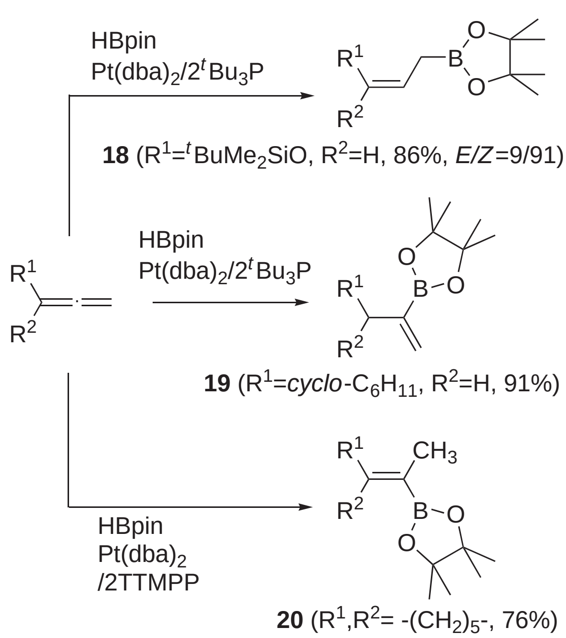
(3)



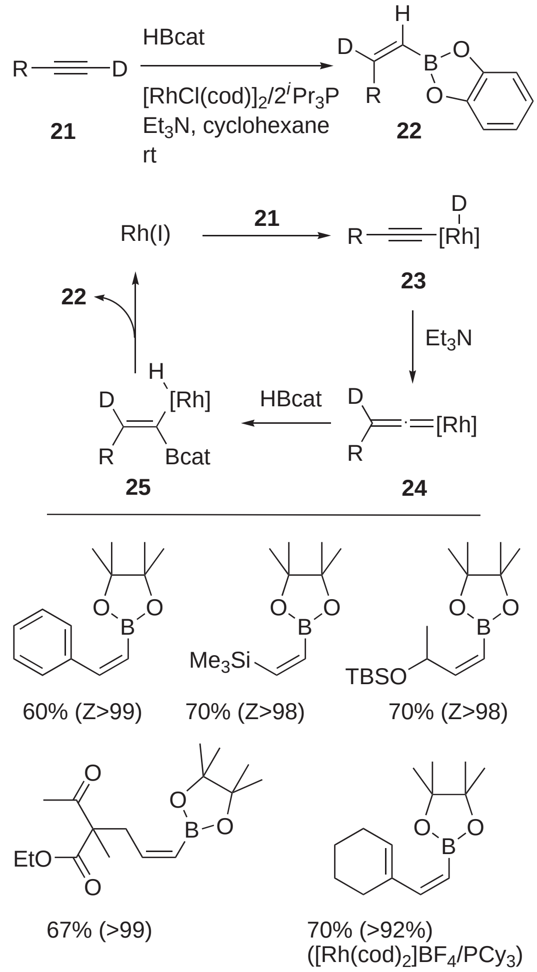
(4)

a) HBcat, $Pd(PPh_3)_4$, benzene, rt; b) PhCHO
c) HBcat, $Pd(PPh_3)_4$ or $NiCl_2$(dppe)

Uncatalyzed hydroboration of allenes results in the formation of a mixture of four possible isomers; however, such regio- and stereoselectivity can be controlled by the ligands used for catalysts (Scheme 3).[34] A platinum(0)/2^{t}Bu$_3$P complex affords the internal products **19** for alkoxyallenes or the terminal *anti*-Markovnikov products **18** for aliphatic and aromatic allenes. On the other hand, a bulky and basic



Scheme 3.

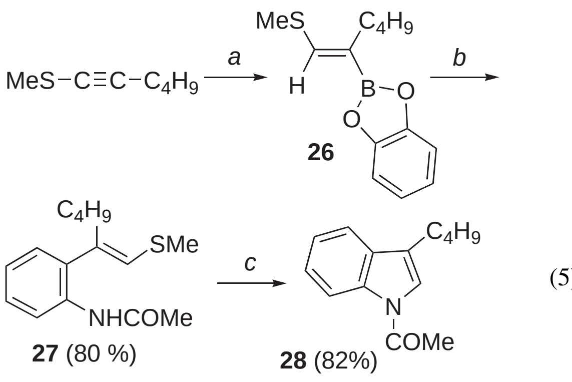


Scheme 4.

tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP) changes the regioselectivity to the Markovnikov addition **20** for the representative terminal allenes.

A rhodium(I)/^{i}Pr$_3$P complex catalyzes novel trans hydroboration of terminal alkynes giving *cis*-1-alkenylboron compounds **22** (Scheme 4).[35] The dominant factors reversing the conventional cis hydroboration to the trans hydroboration are the use of alkyne in excess of HBcat and the presence of more than 1 equivalent of Et_3N to HBcat for a rhodium(I) catalyst possessing two equivalents of bulky and donating alkylphosphine. Since the deuterium label at the terminal carbon of **21** selectively migrates to the internal carbon, a vinylidene complex **24** is proposed as a key intermediate of this formal trans hydroboration.

The hydroboration of thioalkynes with HBcat in the presence of a nickel catalyst selectively yields β-(alkylthio)-1-alkenylboronates **26**, in contrast to uncatalyzed hydroboration that yields opposite α-(alkylthio) derivatives (eq 5).[36] Since the vinylic sulfide is synthetically equivalent to a carbonyl compound, its cross-couplings with aromatic halides having a 2-NHAc or 2-OMOM group provide valuable precursors for the syntheses of indole and benzofuran derivatives.[37] For example, a stepwise one-pot three-step reaction affords indole (**28**) in good yield (eq 5).

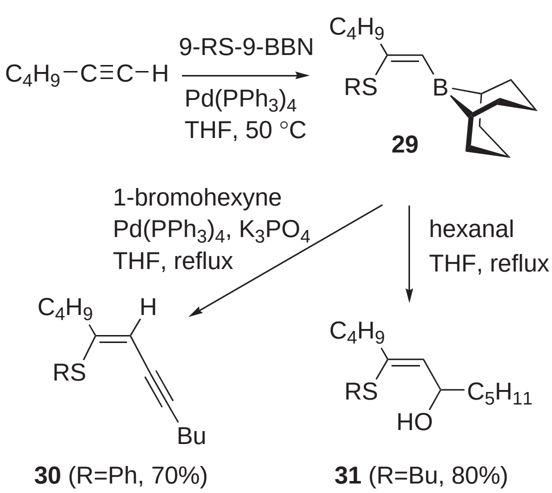


(5)

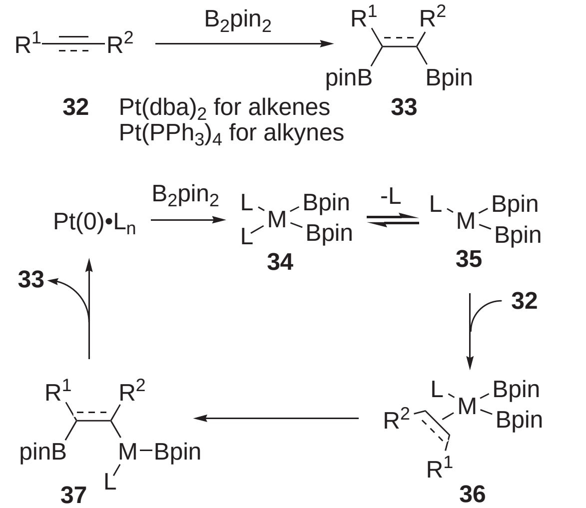
a) HBcat, $NiCl_2$(dppp), benzene, r.t.
b) 2-(NHAc)C_6H_4I, $Pd(PPh_3)_4$, aq. NaOH
c) $HgCl_2$, MeCN-H_2O

2.3 Addition of 9-RS-9-BBN to Terminal Alkynes (Thioboration). β-(Alkylthio)-1-alkenylboranes **29** can be synthesized by thioboration of terminal alkynes with 9-RS-9-BBN (9-BBN = 9-borabicyclo[3.3.1]nonane). A selective cis addition catalyzed by a palladium(0) complex affords **29**, which exhibits exceptionally high reactivity toward protonolysis with methanol, cross-coupling reaction with organic halides **30**, and nucleophilic addition to carbonyl compounds **31** (Scheme 5).[15] A palladium(0) complex also works as a catalyst for synthesis of 9-RS-9-BBN from RSH and 9-BBN.

2.4 Additions of Diborons to Alkenes and Alkynes (Diboration). The addition of B_2X_4 (X = F, Cl, and Br) to unsaturated hydrocarbons was first discovered by Schlesinger in 1954. Although stable alkoxo derivatives are very inert to alkenes and alkynes, they are oxidatively added to a low-valent transition-metal complex with the B–B bond cleavage, thus allowing the catalyzed transfer of the B–B bond to unsaturated organic substrates **33** (Scheme 6).[8] $Pt(PPh_3)_4$, $Pt(C_2H_4)(PPh_3)_2$, $Pt(CO)_2(PPh_3)_2$, and Pt(norbornene)$_2$/P(2-MeC$_6$H$_4$)Ph$_2$ or PCy_3 catalyze the addition of B_2pin_2 to alkynes.[20–22,38] The proposed catalytic cycle[8,20–22] involves oxidative addition, insertion and reductive elimination processes. The reaction is accelerated significantly with an unsaturated platinum(0) complex having a donating phosphine ligand and is slowed down



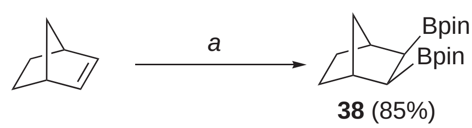
Scheme 5.



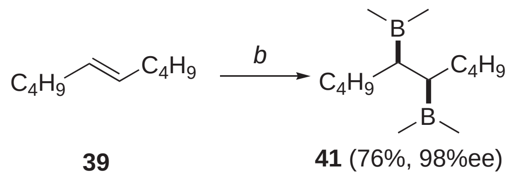
Scheme 6.

in the presence of PPh_3 added to $Pt(PPh_3)_4$, thus suggesting a rate-determining role of both oxidative addition and phosphine dissociation (**34** to **35**).

Phosphine-based platinum(0) catalysts are inefficient for diboration of alkenes, but phosphine-free $Pt(dba)_2$[39,40] and $Pt(cod)_2$[41] are good catalysts allowing insertion of an alkene into the B–Pt bond. Disubstituted alkenes result in no addition, but the reaction proceeds smoothly for terminal alkenes and cyclic alkenes having an internal strain such as 1-decene, styrene, cyclopentene, and norbornene (eq 6). An asymmetric version has recently been demonstrated by using B_2cat_2 and chiral rhodium(I) catalyst **40** (eq 7).[42]

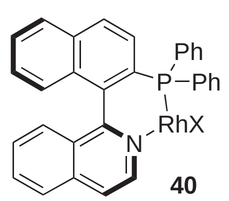


(6)

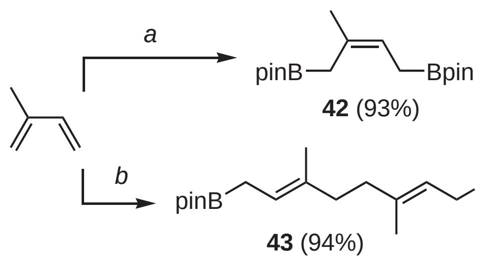


(7)

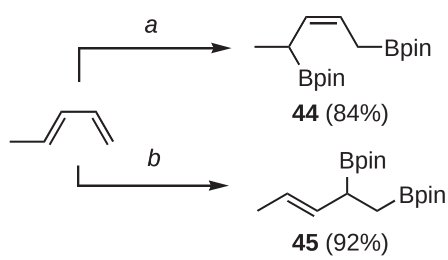
a) B_2pin_2, $Pt(dba)_2$, toluene, 50 °C
b) B_2cat_2, catalyst (**40**), THF



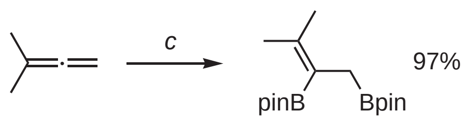
The addition of diborons to 1,3-dienes affords a new class of allylboron compounds that dramatically changes the products between phosphine-based platinum(0) catalysts and phosphine-free catalysts (eqs 8 and 9).[43] $Pt(PPh_3)_4$ stereoselectively yields cis 1,4-addition products **42** and **44** for representative aliphatic and alicyclic 1,3-dienes.[43] In contrast, phosphine-free $Pt(dba)_2$ results in the formation of a 1,2-addition product **45** for 1,3-pentadiene and a double insertion product **43** for isoprene. There have also been systematic studies on diboration of allenes giving allylboron compounds (eq 10).[44,45]



(8)



(9)

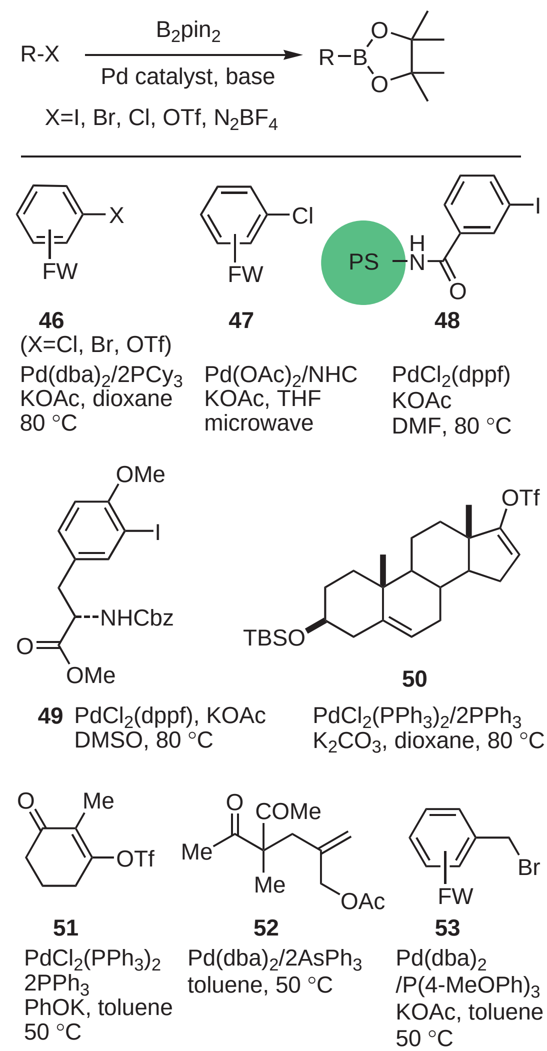


(10)

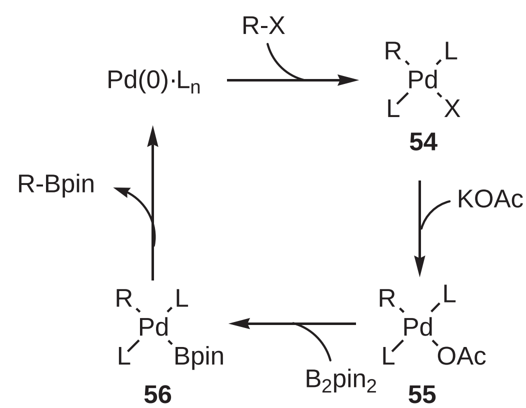
a) B_2pin_2, $Pt(PPh_3)_4$, toluene, 80 °C
b) B_2pin_2, $Pt(dba)_2$, toluene, rt
c) B_2pin_2, $Pt(dba)_2/PCy_3$, toluene, 50 °C

2.5 Coupling Reactions of Diboron with C–X Bonds. Metal-catalyzed cross-coupling reactions of disilanes and distannanes with organic halides have been used for the synthesis of organosilicon and -tin compounds. Although the lack of suitable boron nucleophiles has limited this protocol for boron compounds, tetra(alkoxo)diborons such as B_2pin_2 act as boron-nucleophiles for palladium-catalyzed cross-coupling reactions of organic halides and triflates.[8,18] Analogous coupling reaction of HBpin with aryl or vinyl halides is an economical alternative reported by Masuda, Murata, and co-workers.[19] Borylation of aryl, 1-alkenyl, allyl, and benzyl halides[18,46] or triflates[47] proceeds in the presence of KOAc and a palladium catalyst (Scheme 7). $PdCl_2(dppf)$ has been used for representative aromatic iodides and bromides **48** and **49**,[18] and a combination of a palladium precursor and an electron-donating PCy_3 **46**[46] or N-heterocyclic carbene (NHC, **47**)[48] can be advantageous for achieving high yields for aryl chlorides and electron-rich aryl bromides or triflates. The reaction can be further accelerated by irradiation with microwaves.[48] The borylation of 1-alkenyl halides or triflates **50** and **51** proceeds while completely retaining their stereochemistry.[49,50] Borylation of allyl acetates **52** provides a simple access to variously functionalized allyboronic esters.[51,52] Electron-rich tris(*p*-methoxyphenyl)phosphine is effective for borylation of benzyl halides **53**.[53]

The presence of a base such as KOAc is critical for the coupling of diborons, suggesting transmetalation occurring from Ar–Pd–OAc generated by displacement of X on Ar–Pd–X with an acetate anion (Scheme 8).[18] *trans*-$PhPd(OAc)(PPh_3)_2$ (**55**, R = Ph) is obtained quantitatively when *trans*-$PhPdBr(PPh_3)_2$ (**54**, R = Ph) is treated with an excess of KOAc. Indeed, reaction between **55** and B_2pin_2 gives PhBpin, whereas no reaction is observed between **54** and B_2pin_2. Thus, the coupling with allyl acetates (**52**, Scheme 7) which directly generate **55** via oxidative addition smoothly takes place in the absence of any bases.



Scheme 7.



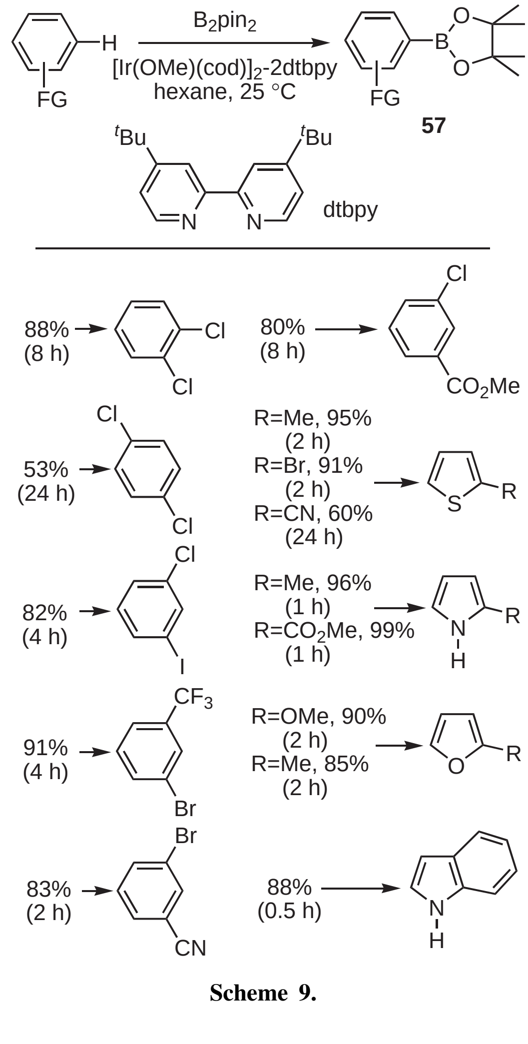
Scheme 8.

2.6 Coupling Reactions of B_2pin_2 and HBpin with C–H Bonds (C–H Borylation). Direct borylation of arenes by HBpin or B_2pin_2 is highly attractive as a convenient, economical, and environmentally benign process for the synthesis of aromatic boron compounds, which has been studied extensively by Hartwig and Smith.[11,54,55] We reported that a class of Ir^I complexes possessing a 2,2′-bipyridine (bpy) or 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) ligand exhibits excellent activity and selectivity for aromatic C–H borylation with B_2pin_2[11d,26,56] or HBpin.[57] An Ir catalyst prepared from $1/2[IrCl(coe)_2]_2$ (coe = cyclooctene) and dtbpy achieves a maximum turnover number (8000 TON) with 0.02 mol % catalyst loading at 100 °C. The reaction was first demonstrated at 80–100 °C using an Ir–Cl complex, but it proceeds smoothly even at room temperature when the catalyst is prepared from $1/2[Ir(OMe)(cod)]_2$ (cod = 1,5-cyclooctadiene) and dtbpy (Scheme 9).[11e,56] Both 1,2- and 1,4-disubstituted arenes bearing identical substituents and 1,3-disubstituted arenes afford isomerically pure single products, whereas monosubstituted arenes resulted in a mixture of para and meta coupling products. Under conditions analogous to those used for typical arenes, heteroarenes are also borylated with B_2pin_2 or HBpin (Entries 7–13). The protocol has been used successfully for borylation of C–H bonds of azulene,[58] ferrocene and Cp–metal complexes,[59] polycyclic aromatic hydrocarbons such as naphthalene, pyrene and perylene,[60] porphyrins,[61] and nitrogen-containing heterocycles.[62]

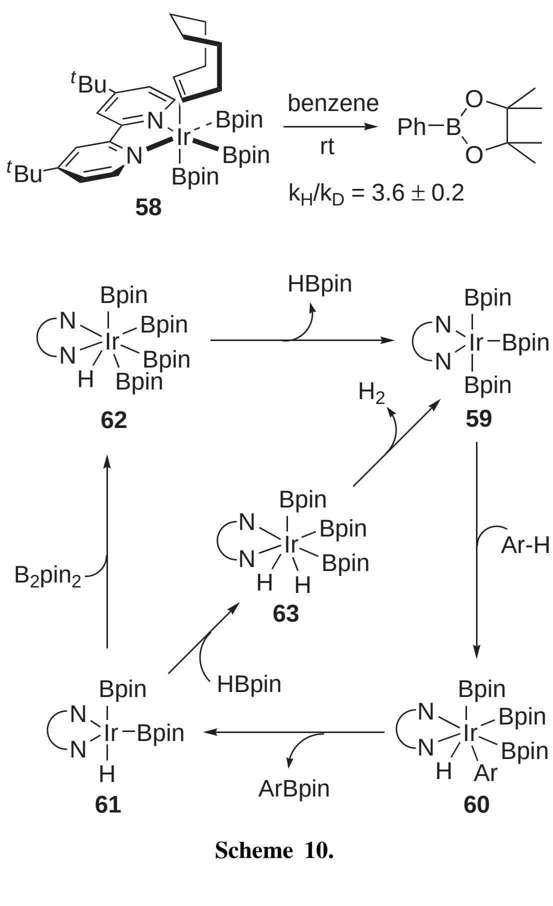
Mechanistic studies have shown that an Ir^{III}–tris(boryl) complex **7** is an active component involved in the catalytic cycle as is discussed in Scheme 2.[11] ^1H NMR spectroscopy for the reaction of B_2pin_2 and $1/2[IrCl(cod)]_2$/dtbpy showed the formation of a tris(boryl)Ir^{III} complex **58**, which was finally isolated and characterized by X-ray analysis.[11d] When **58** is dissolved in benzene at room temperature, 3 equivalents of pinacol phenylboronate (80%) are produced instantaneously. Thus, the reaction proceeds through a catalytic cycle analogous to that proposed for the Rh^I-catalyzed borylation of alkanes[11a] (Scheme 10). A small steric hindrance from the planar bipyridine ligand as well as its electron donation to the metal center allows smooth oxidative addition of an arene C–H bond, giving an Ir^V intermediate **60**. The small steric influence of the planar dioxaboryl rings (Bpin) and an aryl ring (Ar) can also be critical for the formation of such sterically hindered hepta-coordinated intermediates. These processes have been supported by recent theoretical studies by Sakaki et al.[11g]

A chelation-controlled ortho selective C–H borylation of benzoates is achieved when an $Ir^I/2P[C_6H_3(CF_3)_2]_3$ complex is used at 80 °C (Scheme 11).[63] Although HBpin thus generated from B_2pin_2 does not participate in the next catalytic cycle, all reactions are remarkable in their high regiospecificity for selective functionalization of ortho carbons.

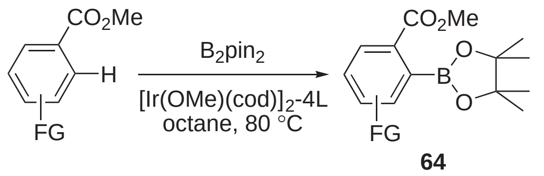
A simple extension of this protocol to vinylic C–H borylation of typical alkenes resulted in formation of a complex mixture of boron compounds, but electron-rich vinyl ethers exceptionally allow selective C–H borylation. Although simple vinyl



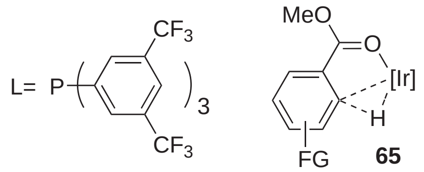
Scheme 9.



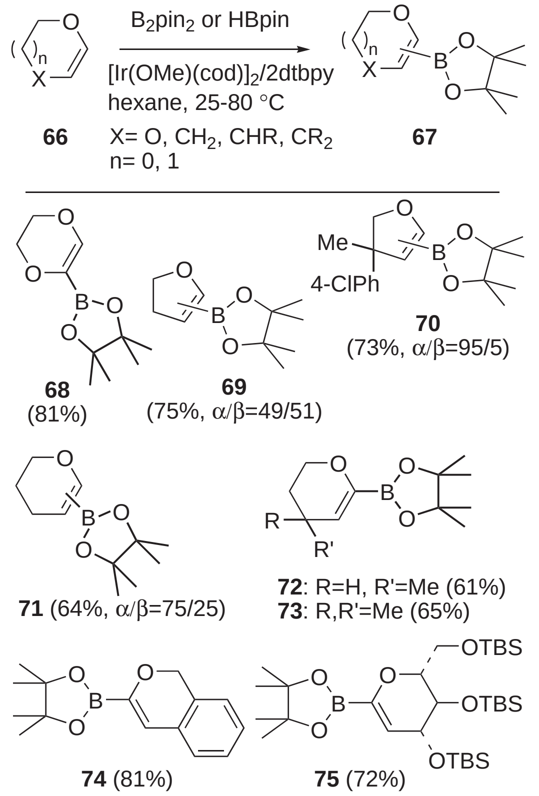
Scheme 10.



FG= *o*-CF_3 (98%), *o*-NMe_2 (97%), *m*-Br (64%), *m*-NMe_2 (99%), *p*-Me (99%), *p*-OMe (66%)



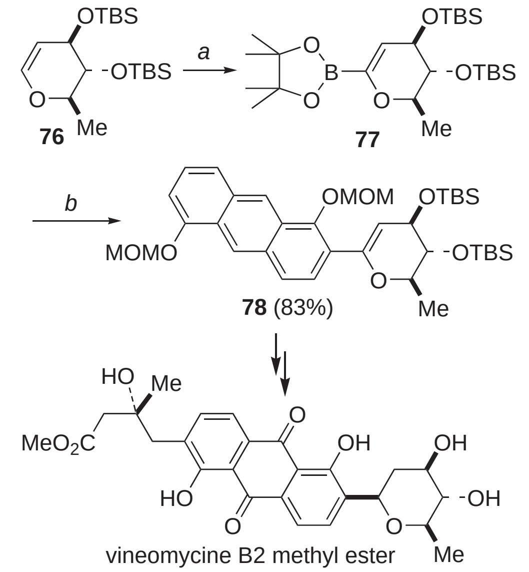
Scheme 11.



Scheme 12.

ethers such as butyl vinyl ether resulted in ca. 30% of (*E*)-BuOCH=CHBpin along with several boron-containing by-products, cyclic vinyl ethers are substrates that achieved selective coupling at the vinylic C–H bond (Scheme 12).[64,65] The reactions with dihydrofurans **69** suffer from low regioselectivities, giving a mixture of α- and β-coupling products even for γ-disubstituted analogues **70**, but dihydropyran derivatives possessing substituents at the γ-position **72**–**74** and protected D-glucals (**75**) provide single coupling products at the α-carbon.

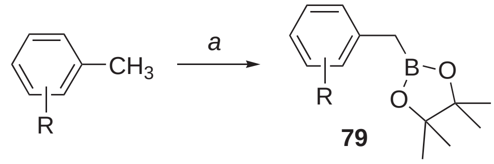
C-Glucals are an important class of compounds due to the frequent occurrence of these fragments in pharmaceuticals. A key skeleton **78** previously used as a precursor of vimeomycinone B2 methyl ester is synthesized in 83% yield when the preparation of 1.1 equivalents of **77** is directly followed by cross-coupling (eq 11).[65]



(11)

a) B_2pin_2, Ir(OMe)(cod)/dtbpy, octane, 80 °C, 16 h
b) ArI, $PdCl_2(PPh_3)_2$, K_3PO_4, dioxane, 80 °C, 8 h

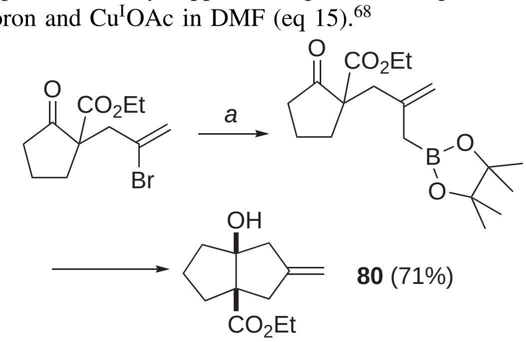
A palladium on carbon (10% Pd/C) catalyzes the selective coupling at the benzylic C–H bond (eq 12).[66]



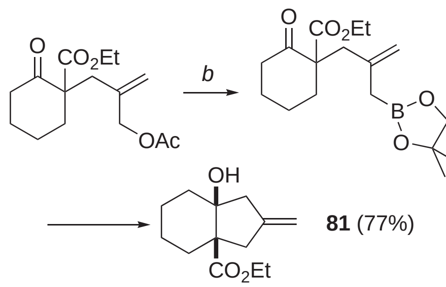
(12)

a) B_2pin_2, Pd/C (3-6 mol%), 100 °C, 16 h.
R= H (74%), 2-Me (77%), 4-Me (72%), 3,4-Me_2 (64%), 4-MeO (13%), 4-F (26%)

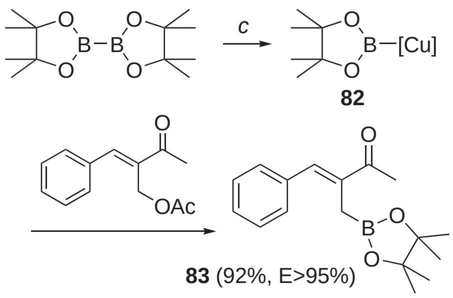
2.7 Synthesis of Allyl- and Benzylboron Compounds. Allylboron compounds are valuable reagents in organic synthesis since their addition to a carbon–oxygen or the carbon–nitrogen double bond diastereoselectively provides homoallylic alcohols or amines via a chair-like, six-membered cyclic transition state. Cross-coupling reaction of Knochel's borylmethylzinc reagent with haloalkenes (eq 13)[67] and borylation of allyl acetates with diboron (eq 14)[51,52] provide a variety of 5–5, 6–5, and 7–5 cis fused exomethylene cyclopentanols from β-ketoesters or -diketones via a cross-coupling/intramolecular allylboration sequence. An alternative boron nucleophile convenient for synthesis of functionalized allylboron compounds is borylcopper(I) reagent in situ generated from diboron and Cu^IOAc in DMF (eq 15).[68]



(13)



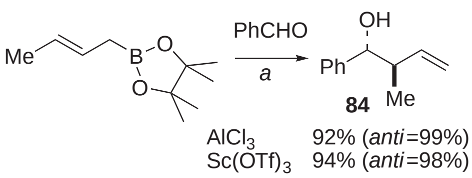
(14)



(15)

a) $IZnCH_2Bpin$, $Pd(OAc)_2/_3PPh_3$
b) B_2pin_2, $Pd(dba)_2/2AsPh_3$, toluene, 50 °C
c) CuCl, LiCl, KOAc, DMF, r.t.

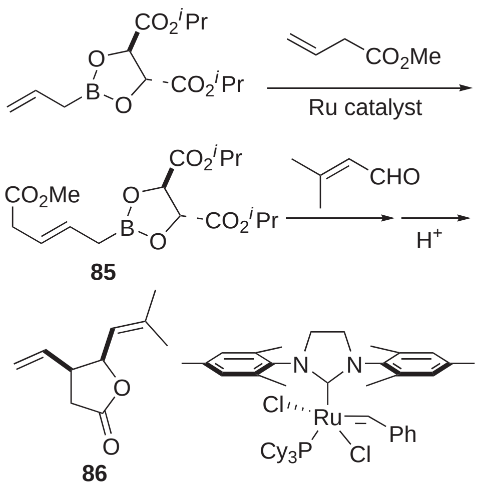
Allylboration of carbonyl compounds with these bulky pinacol esters is very slow at room temperature, but the reaction can be catalyzed by Lewis acids. Addition of pinacol (*E*)- and (*Z*)-crotylboronate to benzaldehyde diastereoselectively proceeds at −78 °C in the presence of $AlCl_3$ or $Sc(OTf)_3$ (10 mol %) (eq 16).[69]



(16)

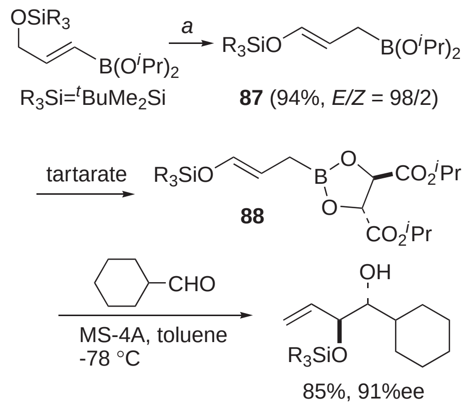
a) catalyst (10 mol%), toluene, -78 °C, 4 h

Ruthenium-catalyzed olefin cross-metathesis has resulted in a one-pot three-component coupling for the synthesis of homoallylic alcohols. The utility of this protocol was demonstrated in enantioselective allylboration (eq 17).[70]



(17)

Metal-catalyzed positional isomerization of the double bond provides a simple access to γ-(alkoxy)allylboronates, which are reagents for diastereoselective preparation of 1,2-diols. The use of a cationic iridium complex obtained via hydrogenation of $[Ir(cod)(PPh_2Me)_2)]PF_6$ in ethyl acetate results in a quantitative isomerization within 10 min without stereochemical isomerization (**87**, E > 98%) (eq 18).[71] For intramolecular allylboration, the isomerization of **89** is followed by deprotection the acetal and cyclization catalyzed by $Yb(OTf)_3$ (eq 19).[72]



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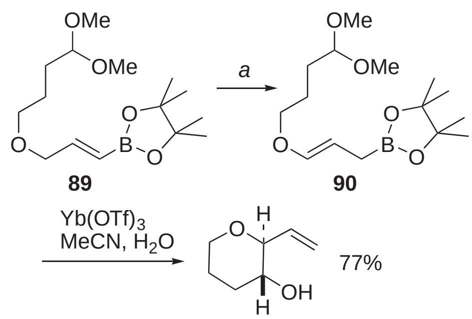
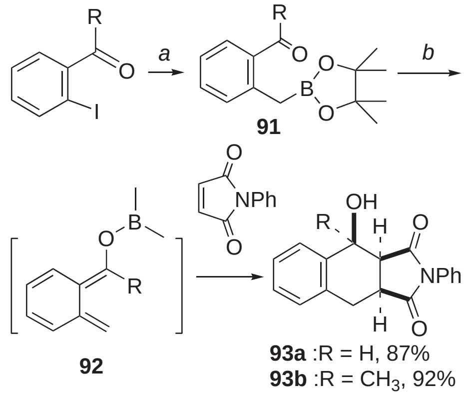


(19)

a) $[IrH_2(PPh_2Me)_2]PF_6$, AcOEt, r.t.

The synthesis of benzylboronates via coupling reactions of B_2pin_2 is shown in Scheme 7 (**53**) and eq 12 (**79**). *ortho*-Acylbenzylboronates synthesized by cross-coupling reaction of Knochel's borylmethylzinc reagent with haloarenes work as stable *ortho*-quinodimethane precursors that can be trapped by dienophiles (eq 20).[73]

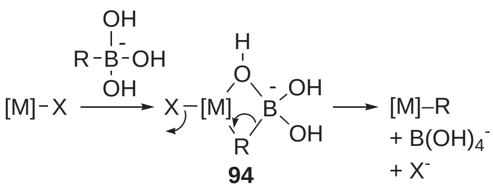


(20)

a) $IZnCH_2Bpin$, $PdCl_2(PPh_3)_2$, THF
b) 100 °C or hν

3. C–C and C–N Bond-Forming Reactions

3.1 Transmetalation to Transition-Metal Complexes. Transmetalation between organometallic reagents and transition-metal complexes is a fundamental process involved in metal-catalyzed bond-forming reactions. It is the first step in metal-catalyzed 1,4-addition of organic electrophiles to α,β-unsaturated carbonyl compounds[9] and the second step in palladium- or nickel-catalyzed cross-coupling reactions of organoboron compounds with nucleophiles.[6] Main group nonmetallic compounds such as boron and silicon compounds are attractive for use in organic syntheses due to their high degrees of thermal stability and air stability for isolation or handling and due to their compatibility with a wide range of functional groups, but transmetalation is very slow due to low nucleophilicity of the nonmetal organoelement compounds. However, they transfer the organic groups to transition-metal complexes by one of the following three processes (eqs 21, 22, and 23).[6,74] The addition of a base such as alkoxy, hydroxy, or fluoride anion exerts a remarkable accelerating effect on the cross-coupling reactions of organoboron and -silicon compounds (eq 21).[6h,75,76] Thereby, the coordination of a negatively charged base enhances the nucleophilicity of the organic group so that ligand exchange between [M]–X (X = halogen) and an organometallic reagent proceeds via a four-centered σ-bond metathesis (**94**).

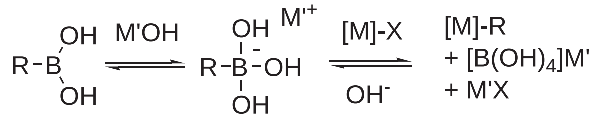


94 (21)

[M]=Pd(II), Ni(II), Rh(I); X=halogen

The effects of bases and counter cations on such a base-assisted transmetalation can be roughly estimated by the basic strength, affinity of counter cations for halide ions (stability constant)[77] and solubility of M′X (Scheme 13). The transmetalation is a reversible process that involves nucleophilic displacement of [M]–X (M = Pd^{II} and Ni^{II}) with $[RB(OH)_3]M'$ **95** to yield [M]–R, $B(OH)_3$, and M′X. The concentration of hydroxyborate anion **95**, which exists in an alkaline solution in equilibrium with a free organoboronic acid, increases by increasing the basic strength ($OH^- > MPO_4^- > MCO_3^- > HCO_3^-$). For each series of bases, cesium may yield a higher concentration of **95** than do the corresponding smaller alkali metals because the stability constant of OH^- becomes smaller as we move down the periodic table ($Cs^+ < K^+ < Na^+ < Li^+$). Transmetalation can be fast for counter cations (M'^+) that have a high stability constant for halide ions ($Ag^+ > Tl^+ > R_4N^+ > Ba^{2+} > Cs^+ > K^+$). Precipitation of insoluble AgX, TlX, and BaX_2 is also a strong driving force of transmetalation.

The second process is transmetalation to [M]–OR′ (M = Pd, Rh, and Re; R′O = OAc, OMe, and OH) complexes (eq 22). Due to the high oxophilicity of boron and silicon compounds and high basicity of [M]–OR′ complexes, transmetalation takes place without any assistance of a base for these Pd, Rh, and Re complexes. Thus, cross-coupling reactions often proceed under neutral conditions for organic electrophiles, directly yielding RO–Pd complexes via oxidative addition. Reactions of boron or silicon compounds with allylic acetates,[78] allylic carbonates,[79] 1,3-butadiene monoxide,[80] propargyl carbonates,[81] acetic anhydrides,[82] and phenyl trifluoroacetate[83] have been carried out in the absence of a base.



95

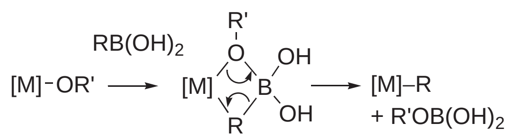
stability constants for OH^- (log K at 25 °C)

Li^+	Na^+	K^+	Cs^+
0.36	-0.2	-0.5	-

stability constants for X^- (log K at 25 °C)

	K^+	Cs^+	Ba^{2+}	Bu_4N^+	Tl^+	Cu^+	Ag^+
Cl^-	-0.7	-0.39	-0.13	0.40	0.49	2.7	3.3
Br^-	-	0.03	-	0.49	0.91	5.9	4.7
I^-	-0.19	-0.03	-	0.78	-	8.9	6.6

Scheme 13.

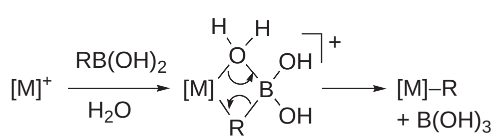


96 (22)

[M]=Pd(II), Rh(I), Re(I); R'=H, Me, COMe

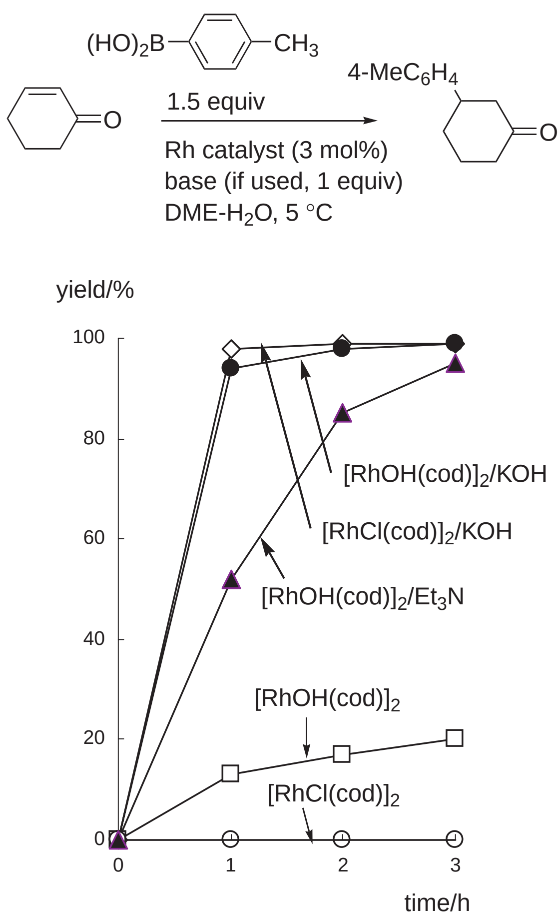
Although the transmetalation shown in eq 22 takes place under neutral conditions, there is a strong accelerating effect of bases (Scheme 14).[84] For example, addition of KOH to a mixture of *p*-tolylboronic acid, 2-cyclohexenone, and a rhodium complex in aqueous DME at 5 °C exerts a remarkable accelerating effect. The RhOH complex, that is believed to be an active species for transmetalation (□), is a better catalyst than the RhCl complex (○), but addition of aqueous KOH results in completion of both reactions within 1 h (● and ◇). Thus, quarternization of arylboronic acids with a base greatly facilitates transmetalation to both RhCl and RhOH complexes.

The third process is transmetalation to cationic metal complexes (eq 23). Cross-coupling reactions of organoboron and silicon compounds with Ph_2IBF_4[85] or ArN_2BF_4,[86] which affords an Ar–[Pd]$^+$ intermediate via oxidative addition, have been carried out in the absence of a base because transmetalation takes place smoothly under neutral conditions.



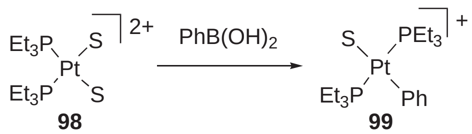
97 (23)

$[M]^+$=Pd^{2+}, RPd^+, Pt^{2+}, Rh^+

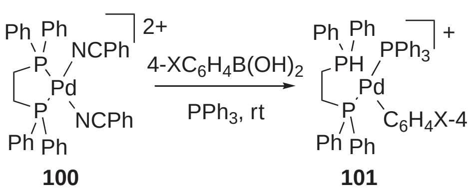


Scheme 14.

It has been reported that a stoichiometric reaction between $[Pt(S)_2(PEt_3)_2][CF_3SO_3]_2$ (**98**, S = MeOH or H_2O) and $[Ph_4B]Na$, Ph_3B, or $PhB(OH)_2$ gives $[Pt(Ph)(S)(PEt_3)_2]^{2+}$ (**99**) without any assistance of bases (eq 24).[87] Another example reported in this category is interaction of $[Pd(dppe)(PhCN)_2](BF_4)_2$ (**100**) with $PhB(OH)_2$ to provide a monocationic $[Pd(Ph)(dppe)(S)]^+$ (**101**, S = H_2O and PhCN) (eq 25). Isolation of this intermediate failed due to its thermal instability, but addition of PPh_3 (1 equiv) gives **101** (X = H), which is identical to an authentic material obtained from *trans*-$[Pd(Ph)(Br)(PPh_3)_2]$, dppe and $AgBF_4$.[75]

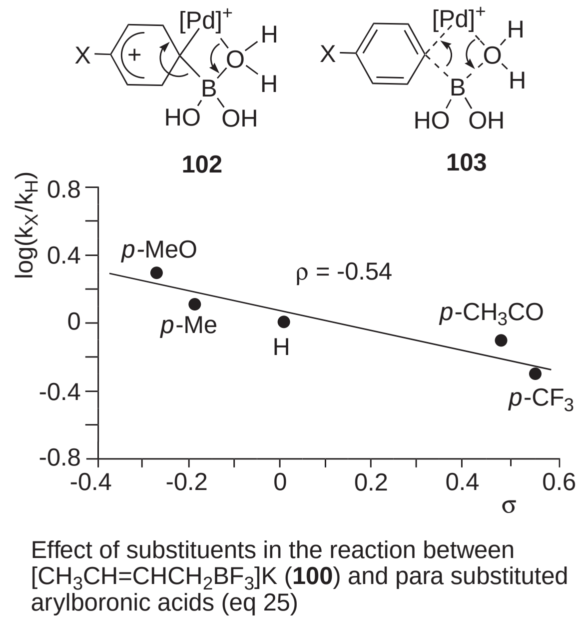


(24)



(25)

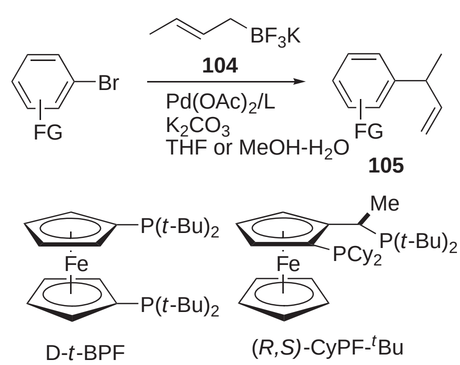
Transmetalation is a critical process involved in various metal-catalyzed bond-forming reactions; however, little is known about the mechanistic features, including its kinetics. The electronic effect on transmetalation of a series of para sub-



Scheme 15.

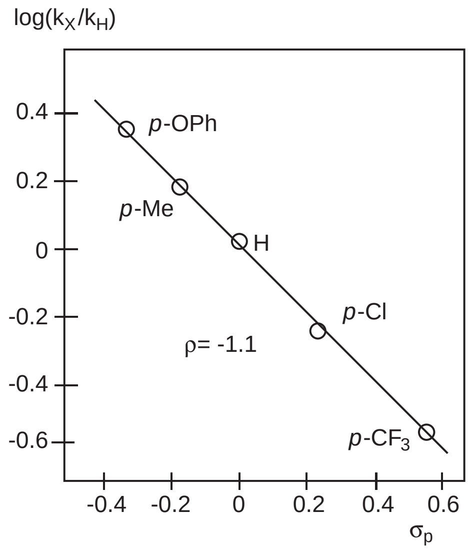
stituted arylboronic acids shows a negative ρ value (−0.54), demonstrating that the donating substituents accelerate the reaction (Scheme 15).[75] Aromatic C–B or C–Si bond cleavage with water or halogens and cleavage of aromatic main metal–carbon bonds with cationic palladium or platinum complexes are believed to proceed through a chelated Wheland intermediate **102**.[88] However, the observed effect is ca. 10-times smaller than that of protonolysis or halogenolysis of aromatic C–B and C–Si bonds via this transition state. For example, the ρ value reported for bromonolysis of aromatic C–B bonds is −3.87.[89] Thus, this effect of substituents can be best interpreted by assuming interaction of an empty d orbital of palladium with the σ C–B bond rather than with the π-orbital of the aromatic ring **103**.

We reported the efficiency of D-*t*-BPF for γ-selective coupling of potassium allyltrifluoroborates **104** with bromoarenes and asymmetric reaction using (*R*,*S*)-CyPF-*t*-Bu as the chiral auxiliary (eq 26).[90,91] It is interesting that kinetic and theoretical studies have revealed a hitherto unknown process that involves the formation of cationic palladium(II) species before transmetalation.[92]



(26)

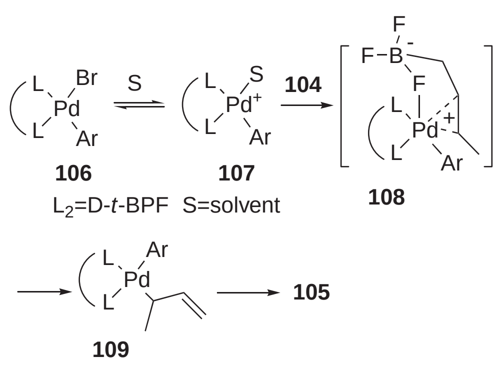
The reaction between (*E*)-$CH_3CH=CHCH_2BF_3K$ (**104**) and para substituted bromoarenes with Pd^0/D-*t*-BPF in refluxing THF showed a negative linear Hammett's correlation



Effect of substituents in the reaction between **104** and para substituted bromoarenes with Pd^0/D-*t*-BPF in refluxing THF (eq 26)

Scheme 16.

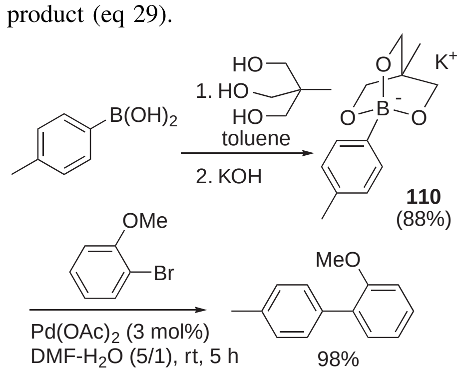
(Scheme 16).[92] Among steps involved in the catalytic cycle of cross-coupling, oxidative addition exhibits a positive correlation accelerated by withdrawing groups. It is also difficult to conclude that it is due to the rate-determining role of reductive elimination. A possible mechanism which accounts for the electronic effect of substituents is one proceeding through a cationic palladium(II) species by elimination of a bromine ligand before reaction with $CH_3CH{=}CHCH_2BF_3K$ (**104**) (eq 27). A donating ability of D-*t*-BPF strongly stabilizing cationic palladium(II) species was previously demonstrated by Hartwig in the equilibrium formation of $[Pd(Ar)(D\text{-}t\text{-}BPF)]^+$ **107** from Pd(Ar)(D-*t*-BPF)(Br) **106** in polar solvents such as THF.[93] Indeed, the reaction between **104** and $[Pd(4\text{-}MeO_2CPh)(D\text{-}t\text{-}BPF)]BF_4$ shows a perfect γ-selectivity. Theoretical calculation suggested transmetalation proceeding through a chelated cyclic transition state **108** analogous to **97** in eq 23.



(27)

3.2 Cross-Coupling Reactions. In 1979, we reported cross-coupling reactions of organoboron compounds, which involve transmetalation to palladium(II) halides as a key step. The protocol has been proved to be a general reaction for a wide range of selective C–C bond formations, in addition to related coupling reactions of organomagnesiums, -zincs, -silicones, and -stannanes. The reaction has been reviewed extensively.[6] In view of space limitation, this review is restricted to other metal-catalyzed bond-forming reactions of organoboronic aids. The mechanism of cross-coupling is discussed in Section **3.1** and some synthetic application are shown in eqs 5, 11, 26, 28, and 29 and in Schemes 5, 7, and 20.

3.3 Cyclic Triolborates for C–C and C–N Bond-Forming Reactions. The C–B bond of organoboronic acids is totally covalent which is inert to ionic reactions, but nucleophilicity of organic groups on a boron atom are significantly enhanced by quaternarization by an anionic ligand. Thus, tetracoordinated ate-complexes are a key species that has been successfully used for addition and coupling reactions of organoboron compounds, including metal-catalyzed reactions of organoboronic acids.[6,9] Air- and water-stable trifluoroborates $[RBF_3]M^+$ ($M = K$ and NR_3) are typical ate-complexes that are advantageous over boronic acids in preparation and handling of pure and water-stable crystalline materials.[94] However, their metal-catalyzed bond-forming reactions are very slow in the absence of bases because of the low nucleophilicity of organic groups due to high electronegativity of fluorine atoms. Thus, sodium trihydroxyborates $[RB(OH)_3]Na$ were recently synthesized as isolated discrete species for cross-coupling in anhydrous solvents.[95] We reported novel cyclic triolborates **110** and **111** that have exceptionally high levels of stability in air and water and higher solubility in organic solvents than that of potassium trifluoroborates.[96] High performance of lithium or potassium triolborates for transmetalation is demonstrated in palladium- and copper-catalyzed C–C and C–N bond-forming reactions (eqs 28 and 29).[96,97] The cross-coupling reactions of arylboronic acids in aqueous solvents often suffers from low yields due to competitive hydrolytic B–C bond cleavage. 2-Pyridylboronic acid is a typical boron compound that results in such cleavage with water during couplings. It is remarkable that 2-pyridineboronate (**111**) affords a high yield of the coupling product (eq 29).



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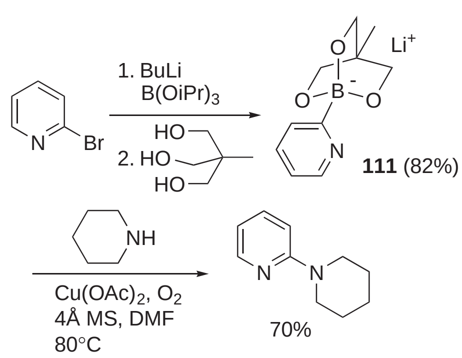
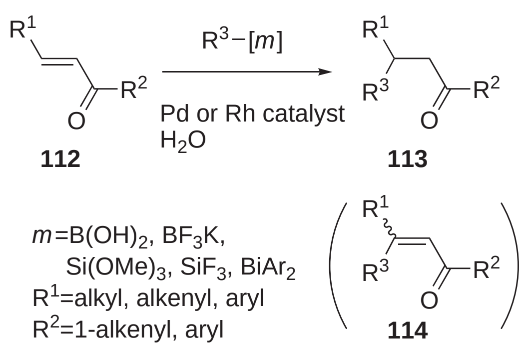


(29)

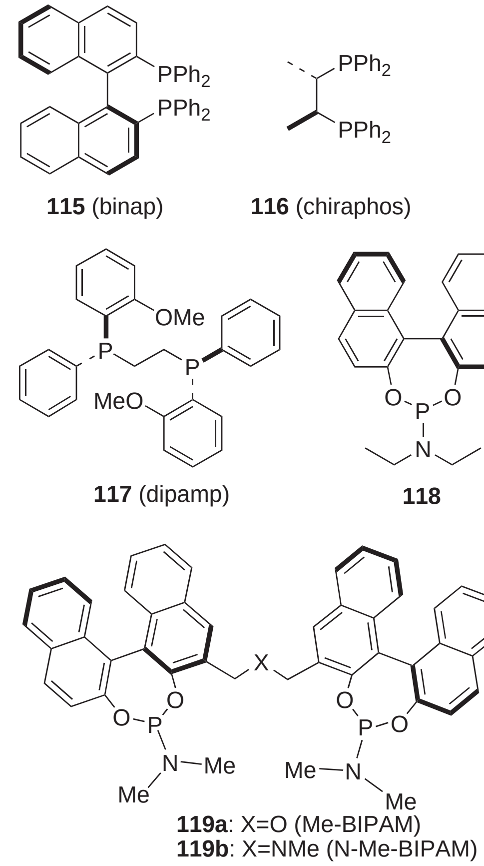
3.4 Conjugate Additions to α,β-Unsaturated Carbonyl Compounds. 1,4-Additions of electrophiles to α,β-unsaturated carbonyl compounds are a versatile methodology for forming carbon–carbon bonds. Since the reaction yields a stereogenic center at the β-carbon, considerable efforts have been devoted to the development of asymmetric syntheses via metal-catalyzed 1,4-addition of organometallic and nonmetallic compounds. In this field, we developed a new catalytic cycle starting from transmetalation to give an aryl- or 1-alkenylrhodium(I) or -palladium(II) intermediate for 1,4-addition of organoboronic acids to electron-deficient alkenes (eq 30).[9a,9b,84,98–106] 1,4-Additions of aryl- or 1-alkenylboron, -silicon, -tin, -titanium, -zinc, -zirconium, and -indium compounds to α,β-unsaturated carbonyl compounds and to other activated or unactivated C–C, C–O, and C–N double bonds or triple bonds are efficiently catalyzed by rhodium(I) complexes.[9c–9h] The corresponding reactions using palladium catalysts are rare; however, we reported that arylboronic acids easily transmetalate to dicationic palladium(II) complexes such as $[Pd(dppe)(PhCN)_2]^{2+}$, in which 1,4-addition of $ArB(OH)_2$, $[ArBF_3]K$, $ArSiF_3$, and Ar_3Bi to enones smoothly took place in an aqueous solvents.[75,107–116]



(30)

The rhodium(I)–binap **115** catalyst was first introduced for enantioselective 1,4-addition of aryl- and 1-alkenylboronic acids to cyclic and acyclic enones (Scheme 17).[9b] Other ligands effective for rhodium(I) catalysts are bisphosphine ligands of chiraphos (**116**)[117] and diphosphonites,[118] P–N ligands of amidomonophosphines,[119] bis(alkene) ligands based on a norbornadiene skeleton,[120] monophosphine ligands of phosphoramidites **118**,[103,121] and bidentate phosphoramidite (**119a**, Me-BIPAM)[104,106] synthesized from linked-(*R*)-BINOL. For the corresponding palladium-catalyzed reactions of organoboron, -silicon, and -bismuth compounds, bisphosphines bridged by two carbons, such as chiraphos (**116**) and dipamp (**117**), result in high yields and high enantioselectivities.[75,107–116]

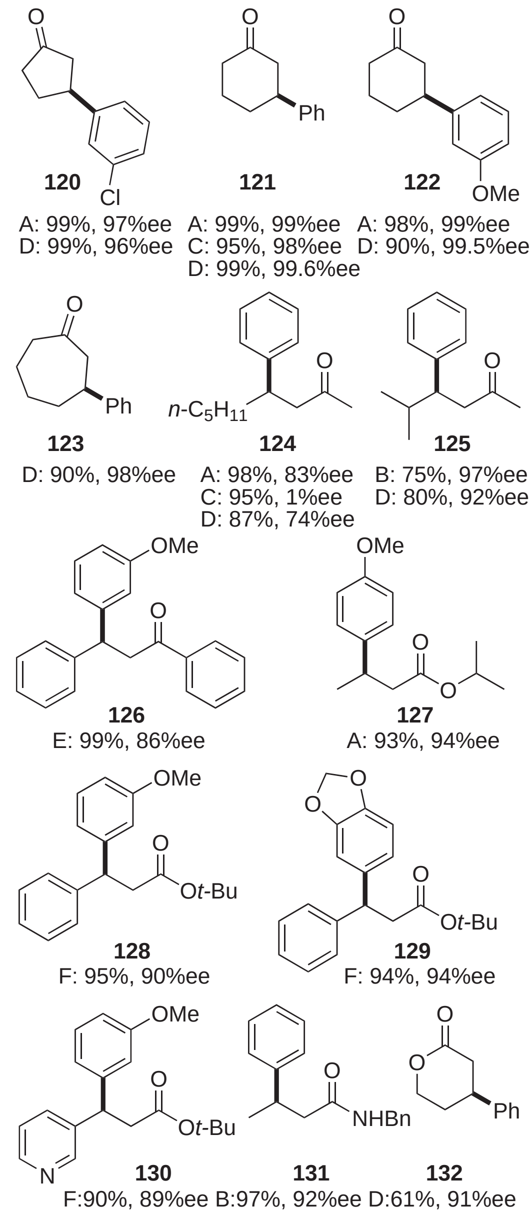
Performance of these chiral ligands for enantioselectivities is shown in Scheme 18. The binap ligand **115** achieves high enantioselectivities for both cyclic and acyclic substrates. For example, it gives enantioselectivities of up to 99% ee for cyclic enones (e.g., **120–122**), 83–97% ee for acyclic enones (e.g., **124** and **125**), 94% ee for acyclic esters **127**, and 92% ee for amides **131** (Methods A and B).[84] Monodentate (Method C)[103] and bidentate phosphoramidite (Method D)[104,106] also achieve high selectivities under analogous conditions. The traditional chiraphos ligand **116** is better than binap for introducing two different aryl-fragments at the β-carbon via addition of aryl metal reagents to β-aryl unsaturated carbonyl compounds. The catalyst in situ prepared from $[Rh(nbd)_2]BF_4$ and chiraphos achieves enantioselectivities in the range of 83–89% for β-aryl ketone derivatives **126** (Method E)[105] and in the range of 78–94% for *t*-butyl β-arylacrylate derivatives (e.g., **128–130**) (Method F).[105]



Scheme 17.

Results of palladium-catalyzed asymmetric 1,4-additions are shown in Scheme 19. Since the catalyst efficiency is specific for bisphosphines bridged by two carbon atoms, dipamp (**117**) and chiraphos (**116**) are ligands that meet this requirement. Enantioselectivities giving β-aryl ketones up to 99% are achieved when using chiraphos for 2-cyclopentenone **133** and acyclic (*E*)-enones **124–134**, whereas dipamp results in the best selectivities for 2-cyclohexenone **121** and 2-cycloheptenone **123** (89–96% ee). Addition of boronic acids require the presence of a silver co-catalyst (Method A)[112] whereas $[ArBF_3]K$ smoothly add to enones without any such an additive (Method B).[110,111] The palladium–chiraphos complex catalyzes the addition of $PhSiF_3$ at 0 °C in the presence of ZnF_2 (0.5 equiv) (Method C).[111] The corresponding reaction of Ar_3Bi suffers from decomposition of the catalyst, resulting in the formation of a homo-coupling biaryl with precipitation of palladium black. Thus, the presence of a reoxidant such as $Cu(BF_4)_2$ is critical to recycle the precipitated palladium(0) species (Method D).[109]

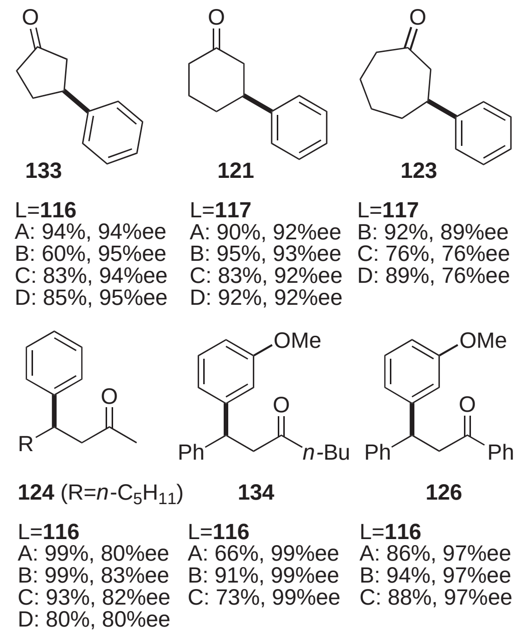
High performance of a chiraphos ligand for β-arylenones is demonstrated in the enantioselective synthesis of carbonyl compounds possessing two aryl groups at the β-carbon. 1,4-



All reactions were conducted in dioxane-H_2O.
A: [Rh(binap)(nbd)]BF_4, Et_3N, rt, 6 h.
B: [Rh(binap)(nbd)]BF_4, Et_3N, 50 °C, 16 h
C: Rh(acac)$(C_2H_4)_2$, **118**, KOH, 50 °C, 6 h.
D: $[Rh(nbd)_2]BF_4$, **119a**, Et_3N, rt, 1-16 h.
E: $[Rh(nbd)_2]BF_4$, **116**, K_2CO_3, 20 °C, 5 h.
F: $[Rh(nbd)_2]BF_4$, **116**, KOH, 50~60 °C, 6 h.

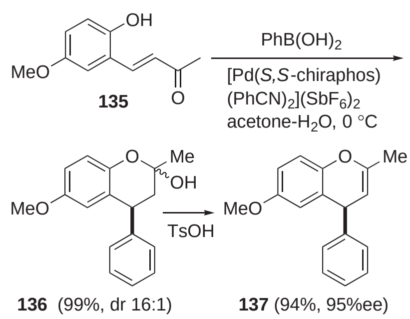
Scheme 18.

Addition of arylboronic acids to **135** affords a diastereomeric mixture of hemi acetals **136**, which give optically active chromens with 95% ee via acid-catalyzed dehydration (eq 31).[112] 1,4-Addition to unsaturated aldehydes is very slow due to the formation of hemi acetal in aqueous solution. The reaction with *trans*-β-arylenals proceeds smoothly in the presence of HBF_4 to afford optically active 3,3-diarylalkanals with high enantioselectivities in the range of 86–97% ee. The protocol provided a method for short-step synthesis of optically active (+)-(*R*)-CDP 840 (eq 32).[113]

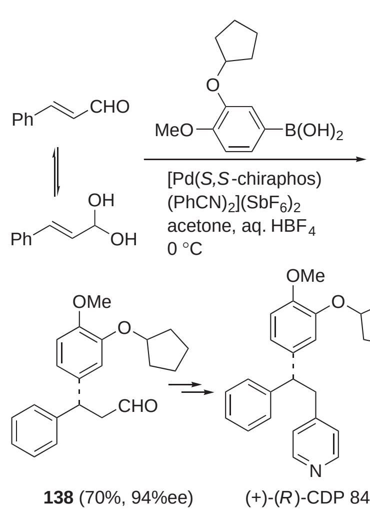


A: $ArB(OH)_2$, $[Pd(L)(PhCN)_2](SbF_6)_2$, $AgBF_4$, acetone-H_2O, 0 °C.
B: $[ArBF_3]K$, $[Pd(L)(PhCN)_2](SbF_6)_2$, MeOH-H_2O, -15~5 °C.
C: $ArSiF_3$, $[Pd(L)(PhCN)_2](SbF_6)_2$, ZnF_2, MeOH-H_2O, 0~5 °C.
D: Ar_3Bi, $[Pd(L)(PhCN)_2](SbF_6)_2$, $Cu(BF_4)_2$, MeOH-H_2O, -5~10 °C.

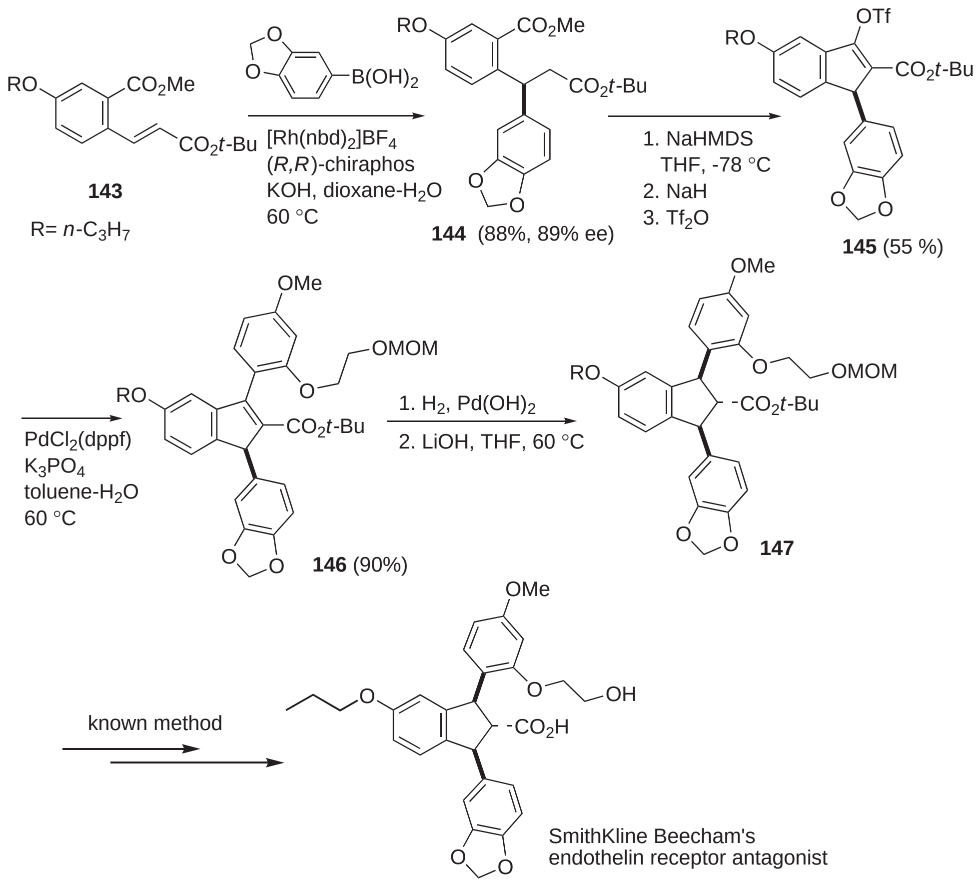
Scheme 19.



(31)

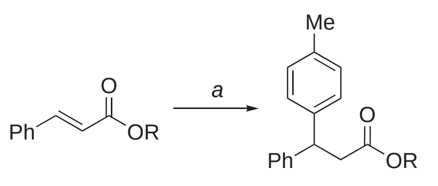


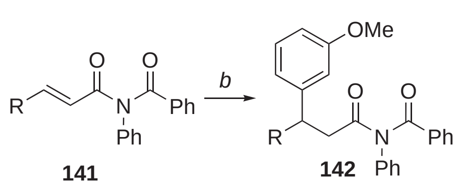
(32)



Scheme 20.

Although the palladium-catalyzed protocol has been limitedly used for unsaturated ketone and aldehyde derivatives, additions to aryl esters (**139**, R = Ph and 4-MeCOPh)[122] and *N*-acylamides (**141**)[115] exceptionally provide 1,4-addition products (eqs 33 and 34). The dicationic palladium–chiraphos catalyst is again recognized to be the best catalyst to afford optically active esters **140** with enantioselectivities of up to 97% ee and amides **142** of up to 98% ee.

 (33)

 (34)

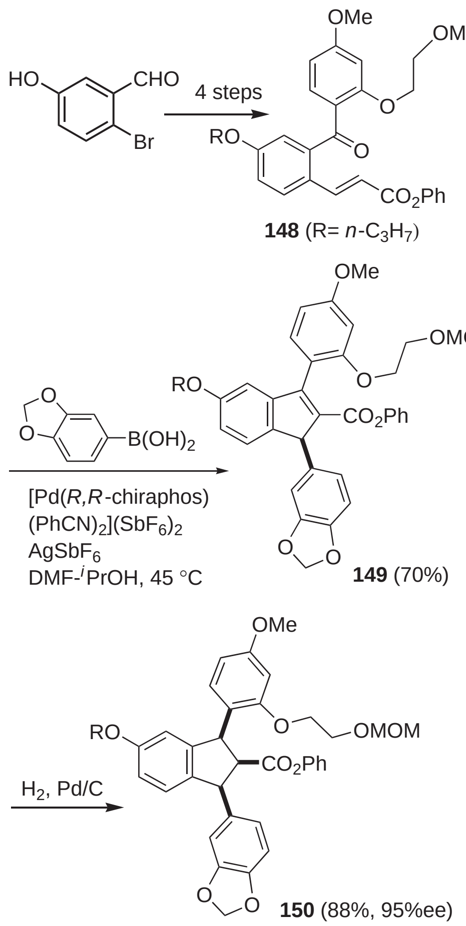
R= Ph (74%, 98%ee), CH_3 (96%, 92%ee)
n-C_3H_7 (77%, 90%ee)

a) 4-$MeC_6H_4B(OH)_2$, [Pd(*S,S*-chiraphos)$(PhCN)_2$]$(SbF_6)_2$, acetone-H_2O, 50 °C
b) 3-$MeOC_6H_4B(OH)_2$, [Pd(*S,S*-chiraphos)$(PhCN)_2$]$(SbF_6)_2$, DMF-H_2O, 50 °C

1,3-Diarylindane-2-carboxylic acids such as **147** are highly potent antagonists, selective for endothelin receptors among non-peptide antagonists reported by SmithKline Beecham[123] and Merck–Banyu.[124] The first catalytic synthesis was accomplished by 1,4-addition catalyzed by a rhodium–chiraphos complex (Scheme 20).[105] The strategy has a structural flexibility for both top and bottom aryl groups for parallel synthesis of drug candidates.

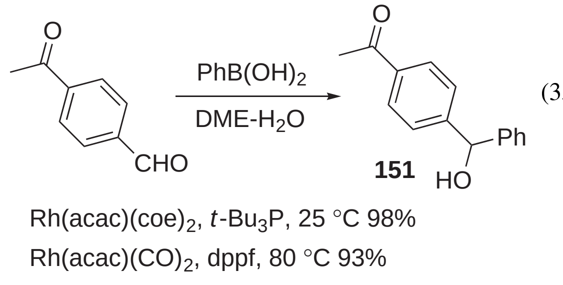
One-step enantioselective synthesis of optically active 1-aryl-1*H*-indenes **149** is achieved by tandem 1,4-addition and aldol condensation using a palladium(II)–chiraphos catalyst in acidic media (Scheme 21).[114,122] The desired **149** are provided in 60–99% yields and with 90–97% ee in the presence of HBF_4. The protocol provides a simple, short-step access to an indene intermediate **146** employed for the total synthesis of an endothelin receptor antagonist **147** shown in Scheme 20.

3.5 Nucleophilic Additions to C=O and C=N. Less attention has been paid to Grignard-type reactions of nonmetal element compounds, but metal-catalyzed reactions of B and Si compounds are of interest due to their compatibility with a wide range of functional groups and their potential applications to asymmetric synthesis. In this field, the rhodium(I)-catalyzed addition of arylstannanes to ketones and aldehydes was first reported by Oi, Inoue, and co-worker in 1997.[125] This discovery was followed by reports of analogous reactions of B, Si, and Bi compounds with aldehydes,[102,126–129] ketones, and aldimines.[130,131] The reaction of arylboronic acids

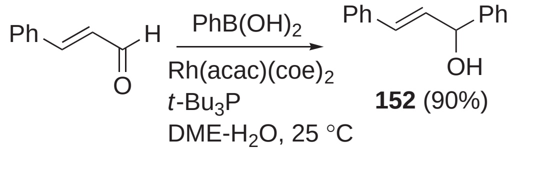


Scheme 21.

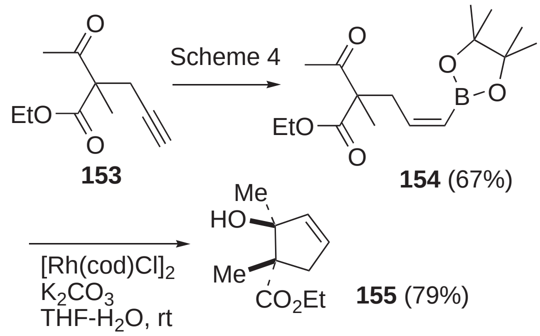
is catalyzed by rhodium(I)–bisphosphine complexes having a large P–Rh–P angle such as dppf,[126] but bulky and donating monophosphines such as i-Pr_3P and t-Bu_3P remarkably accelerate the reaction when one equivalent of phosphine to a rhodium metal complex is used (eqs 35 and 36).[102,127] The reaction is used for a catalytic ring closure via the intramolecular addition of **156** to a ω-keto carbonyl group (eq 37).[102,128] The required key intermediates **155** are available by Z selective hydroboration of the corresponding terminal alkynes shown in Scheme 4.



(35)

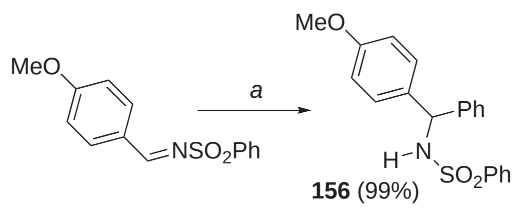


(36)

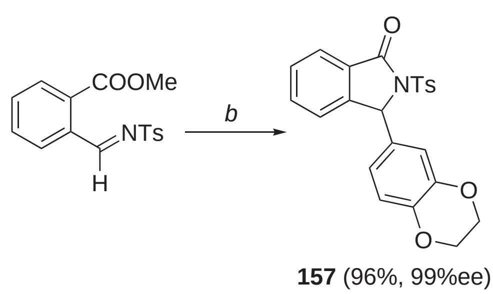


(37)

The addition of arylboronic acids to N-phenylsulfonyl aldimines, $RCH{=}NSO_2Ph$ (R = alkyl, aryl, and 1-alkenyl), takes place at 95 °C in the presence of a rhodium catalyst (eq 38).[130–132] $[Rh(cod)(MeCN)_2]BF_4$ (3 mol %) is recognized to be the best catalyst for aryl aldimines and $Rh(acac)(coe)_2/$ i-Pr_3P for alkyl and 1-alkenyl aldimines. Analogous reactions of arylboronic esters, such as 1,2-ethanediol and 1,3-propanediol esters, are slower than those of arylboronic acids, but they smoothly occur in the presence of two equivalents of Et_3N. For enantioselective addition, the bidentate phosphoramidite (**119b**, N–Me–BIPAM) results in high enantioselectivities of up to 99% ee (eq 39).[133]



(38)



(39)

a) $PhB(OH)_2$, $[Rh(cod)(MeCN)_2]BF_4$, dioxane, 95 °C
b) 1) $ArB(OH)_2$, $Rh(acac)(=)_2/(R)$-N-Me-BIPAM (**119b**), DME, 50°C, 2) K_2CO_3

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