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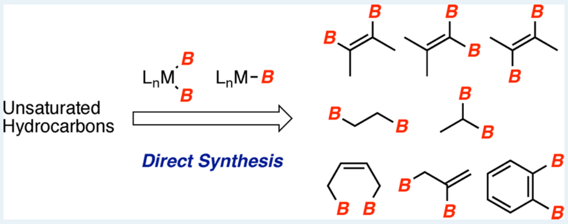
Catalytic, Direct Synthesis of Bis(boronate) Compounds

Jun Takaya and Nobuharu Iwasawa*

Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

ABSTRACT: Bis(boronate) compounds have been attracting much attention as versatile building blocks for concise synthesis of complex molecules because these compounds enable multiple C−C bond formations and functionalizations at the C−B bonds. Transition metal-catalyzed diboration reactions of unsaturated hydrocarbons with diborons have been utilized as a straightforward and highly useful method for the synthesis of bis(boronate) compounds. This perspective article will summarize recent development in substrate generality, asymmetric synthesis, and discovery of new metal catalysts in the diboration chemistry. Moreover, another approach to bis(boronate) compounds via sequential monoborylation reaction will also be described, expanding diversity of the direct synthesis of bis(boronate) compounds.



KEYWORDS: *bis(boronate) compound, diboration, hydroboration, borylation, metal catalyst*

1. INTRODUCTION

Organoboronates are recognized as versatile building blocks in organic synthesis since these compounds are usually storable and easy to handle and enable further transformations based on the unique reactivity of the C−B bond.[1] Among them, bis(boronate) compounds, which possess two boronate moieties in a single molecule, are expected to be a highly useful synthetic module for concise synthesis of complex molecules through multiple C−C bond formation, functionalization reactions of the C−B bonds, or both.

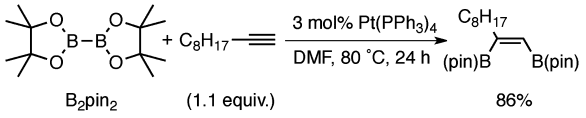
Many methods for the preparation of these classes of compounds have been reported.[2,3] Borylation of premonoborylated compounds is a simple way to obtain bis(boronate) compounds. For example, Pd-catalyzed Miyaura-borylation of 2-bromoethenylboronic ester with diboron afforded a diborylalkene, which was utilized in a concise total synthesis of natural products.[4] Moreover, several one-step preparative methods of bis(boronate) compounds have been developed on the basis of the reactions of multiborylmethanes or *gem*-diboration reactions of lithium carbenoids with diboron.[5,6] However, these methods necessitate multistep procedures or the use of specific reagents as a B-source or substrate. Thus, there has been a growing interest in developing a direct, catalytic method for the preparation of bis(boronate) compounds starting from simple, easily available substrates and boron sources to expand the utility of bis(boronate) compounds.

The transition metal-promoted borylation reaction is a powerful tool for facile synthesis of various types of organoboronate compounds since the key intermediate, borylmetal complex, can be generated in various ways and react with various organic substrates.[7−9] This review article will describe recent development of transition metal-catalyzed direct synthesis of bis(boronate) compounds from unsaturated hydrocarbons and diborons (or boranes) as a boron source. The reactions are divided into two major categories of reactions: One is the diboration reaction in which two boronate groups of diboron add to unsaturated hydrocarbons concurrently in a single *catalytic cycle* (sections 2−4). The other is a sequential monoborylation reaction in which monoborylation reactions (such as hydroboration and dehydrogenative borylation) proceed sequentially to afford bis(boronate) compounds in a single *reaction* (section 5). The diboration reactions will be further classified by the kind of metal catalysts (section 2 and 3) and substrates (section 4).

2. PT-CATALYZED DIBORATION REACTIONS OF CARBON−CARBON MULTIPLE BONDS

The addition reactions of the B−B bond of diborons to carbon−carbon (or carbon−heteroatom) multiple bonds catalyzed by platinum catalysts have been studied most extensively since the discovery of the Pt-catalyzed diboration reaction of alkynes with bis(pinacolato)diboron (B_2pin_2) by Suzuki, Miyaura, and co-workers in 1993 (Scheme 1).[10] Various substrates, such as alkynes, dienes, allenes, and alkenes, have been reported to be applicable to the reaction for the synthesis of a variety of synthetically useful bis(boronate) compounds (Figure 1).[11−14] The general catalytic cycle is depicted in Scheme 2. The reaction is proposed to proceed via (a) oxidative addition of the B−B bonds to Pt(0), (b) insertion of

Scheme 1. Pt-Catalyzed Diboration of Alkynes



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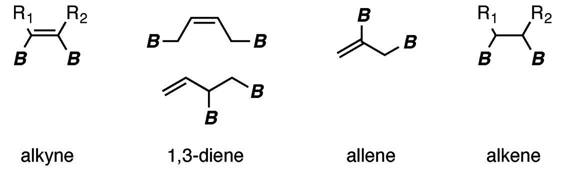
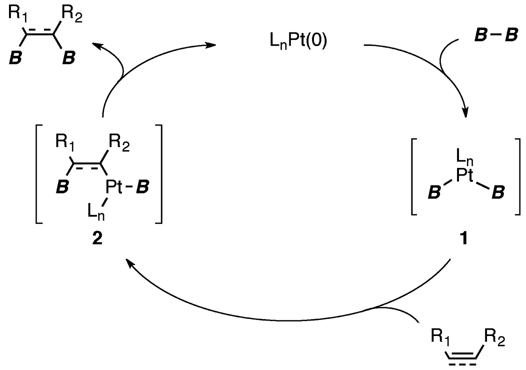


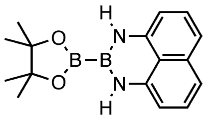
Figure 1. Bis(boronate) compounds Accessible by Pt-Catalyzed Diboration Reaction.

Scheme 2. General Catalytic Cycle of Pt-Catalyzed Diboration Reaction



C–C multiple bonds into the Pt–B bonds, and (c) reductive elimination of the C–B bonds with regeneration of the catalytically active Pt(0). Both boron atoms of the diborons add to the same unsaturated hydrocarbons in the sequence. The reactions usually proceed under neutral conditions without any additives for activation of substrates and, thus, are a highly atom-economical process. The characteristic syn-stereospecific addition of B–B bonds enables stereoselective synthesis of bis(boronate) compounds, such as *cis*-1,2-diborylalkenes. Because there has been growing interest in the stereoselective organic synthesis via transformation of boronic esters, the Pt-catalyzed diboration reaction has been attracting much attention as a versatile method for introducing two boryl groups in a stereoselective manner. In this section, we deal with mainly recent progress in substrate scope and asymmetric synthesis based on this Pt-catalyzed diboration reaction.

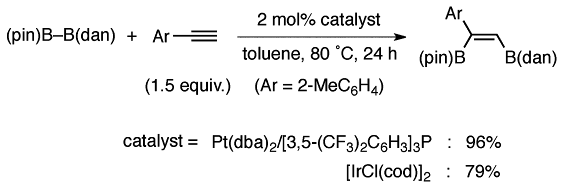
2.1. Substrate Scope. Most Pt-catalyzed diboration reactions have employed symmetrical diborons, such as bis(pinacolato)diboron and bis(catecholato)diboron (B_2cat_2). Recently, Suginome and co-workers reported Pt-catalyzed diboration reaction of alkynes with an unsymmetrical diboron, (pin)B–B(dan) (pin = pinacolato, dan = naphthalene-1,8-diaminato, Figure 2).[15] The reaction proceeded with various terminal alkynes regioselectively in the presence of a platinum catalyst ($Pt(dba)_2/[3,5\text{-}(CF_3)_2C_6H_3]_3P$) or an iridium catalyst ($[IrCl(cod)]_2$ without phosphine ligand), giving 1,2-diborylalkenes in good yield (Scheme 3). It should be noted that Ir has rarely been utilized as a catalyst in a diboration reaction (vide infra). Notably, the diboration products possessed the B(dan) at the terminal position and realized the internal-selective Suzuki–Miyaura coupling as a result of the lower reactivity of the alkenyl B(dan) (Scheme 4). This is in sharp contrast to the diboration with B_2pin_2, in which the resulting 1,2-diborylalkenes selectively undergo coupling reaction at the terminal B(pin) moiety. This type of diboration using unsymmetrical diborons is highly useful for stereoselective synthesis of π-conjugated materials and polyene natural products.[16,17]



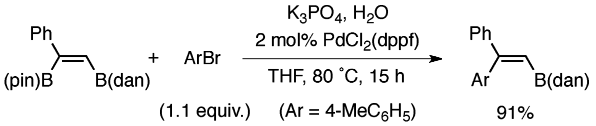
(pin)B–B(dan)

Figure 2. Differentially protected diboron, (pin)B–B(dan).

Scheme 3. Diboration of Alkynes Using (pin)B–B(dan)

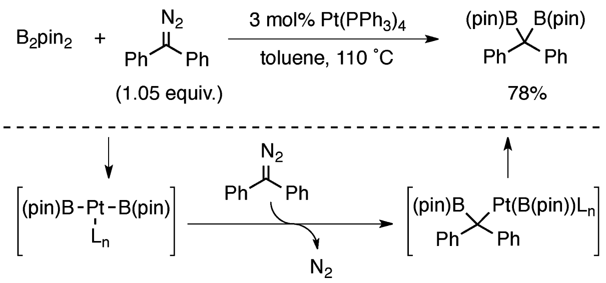


Scheme 4. Internal-Selective Suzuki–Miyaura Coupling



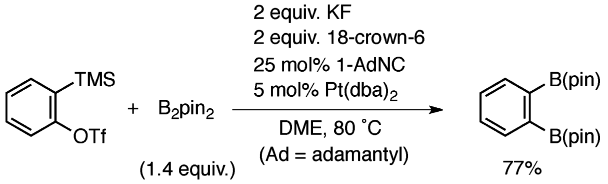
Not only carbon–carbon multiple bonds but also carbenes undergo diboration by using diazoalkanes as a substrate in the Pt-catalyzed reaction. Srebnik et al. reported that $Pt(PPh_3)_4$ efficiently catalyzed a diboration reaction of several diazoalkanes with B_2pin_2 in toluene at 110 °C to afford 1,1-diborylalkanes in good yield (Scheme 5).[18,19] 1,1-Diborylalkanes are unique, highly valuable synthetic building blocks that enable multiple C–C bond formations via Suzuki–Miyaura coupling,[20,21] and therefore, development of an efficient synthetic method for such compounds is useful. Generation of carbenes from diazoalkanes and insertion of the carbenes to the B–Pt bond of the bis(boryl)platinum(II) complex followed by reductive elimination was proposed as a reaction mechanism.

Scheme 5. Diboration of Diazoalkanes



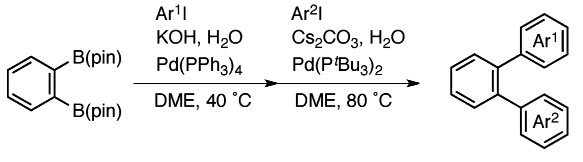
Arynes are highly reactive aromatic intermediates that could be considered as strained alkynes. Yoshida reported the Pt-catalyzed diboration of the C–C triple bond of arynes, which were generated in situ from 2-(trimethylsilyl)phenyltriflate derivatives, KF, and 18-crown-6 (Scheme 6).[22] The reaction proceeded at 80 °C in DME in the presence of a platinum isocyanide complex as catalyst to afford various 1,2-diborylarenes in good yield, although the reaction mechanism has not been clarified. Selective syntheses of unsymmetrical *ortho*-

Scheme 6. Diboration of Arynes



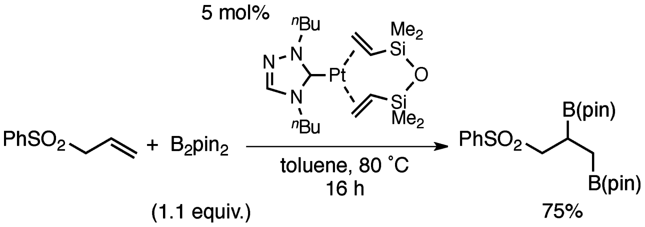
terphenyls via the stepwise Suzuki–Miyaura coupling utilizing these products were successively demonstrated (Scheme 7).

Scheme 7. Synthesis of *ortho*-Terphenyls



1,2-Diboration of aryl allylic sulfones was achieved by utilizing a platinum complex bearing an NHC ligand (N-heterocyclic carbene) (Scheme 8).[23] The reaction proceeded smoothly without any formation of undesired byproducts caused by alkene isomerization, providing a useful method for the synthesis of 1,2-dihydroxysulfones. Interestingly, commonly employed catalysts in diboration reaction, such as $[RhCl(PPh_3)_3]$, $[Rh(cod)(PPh_3)_3]BF_4$, or $Pt(PPh_3)_4$, did not promote the reaction.

Scheme 8. Diboration of Aryl Allylic Sulfones Catalyzed by NHC–Pt Complex

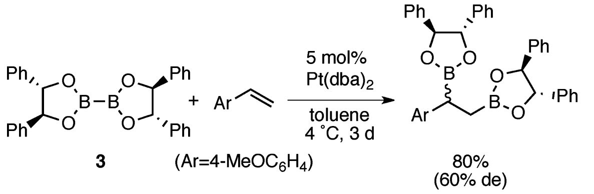


2.2. Asymmetric Reaction.

Asymmetric addition of B–B bonds to carbon–carbon double bonds affords chiral bis(boronate) compounds, which are utilized as highly useful synthetic building blocks in organic synthesis.[24] For example, oxidation of the C–B bonds of diborylalkanes proceeds with retention of the stereochemistry to give chiral 1,2-diols, providing an alternative method to osmium-catalyzed enantioselective 1,2-dihydroxylation of alkenes. Moreover, stereoselective construction of chiral carbon–carbon bonds is possible through various types of C–C bond formations, such as allylboration of aldehydes, homologation reaction with chloromethyllithium, and Pd-catalyzed Suzuki–Miyaura coupling, leading to synthetically valuable chiral organic molecules.

Asymmetric diboration was first reported by Marder and Norman in 1998 (Scheme 9).[25] The reaction was a diastereoselective diboration of alkenes using chiral diborons derived from chiral diols and $B_2(NMe_2)_4$ as a B source catalyzed by phosphine-free platinum $[Pt(dba)_2]$. Among several chiral diborons investigated, diboron **3** derived from (*R*,*R*)-1,2-diphenylethane-1,2-diol was found to give the best result. However, the diastereoselectivity was not satisfactory (up to 60% de), even when the reaction was carried out at low temperature for a long time. Although the reaction was expanded to 1,4-diboration of 1,3-dienes, the reaction required the use of a bisphosphine-platinum complex, $(PPh_3)_2Pt(C_2H_4)$, as a catalyst, which necessitates heating conditions to liberate a phosphine ligand, resulting in poor asymmetric induction.[26]

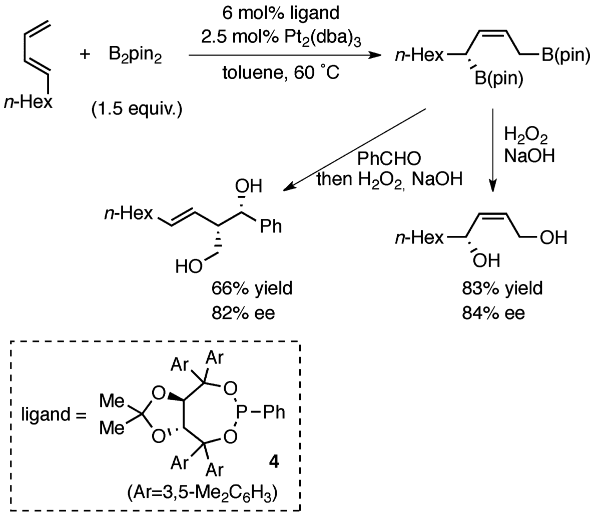
Scheme 9. Initial Attempts toward Asymmetric Diboration



Chiral catalyst-based enantioselective diborations would be an ideal method for asymmetric synthesis of bis(boronate) compounds; however, mechanistic studies on the phosphine-platinum complex-catalyzed diboration of alkynes suggested that insertion of alkynes proceeds via dissociation of a phosphine ligand from $(PR_3)_2(B(OR')_2)_2Pt(II)$, followed by coordination of the alkynes to the monophosphine-platinum complex.[27−29] Thus, development of an efficient platinum catalyst bearing a chiral *monodentate* ligand is required for the enantioselective diboration reaction.

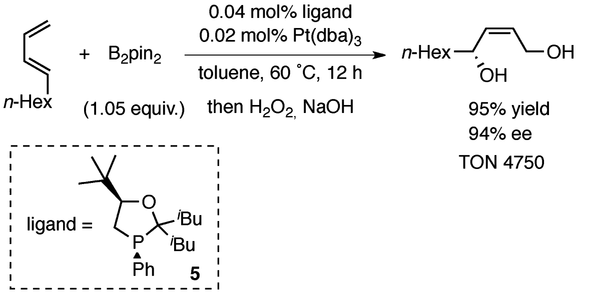
Enantioselective diboration using a chiral platinum catalyst was first reported by Morken in 2009.[30] The combination of $Pt_2(dba)_3$ and a monodentate, TADDOL-based phosphonite ligand **4** was effective for the enantioselective 1,4-diboration of 1,3-dienes with B_2pin_2 (Scheme 10). The reaction of several 1-substituted-*trans*-1,3-dienes and some cyclohexadiene derivatives successfully afforded *cis*-2-buten-1,4-diol derivatives in good enantiomeric excess (ee) after oxidation of the C–B bonds. The *α*-chiral allylic bis(boronate) was utilized in the stereoselective allylboration of aldehydes. The author also reported that cyclohexadiene derivatives bearing various substituents at the 3-position were employable for the reaction by modifying the TADDOL-based ligand structure.[31]

Scheme 10. Enantioselective 1,4-Diboration of 1,3-Dienes



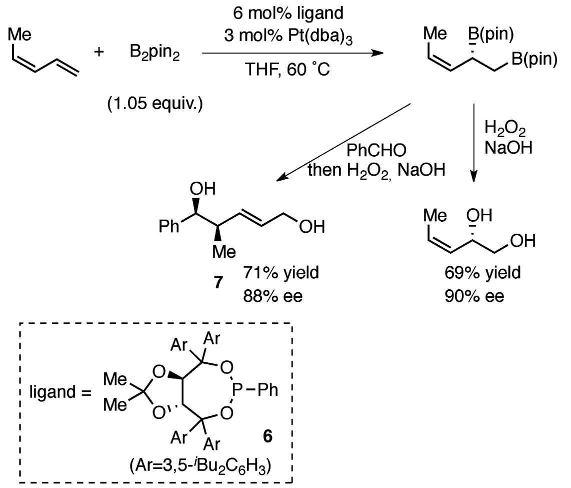
Recently, a modular oxaphospholane was developed as a chiral monodentate ligand and was applied to the Pt-catalyzed enantioselective diboration of 1,3-dienes on the basis of the expectation that the reaction would benefit from the presence of a more electron-rich ligand than the phosphonite described above.[32] In fact, the use of *cis*-*i*Bu-OxaPhos **5** greatly enhanced the catalytic activity and expanded the generality of substrate in the 1,4-diboration of 1,3-dienes (Scheme 11). The turnover number (TON) reached 4750 with high ee, and a variety of acyclic dienes having various substituents were diborated efficiently.

Scheme 11. Enantioselective 1,4-Diboration of 1,3-Dienes using a Chiral Oxaphospholane Ligand



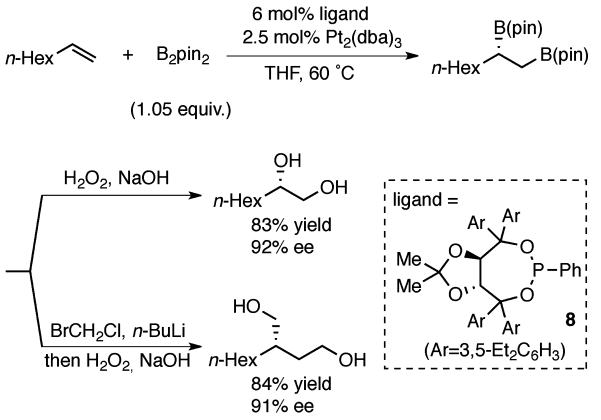
The regioselectivity of the diboration reaction of 1,3-dienes is highly dependent on the substitution pattern of the dienes. Thus, Morken et al. found that enantioselective 1,2-diboration proceeded selectively by using *cis*-1,3-dienes or 1,1-disubstituted-1,3-dienes as substrate under mostly the same reaction conditions as shown in Scheme 10 (Scheme 12).[33] It should be noted that allylboration of 1,2-diborylated products with aldehydes followed by oxidative workup afforded *syn*-homoallylic alcohols **7** bearing a terminal hydroxyl group stereoselectively. These products are highly valuable building blocks for polyketide synthesis, and the reaction is a good alternative to *syn*- and enantioselective vinylogous aldol reactions.

Scheme 12. Enantioselective 1,2-Diboration of 1,3-Dienes



Morken also showed that the reaction was applicable to the enantioselective diboration of terminal alkenes.[34] Various 1,2-diols were obtained in high enantioselectivity after oxidation by using a TADDOL-based phosphonite ligand **8** (Scheme 13). Single-flask transformation of the product was achieved by treatment of the reaction mixture with 2 equiv of $ClCH_2Li$ at −78 °C to give a homologation product, which was converted to 1,4-diol in good yield with high enantiomeric purity after oxidative workup.

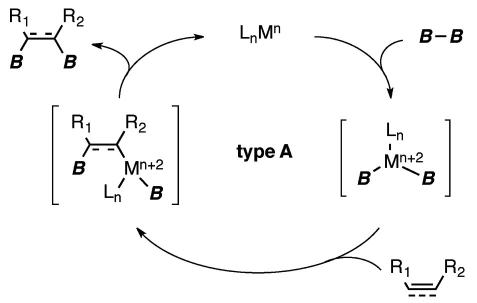
Scheme 13. Enantioselective Diboration of Alkenes



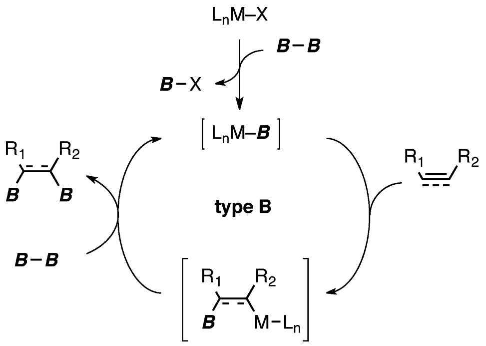
3. DIBORATION OF CARBON–CARBON MULTIPLE BONDS CATALYZED BY OTHER METAL COMPLEXES

Since the first discovery of the Pt-catalyzed diboration, several other transition metal catalysts have been reported to be active for various types of diboration reactions. These reactions can be divided into mainly two categories by the reaction mechanism. One is the reaction, which consists of redox of the metal center via oxidative addition of the B–B bonds and reductive elimination of the C–B bonds, as in the Pt-catalyzed reaction (type A, Scheme 14). The other is the reaction in which borylmetal species are generated by transmetalation or a σ-bond metathesis reaction between the M–X or M–C bonds and the B–B bonds, as often proposed in Cu-catalyzed reactions (type B, Scheme 15). In this case, the valency of the

Scheme 14. Catalytic Cycle via Oxidative Addition of the B–B Bond (type A)



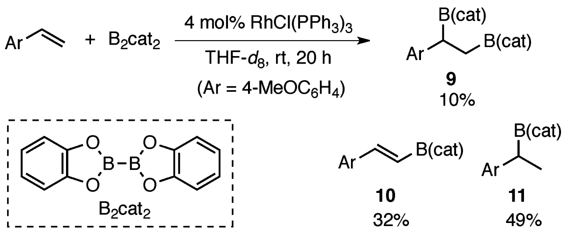
Scheme 15. Catalytic Cycle via Transmetallation (σ-Bond Metathesis) of the B–B Bond (type B)



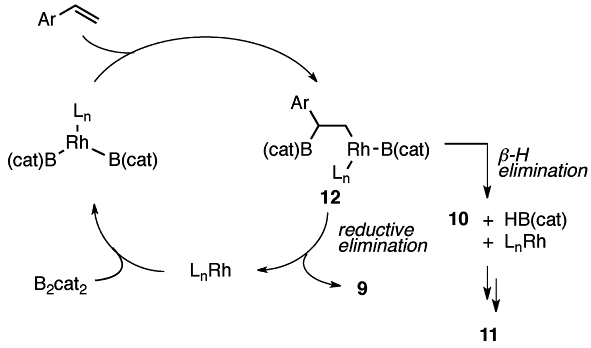
metal is fixed during the catalytic cycle, and the two boron atoms in the diboron are not introduced to the same molecule. A diboration reaction proceeding via the latter mechanism has been reported lately, giving new approaches to bis(boronate) compounds, which are difficult to synthesize by Pt-catalyzed diborations. In this section, recent development of diboration reactions of carbon−carbon multiple bonds catalyzed by transition metals other than platinum will be described. The section is further categorized by the kind of metals in groups 9−11 and nonmetal catalyzed systems.

3.1. Group 9. *3.1.1. Rhodium.* In 1995, two years after the discovery of Pt-catalyzed diboration of alkynes, Baker, Marder, and Westcott reported the first example of Rh-catalyzed diboration of 4-vinylanisole with B_2cat_2 (Scheme 16).[35] The yield of diboration product **9** was moderate because of the inevitable formation of considerable amounts of alkenylboronate **10** and monoborylalkane **11**, which were produced via dehydrogenative borylation and hydroboration, respectively. As in the case of Pt catalysts, the reaction was proposed to proceed via generation of a bisborylrhodium complex, which underwent alkene insertion to give a borylethyl(boryl)rhodium complex (B−C−C−Rh−B) **12**, followed by reductive elimination of the B−C bond. At the stage of reductive elimination from the intermediate **12**, *β*-hydride elimination competed to afford alkenylboronate **10** and HBcat, which was further consumed by Rh-catalyzed hydroboration to give monoborylalkane **11** (Scheme 17). It was demonstrated that B_2cat_2 was more reactive than B_2pin_2 in the oxidative addition to $RhCl(PPh_3)_n$ complex.[36] Further investigation clarified that the use of the zwitterionic η^6-(arene)rhodium complex [(dppm)Rh(η^6-catBcat)], **13**, was effective to suppress these side reactions, and the reaction was applicable to several alkenes, including internal ones (Figure 3).[37]

Scheme 16. Early Report of Rh-Catalyzed Diboration of Alkenes



Scheme 17. Proposed Reaction Mechanism



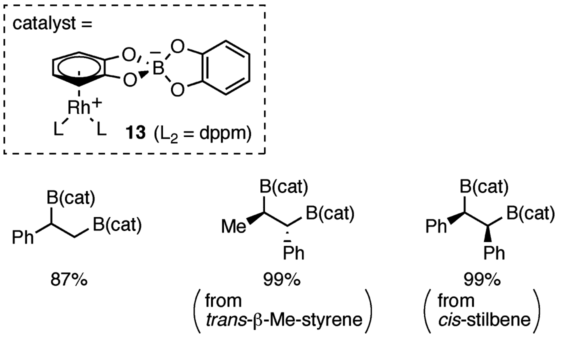
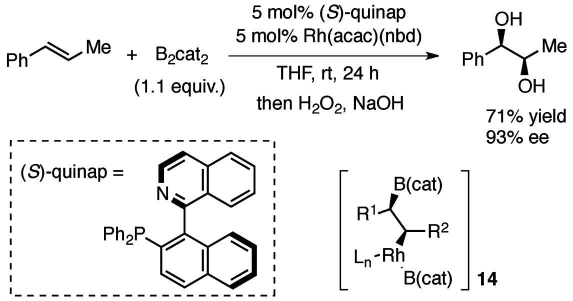


Figure 3. [(dppm)Rh(η^6-catBcat)] **13**-Catalyzed Diboration of Alkenes.

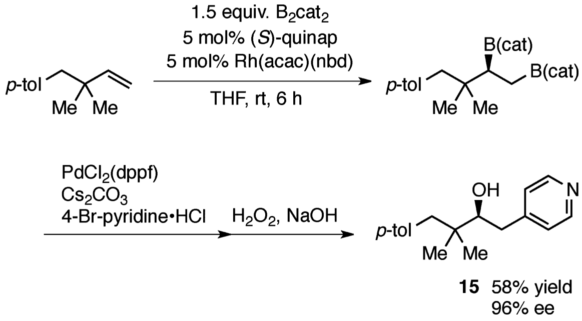
In 2003, Morken and co-workers developed the first example of a chiral bisphosphine-rhodium complex-catalyzed enantioselective diboration of alkenes.[38−41] The combination of (*S*)-quinap/(nbd)Rh(acac) was found to be the best for enantioselective diboration of various internal alkenes, giving corresponding 1,2-diols in good yield with moderate to high ee after oxidative workup (Scheme 18). The reaction of internal aliphatic alkenes and styrene derivatives generally proceeded with high ee. Terminal alkenes resulted in low ee, although those bearing a quarternary carbon center near the alkene moiety improved enantioselectivity. Mechanistic studies suggested that the catalyst suppressed *β*-hydride elimination from the intermediate **14** more efficiently compared with binap-Rh catalyst. It was also demonstrated that selective Suzuki−Miyaura coupling of the diboration product at the less hindered boryl moiety followed by oxidative workup afforded a chiral secondary alcohol **15** as a carbohydroxylation product of alkene without lowering enantiomeric excess (Scheme 19).

Scheme 18. Rh-Catalyzed Enantioselective Diboration of Alkenes



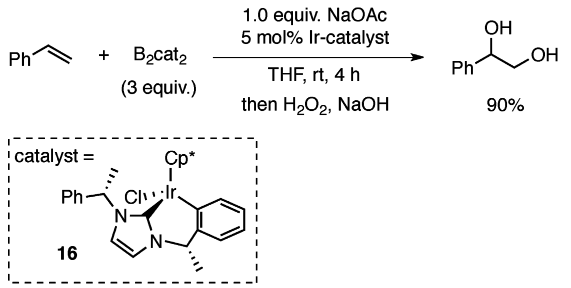
3.1.2. Iridium. Ir-catalyzed diboration of alkenes was first reported by Fernandez and Peris in 2007.[42] The reaction

Scheme 19. Tandem Enantioselective Diboration/Suzuki Coupling/Oxidation

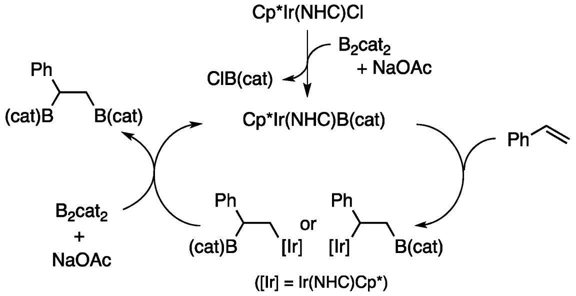


proceeded by treatment of alkenes, excess B_2cat_2, and a stoichiometric amount of NaOAc with a catalytic amount of Cp*Ir(NHC)Cl complex **16** to afford 1,2-diols in high yield after oxidative workup (Scheme 20). The author proposed that the type B mechanism is operative with Ir(III) complex and the added NaOAc promotes heterolytic cleavage of the B−B bond (Scheme 21). Suginome also reported the catalytic activity of $[IrCl(cod)]_2$ in the diboration of alkynes with (pin)B−B(dan), as already mentioned in Scheme 3, although its reaction mechanism was not described.[15]

Scheme 20. Ir-Catalyzed Diboration of Alkenes



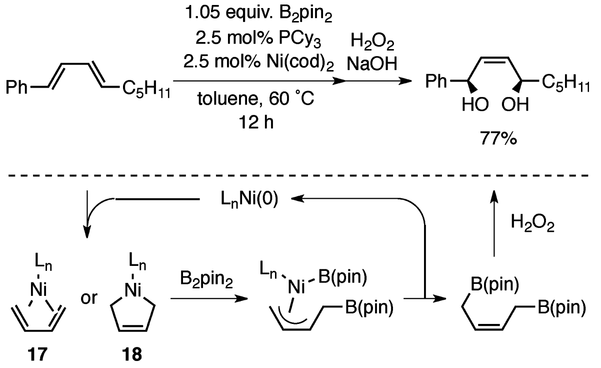
Scheme 21. Proposed Mechanism



3.2. Group 10.

3.2.1. Nickel. Recently, 1,4-diboration of 1,3-dienes with B_2pin_2 catalyzed by $Ni(cod)_2/PCy_3$ was reported by Morken and co-workers (Scheme 22).[43] The diboration occurred selectively at the 1,4-position of the diene moiety, and no formation of 1,2-diboration products was observed for various 1,3-dienes, including 1-, 1,2-, 1,3-, 1,1,3-, or 1,4-substituted derivatives. This perfect 1,4-regioselectivity is in sharp contrast to that observed in the Rh-catalyzed enantioselective diboration reaction, in which the regioselectivity is highly dependent on the substitution pattern of 1,3-dienes (Scheme 12).[33] Synthetically useful (*Z*)-2-alkene-1,4-diol derivatives were obtained in good yield after oxidation of the C−B bonds. Interestingly 1,3-dienes that can easily adopt an s-cis conformation are more reactive than those for which it is difficult to take the s-cis form due to steric repulsion (e.g., *trans*-1,3-pentadiene > *cis*-1,3-pentadiene). Moreover, no borylated products were obtained when styrene was employed as a substrate. The author suggested the reaction via type A mechanism involving the bis(boryl)Ni(II) complex may not be operative, and a new mechanism that involves initial association of Ni(0) with 1,3-diene to form the diene-Ni(0) complex **17** or nickelacyclopentene **18** and its subsequent reaction with B_2pin_2 was proposed.

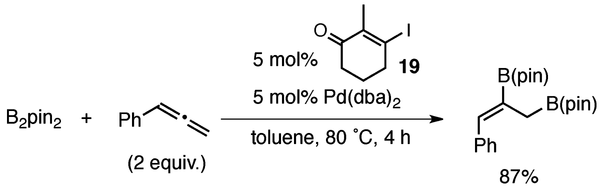
Scheme 22. Ni-Catalyzed 1,4-Diboration of 1,3-Dienes



3.2.2. Palladium. In contrast to widespread use of the platinum(0) catalysts, palladium(0) has not been utilized in diboration of alkynes and alkenes until recently. Early theoretical studies carried out independently by Morokuma and Sakaki suggested that oxidative addition of the B−B bond to palladium(0) is more endothermic than that to platinum(0) although the activation barrier for B−B bond scission itself is energetically possible.[44,45]

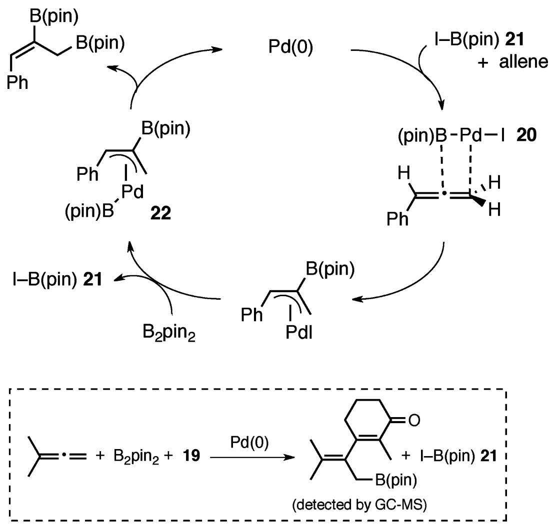
A palladium catalyst was first utilized in a diboration reaction of allenes with B_2pin_2 as reported by Cheng in 2001 (Scheme 23).[46] The reaction was applicable to various monosubstituted allenes, and two boronate groups were introduced at the less hindered terminal C−C double bond with high regio- and stereoselectivity. Some mechanistic investigations disclosed that addition of a catalytic amount of alkenyl iodide **19** was essential to initiate the reaction, and the two boronate moieties of the product come from different diboron molecules. The author proposed the reaction proceeded via boryl(iodo)palladium(II) complex **20**, which was generated by oxidative addition of boryl iodide **21** to Pd(0). The boryl iodide **21** was considered to be formed by three component coupling of allene, alkenyl iodide **19**, and B_2pin_2 because the coupling product was detected by GC/MS. Insertion of an allene into the Pd−B bond followed by transmetalation with diboron produced boryl iodide **21** and allyl(boryl)Pd(II) **22**, which underwent reductive elimination to give the diborated product and catalytically active Pd(0) (Scheme 24).

Scheme 23. Pd-Catalyzed 1,2-Diboration of Allenes

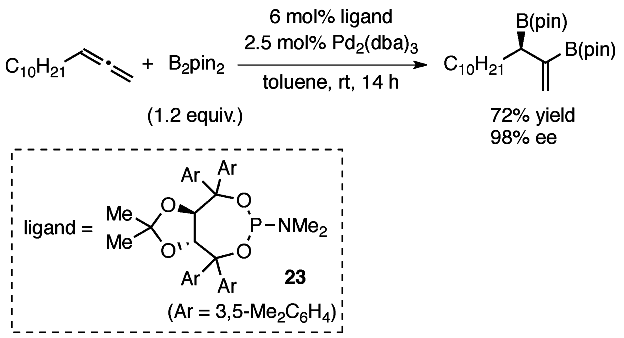


Morken reported Pd-catalyzed enantioselective diboration of allenes with diboron. Treatment of various monosubstituted allenes and B_2pin_2 with catalytic amounts of $Pd_2(dba)_3$ and TADDOL-based phosphoramidite ligand **23** afforded α-substituted-β-borylallylboronate esters in good yield with high enantiomeric excess (Scheme 25).[47] The borylation occurred selectively at the more hindered C−C double bond to give branched products, in contrast to Cheng's case, shown in Scheme 23. The reaction was accelerated when a more electron-rich phosphine ligand was employed, such as PCy_3 and $P(NMe_3)_3$. Experimental and theoretical studies revealed that this reaction proceeded via rate-determining oxidative addition of diboron to Pd(0) (type A mechanism).[48] Insertion

Scheme 24. Proposed Mechanism via Boryl(iodo)palladium(II) Complex

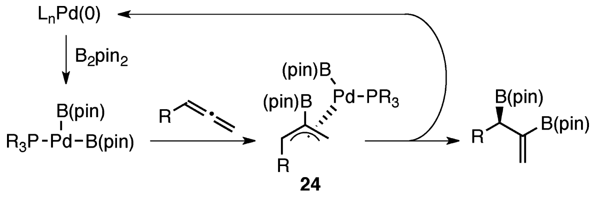


Scheme 25. Pd-Catalyzed Enantioselective 1,2-Diboration of Allenes



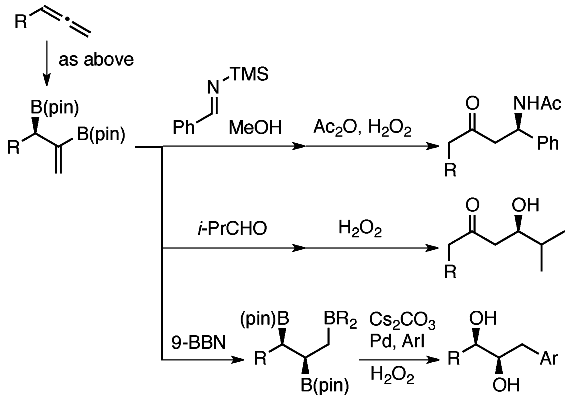
of allenes into the Pd−B bond occurred at the less hindered alkene moiety to provide η^3-allylpalladium(II) complexes **24**, which underwent C−B bond-forming reductive elimination immediately at the more hindered carbon center (Scheme 26).

Scheme 26. Proposed Mechanism via Oxidative Addition of Diboron to Pd(0)



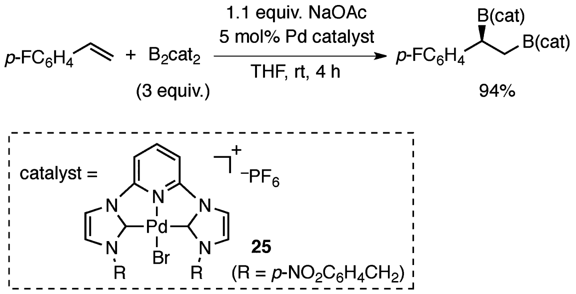
The author demonstrated that the chirality of the C−B bond was successfully transferred to that of the C−C bond via allylboration of imines or aldehydes, leading to synthetically valuable compounds such as β-amino- or hydroxyketones in a one-pot operation.[49,50] Moreover, hydroboration of the diboration products with 9-BBN proceeded stereoselectively to give triborylalkanes, which were converted to chiral 1,2-diols via site-selective Suzuki−Miyaura coupling, followed by oxidation of the remaining C−B bonds (Scheme 27).[51]

Scheme 27. Synthetic Application of Diboration Products



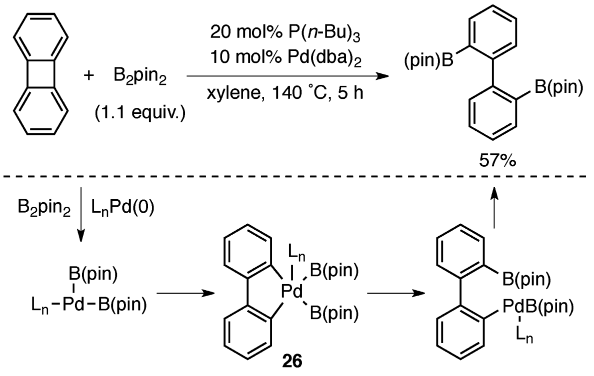
Recently, Bo and Fernandez et al. reported pincer-type NHC-palladium complex **25** catalyzed diboration of styrene derivatives in the presence of NaOAc (Scheme 28).[52] Theoretical calculation suggested that oxidative addition of the B−B bond is unfavorable because of the instability of the Pd(IV) intermediate, and a NaOAc-promoted transmetalation mechanism is proposed for the generation of the borylpalladium (type B).

Scheme 28. NHC-Pd(II)-Catalyzed Diboration of Alkenes



Recently, Pd-catalyzed diboration of the carbon−carbon σ-bond of biphenylene was reported by Matsuda and co-worker, demonstrating a new substrate scope in diboration chemistry.[53] Treatment of biphenylene and 1.1 equiv of B$_2$pin$_2$ with a catalytic amount of Pd(dba)$_2$/P(n-Bu)$_3$ in xylene at 140 °C afforded 2,2′-diborylbiphenyl in 57% yield (Scheme 29). The reaction is proposed to proceed via generation of a bisborylpalladium complex [B(pin)]$_2$Pd(II) by oxidative addition of diboron to Pd(0), which cleaves the strained C−C σ-bond to form a Pd(IV) intermediate, **26**. Successive reductive elimination of two C−B bonds afforded the product.

Scheme 29. Pd-Catalyzed Diboration of Strained σ-Bond

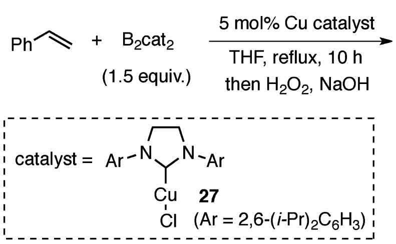


Further studies on the scope, generality, and mechanism of the reaction are desirable to establish this new possibility of the Pd catalyst in diboration reactions.

3.3. Group 11. *3.3.1. Copper.* Utilization of borylcopper complexes as a borylating reagent was first reported by Hosomi's and Miyaura's groups independently in 2000−2001, describing generation of borylcopper species from CuX and B_2pin_2 in the presence of base and its nucleophilic addition to *α,β*-enones.[54,55] Then, Sadighi succeeded in isolation and structural analysis of borylcopper complexes by utilizing a NHC ligand and investigated their stoichiometric reactions with C−C and C−O multiple bonds in detail,[56,57] leading to catalytic diboration reactions of CO_2 and aldehyde (see section 4). These studies formed the basis of recent development of Cu-catalyzed borylation reactions.

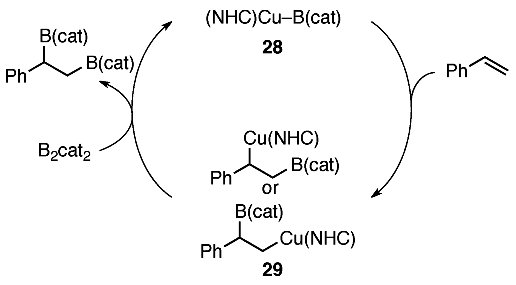
The first example of the Cu-catalyzed diboration reaction of C−C multiple bonds was reported by Pérez and Fernández in 2007.[58] Diboration of styrene with B_2cat_2 proceeded smoothly in the presence of a catalytic amount of (SIPr)CuCl complex **27** in refluxing THF to give a 1,2-diol after oxidation (Scheme 30). Monoborylation product was obtained as a byproduct in some cases. Diboration of alkynes also proceeded to give *cis*-diborylalkenes under the same reaction conditions, broadening the scope of this reaction. Experimental and theoretical studies indicated oxidative addition of the B−B bond to the Cu(I) catalyst is unlikely. The author proposed a type B mechanism is operative via formation of monoborylcopper(I) complex **28**. Insertion of styrene into the B−Cu bond of **28** forms alkylcopper(I) complex **29**, which reacted with diboron to produce the diboration product with regeneration of the borylcopper complex **28** (Scheme 31). DFT studies by Lin and Marder disclosed the mechanism of each elementary step and the differences in the reactivity of B_2cat_2 and B_2pin_2 in detail.[59,60]

Scheme 30. (NHC)Cu-Catalyzed Diboration of Alkenes

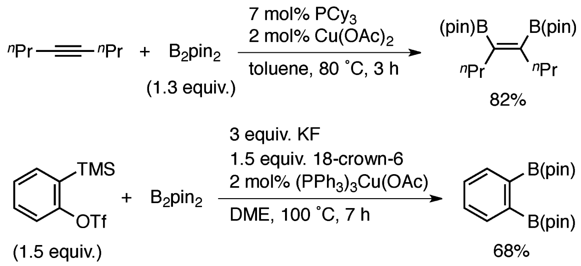


Recently, Yoshida et al. reported a general and practical diboration reaction of alkynes catalyzed by $Cu(OAc)_2/PCy_3$ using B_2pin_2 as a diboron (Scheme 32).[61] The reaction was applicable to various internal alkynes to afford *cis*-1,2-diborylalkenes stereoselectively. Arynes generated in situ from 2-(trimethylsilyl)phenyltriflate derivatives, KF, and 18-crown-6 were also diborated, giving *vic*-diborylbenzene derivatives in good yield. The type B mechanism via borylcopper(I) complex was proposed. Furthermore, unique multiboration was demonstrated when methyl propargyl ethers were employed as substrate, in which diboration of the alkyne moiety and substitution of MeO-group by B(pin) proceeded probably via formation of a borylallene as an intermediate to give tetraborylated product **30**, as shown in Scheme 33.

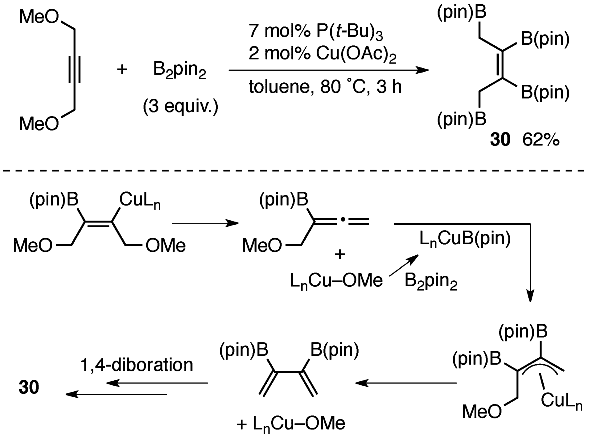
Scheme 31. Proposed Mechanism



Scheme 32. Cu-Catalyzed Diboration of Alkynes



Scheme 33. Cu-Catalyzed Tetraboration of 1,4-Dimethoxy-2-butyne

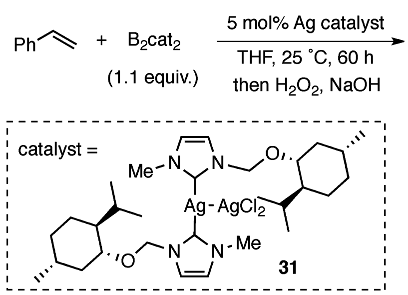


3.3.2. Silver. Silver-catalyzed diboration of alkenes with B_2cat_2 was reported by Peris and Fernandez in 2005.[62,63] A new NHC−silver complex, **31**, bearing a menthyloxymethyl group on nitrogen was employed for 1,2-diboration of styrene and vinylcyclohexane, giving corresponding 1,2-diols in good yield, although almost no asymmetric induction was observed (Scheme 34). Type A mechanism via oxidative addition of the B−B bond to Ag was proposed, although no experimental supports were provided.

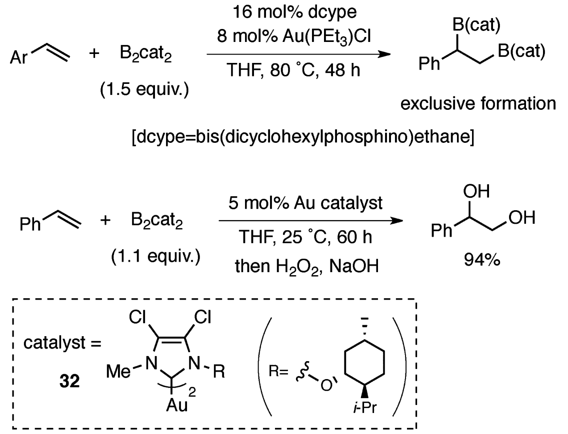
3.3.3. Gold. Baker, Marder, and Westcott first reported the catalytic activity of gold complexes for diboration, together with their report on the Rh-catalyzed diboration reaction in 1995.[35] It was found that the gold complex generated from $Au(PEt_3)Cl$ and dcype in situ catalyzed 1,2-diboration of 4-trifluoromethylstyrene and allylbenzene to give 1,2-diborylalkanes. Afterward, Peris and Fernandez described the catalytic activity of the NHC−gold complex **32** for diboration of styrene and vinylcyclohexane (Scheme 35).[63]

During the investigation of the gold-catalyzed diboration reaction of styrene, Fernandez and co-workers found the catalytic activity of $(binap)Au_2I_2$ was greatly enhanced when the reaction was carried out with an excess amount of B_2cat_2 in the

Scheme 34. Ag-Catalyzed Diboration of Alkenes

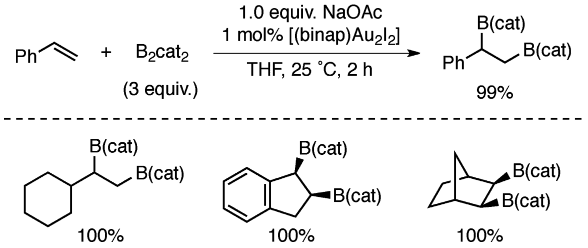


Scheme 35. Au-Catalyzed Diboration of Alkenes

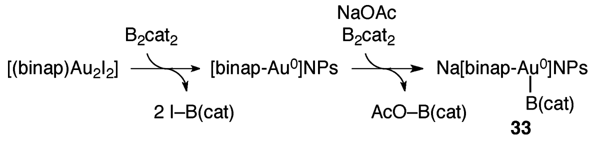


presence of NaOAc (Scheme 36).[64] The reaction was applicable to various alkenes, such as vinylcyclohexane, β-methylstyrene, indene, and norbornene to afford 1,2-diboration products in high yield with excellent cis stereoselectivity. Several mechanistic studies supported that the catalytically active species is the gold nanoparticles, which are generated via reduction of the starting complex by B$_2$cat$_2$ and stabilized by the bidentate phosphine ligand. Heterolytic cleavage of diboron during the catalytic cycle was confirmed by a cross-addition experiment between B$_2$cat$_2$ and bis(4-methylcatecholato)-diboron, and therefore, the catalytic cycle via monoborylated gold nanoparticles **33** was postulated (Scheme 37). Such a nanoparticles-catalyzed heterogeneous diboration reaction would be a practical method for the synthesis of diborylated compounds because of its reusability and easy separation.

Scheme 36. Gold Nanoparticle-Catalyzed Diboration of Alkenes

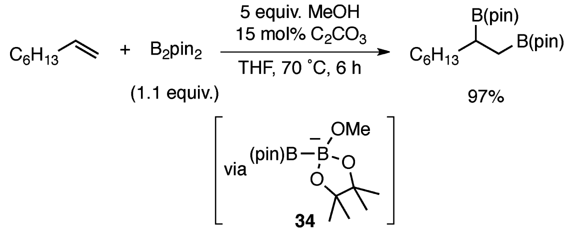


Scheme 37. Proposed Mechanism



3.4. Transition Metal-Free Diboration. Recently, Bo, Gulyas, and Fernandez reported diboration reaction of nonactivated alkenes and allenes with B$_2$pin$_2$ catalyzed by simple Lewis bases.[65] 1,2-Diboration of several alkenes, including both terminal and internal ones, proceeded smoothly in THF at 70 °C in the presence of 5 equiv of MeOH and a catalytic amount of Cs$_2$CO$_3$ or *t*-BuOK as base (Scheme 38).

Scheme 38. Simple Base-Catalyzed Borylation of Alkenes and Allenes



Adduct **34** generated from MeO$^-$ and diboron was proposed to undergo diboration of alkenes via nucleophilic addition of the B-atom. Interestingly, the hydroboration product, generated by borylation and protonation, was rarely observed as a byproduct, even in the presence of an excess amount of MeOH. These transition metal-free diboration reactions are an atom-economical and environmentally benign process, and in addition, development to expand generality and application to asymmetric version are highly desirable.

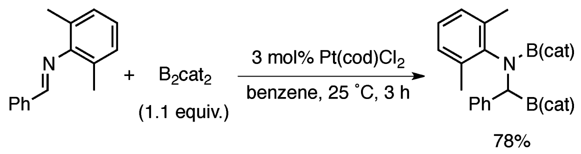
4. DIBORATION OF CARBON−HETEROATOM MULTIPLE BONDS

Not only carbon−carbon multiple bonds but also carbon−heteroatom multiple bonds are employable as substrates in diboration reaction. Such a reaction would afford alkylboronic ester derivatives bearing a heteroatom at the α-position, which are attracting much attention as highly useful building blocks in organic synthesis.

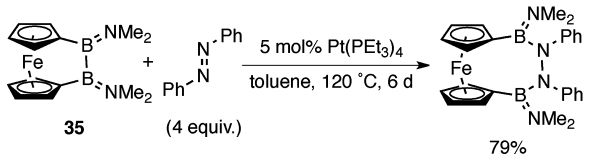
The first example of such a reaction was reported by Baker in 2000, in which diboration of the C−N double bond of aldimines with B$_2$cat$_2$ proceeded smoothly by the use of Pt(cod)Cl$_2$ as a catalyst.[66] Some *N*-benzylidene anilines reacted smoothly to give α-aminoboronates in good yield. However, selective protodeboration of the N−B bond was unsuccessful, and utilization of these products was not demonstrated (Scheme 39). Furthermore, a recent report by Braunschweig demonstrated that Pt-catalyzed diboration of the N−N double bond of azobenzene proceeded by using a rather specific diboron compound, boraferrocenophane, **35** (Scheme 40).[67]

One example of Rh-catalyzed diboration of a thiocarbonyl compound was reported by Baker and Westcott et al. (Scheme 41).[68]

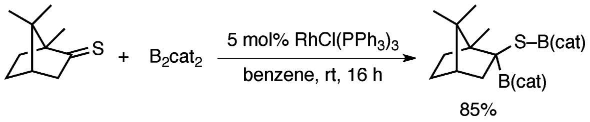
Scheme 39. Pt-Catalyzed Diboration of Aldimines



Scheme 40. Pt-Catalyzed Diboration of Azobenzene

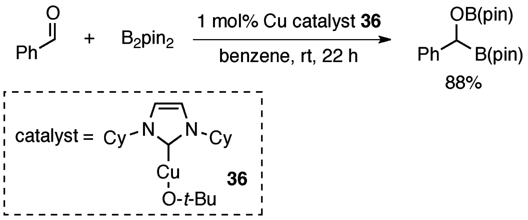


Scheme 41. Rh-Catalyzed Diboration of a Thiocarbonyl Compound

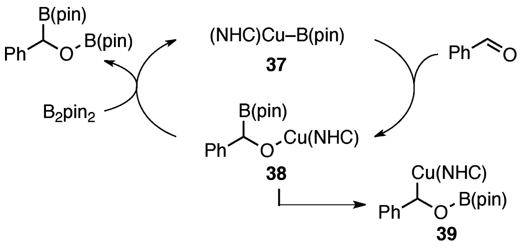


A copper catalyst system is more suitable for diboration of C−X multiple bonds than rhodium and platinum systems, and several reactions have been reported. Sadighi et al. reported the (NHC)Cu complex **36** efficiently catalyzed diboration of aldehydes with B_2pin_2 at room temperature to give diboration products in good yield (Scheme 42).[69] Although these products were stable for weeks when not in the presence of air and light, exposure to oxygen caused slow decomposition to aldehydes and $(Bpin)_2$−O. Mechanistic studies clarified that insertion of the C−O double bond to the Cu−B bond of the borylcopper complex **37** occurred to give B−C−O−Cu intermediate **38**, which underwent σ-bond metathesis with the B−B bond of B_2pin_2 to regenerate the borylcopper species **37** (Scheme 43).[70] In the absence of diboron, the intermediate **38** undergoes rearrangement to give Cu−C−O−B intermediate **39** as an observable intermediate.

Scheme 42. Cu-Catalyzed Diboration of Aldehyde

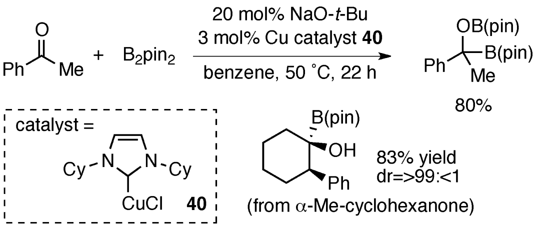


Scheme 43. Proposed Mechanism



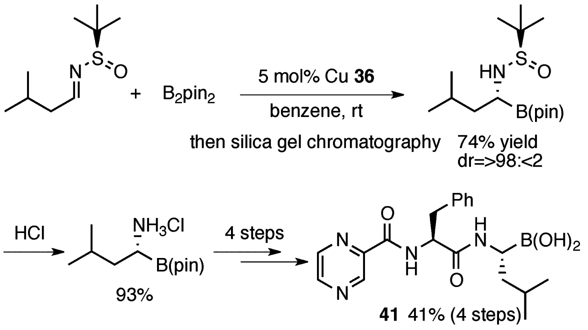
Similarly, (NHC)Cu-catalyzed diboration of ketones was reported by Clark in 2010 (Scheme 44).[71] The reaction showed wide generality, and various functional groups, such as furan, alkene, nitrile, and ester, were tolerated under the reaction conditions. In most cases, the obtained products were isolated as α-hydroxy boronic esters in good yield via selective protonolysis of the O−B bond during silica gel chromatography. Notably, the reaction proceeded with high diastereoselectivity when α-substituted ketones were employed as the substrate.

Scheme 44. Cu-Catalyzed Diboration of Ketones



This system was extended to diastereoselective diboration of chiral *N*-*tert*-butasulfinyl aldimines as a protocol for asymmetric synthesis of α-amino boronic esters.[72] The reaction of various aldimine derivatives with B_2pin_2 proceeded smoothly at room temperature by the use of (ICy)CuO^{t}Bu as a catalyst, giving α-amino boronic esters in good yield with excellent diastereomeric ratio after aqueous workup and rapid silica gel chromatography (Scheme 45). Versatility of this protocol was demonstrated by an efficient, short-step synthesis of bortezomib **41**. α-Amino boronic ester derivatives have recently been utilized as a useful coupling partner in stereoselective Suzuki−Miyaura coupling,[73,74] and therefore, development of an efficient method for the synthesis of these compounds is highly useful.

Scheme 45. Cu-Catalyzed Asymmetric Diboration of *N*-*tert*-Butasulfinyl Aldimines



5. STEPWISE INTRODUCTION OF TWO BORYL GROUPS VIA SEQUENTIAL MONOBORYLATION REACTIONS

In the concurrent diboration reactions, the mode of diboration is limited to vic-diboration, which proceeds via insertion of C−C multiple bonds into the M−B bond to form the B−C−C−M species, followed by a second borylation at the M−C bond. Moreover, by this mechanism, syn addition of two boryl groups occurs, affording only *cis*-1,2-diborylalkenes in diboration of alkynes. Therefore, development of new methods for the direct synthesis of other types of bis(boronate) compounds, such as 1,1-diborylalkanes, 1,1-diborylalkenes, and *trans*-1,2-diborylalkenes, is highly desirable to expand diversity and utility of bis(boronate) compounds in organic synthesis.

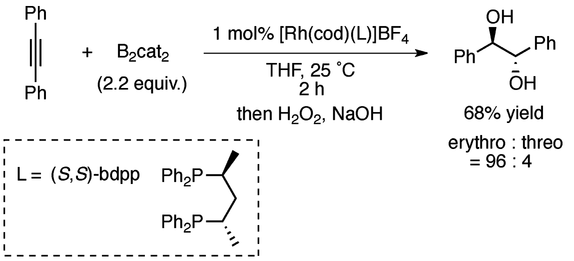
Recently, stepwise introduction of two boronate groups via sequential monoborylation of unsaturated hydrocarbons has emerged as another direct route to bis(boronate) compounds. There are several transition metal-catalyzed monoborylation reactions, and we believe that this protocol will provide many possibilities of synthesizing new bis(boronate) compounds, which are inaccessible by the concurrent diboration reactions. This section describes recent development of such protocols based on the hydroboration reaction and dehydrogenative borylation reaction.

5.1. Double Hydroboration. Transition metal-catalyzed hydroboration of alkynes is a versatile method for the synthesis of alkenylboronic esters from alkynes and boranes under mild conditions.[75−77] Thus, there is a possibility of sequential hydroboration of alkynes by using 2 equiv of borane, in which hydroboration of initially formed alkenylboronic esters further proceeds to give 1,1- or 1,2-diborylalkanes in a single operation. Metal-catalyzed concurrent diboration reaction of alkenes holds some limitations, such as (1) the diboration reaction is not able to synthesize 1,1-diborylalkanes, and (2) substrate generality is not necessarily good because of side reactions via β-hydride elimination of (borylethyl)metal species, especially in the case of Pt- and Rh-catalyzed reactions. Therefore, a sequential hydroboration protocol would be highly useful as an alternative method to diboration of alkenes.

Concerning nonmetal-catalyzed hydroboration reactions using reactive boranes such as $HBCl_2$ and 9-BBN, several examples of sequential hydroboration of alkynes have been reported to give *gem*-diborylalkanes preferentially.[2] Since this review focuses on recent development of metal-catalyzed synthesis of bis(boronate) compounds, details of these classical reactions are not described. In regard to transition metal-catalyzed reactions, however, such a protocol has rarely been developed until recently.

Fernández reported synthesis of diphenyl-1,2-ethanol through Rh-bisphosphine complex-catalyzed double hydroboration of diphenylacetylene with 2.2 equiv of catecholborane, followed by oxidative workup (Scheme 46).[41] A rhodium complex bearing a chiral bidentate phosphine ligand ((*S*,*S*)-bdpp) showed catalytic activity; however, the obtained 1,2-diol was mainly erythro isomer. Formation of a small amount of 1,2-diphenylethanol via hydroboration/hydrogenation and stilbene via hydrogenation product were also observed.

Scheme 46. Rh-Catalyzed Double Hydroboration of Diphenylacetylene

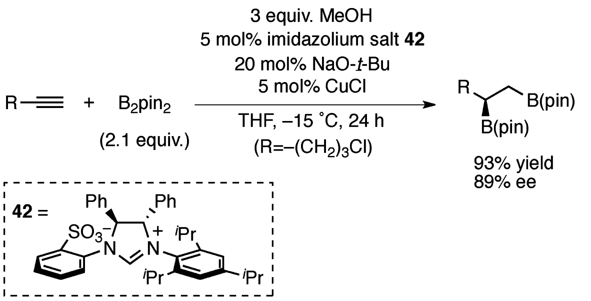


Endo and Shibata reported synthesis of 1,1-diborylalkanes via Rh-catalyzed sequential hydroboration of terminal alkynes with pinacolborane (HBpin) (Scheme 47).[78] The reaction proceeded smoothly at room temperature by the use of $[RhCl(cod)]_2$/dppb as a catalyst, and both hydroboration steps occurred regioselectively to give 1,1-diborylalkanes. Various terminal alkynes bearing an aliphatic or aromatic substituent were employable to give the products in moderate to good yield, although monoborylalkanes, formed by hydrogenation of alkenylboronates, were observed as a byproduct to some extent.

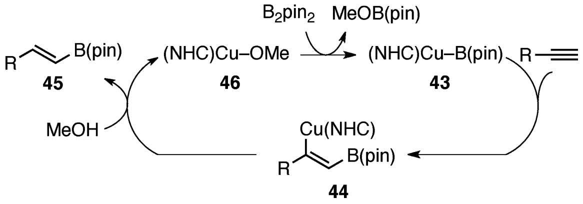
Scheme 47. Rh-Catalyzed Double Hydroboration of Alkynes

Recently, Hoveyda and co-workers developed an enantioselective synthesis of 1,2-diborylalkanes via regioselective, sequential monoborylation of terminal alkynes catalyzed by a chiral NHC-copper catalyst.[79] The reaction proceeded with 2 equiv of B_2pin_2 in the presence of 5.0 mol % of chiral imidazolium salt **42**, CuCl, and 3.0 equiv of MeOH at −15 °C, affording 1,2-diborylalkanes selectively in good yield with high enantioselectivity (Scheme 48). Borylcopper complexes bearing a chiral NHC-ligand **43** underwent the first borylation of alkynes at its terminal carbon to give (boryl)alkenylcopper complexes **44**, which were protonated by MeOH to afford alkenylboronates **45** and (NHC)CuOMe, **46**. Transmetalation of **46** with B_2pin_2 regenerated borylcopper **43**, which underwent the second borylation of alkenylboronates **45** at the β-position to the B-atom regio- and enantioselectively to give 1,2-diborylalkanes (Scheme 49). This reaction was compatible with Cl, carbamate, ether, and alkene functionalities, demonstrating superior substrate generality to previously reported enantioselective diboration of alkenes catalyzed by Rh- and Pt-catalysts.

Scheme 48. Cu-Catalyzed Double Borylation of Alkynes

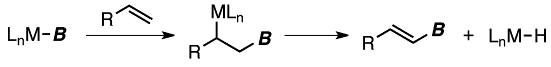


Scheme 49. Proposed Mechanism



5.2. Double Dehydrogenative Borylation. Dehydrogenative borylation of alkenes proceeds through insertion of alkenes into the M−B bond of borylmetal complexes, followed by β-hydride elimination (Scheme 50).[80] This reaction is a formal direct borylation reaction of olefinic C−H bonds leading to alkenylboronates from alkenes and diboron or borane and, thus, is the most straightforward method for the synthesis of

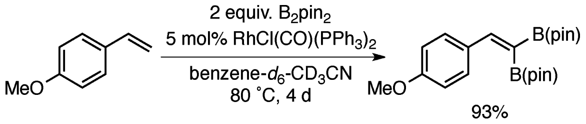
Scheme 50. Dehydrogenative Borylation



alkenylboronates. Furthermore, *β*, *β*-disubstituted alkenylboronates or medium-sized cyclic alkenylboronates, which cannot be obtained by hydroboration of alkynes, are produced by this method. Because use of alkenylboronates as the substrate of dehydrogenative borylation reaction would afford 1,1- or 1,2-diborylalkenes, realization of such double dehydrogenative borylation of alkenes by using excess amounts of a B source in a single reaction would be highly useful as a different approach to diborylalkenes.

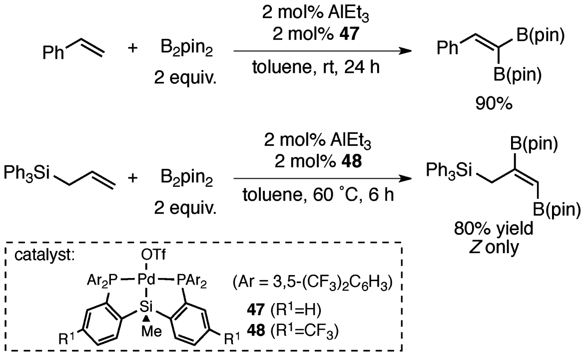
Double dehydrogenative boryation was first reported by Marder and co-workers during the investigation of Rh-catalyzed deydrogenative borylation of alkenes with diboron.[81,82] When the reaction of 4-vinylanisole was carried out with 2 equiv of B_2pin_2 in the presence of 5 mol % of $RhCl(CO)(PPh_3)_2$ in acetonitrile at 80 °C for 4 days, 1,1-diborylalkene was obtained selectively in high yield (Scheme 51).

Scheme 51. Rh-Catalyzed Double Dehydrogenative Borylation



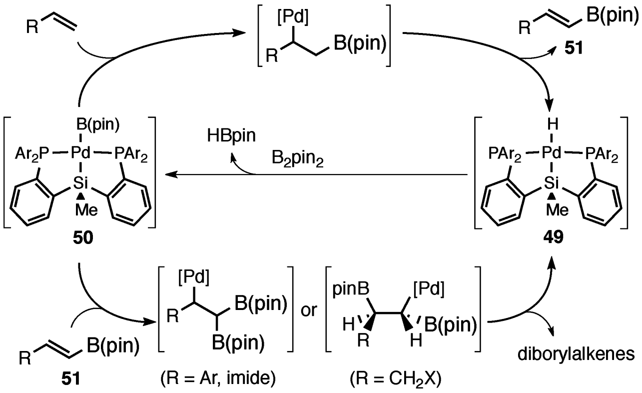
We have recently reported an efficient synthesis of 1,1- and 1,2-diborylalkenes via double dehydrogenative borylation of alkenes with B_2pin_2 catalyzed by a palladium complex bearing a PSiP-pincer type ligand.[83] Treatment of a 1:2 mixture of alkenes and B_2pin_2 with 1−10 mol % of a PSiP-pincer palladium catalyst **47** or **48** and $AlEt_3$ afforded two types of diborylalkenes regioselectively, such as 1,1-diboryl- and 1,2-diborylalkenes, depending on the substituent on the alkenes. Thus, the reaction of terminal alkenes bearing an electronically activated, bulky substituent such as styrene afforded 1,1-diborylalkenes in high yield (Scheme 52). On the other hand, nonactivated, sterically less demanding alkenes such as triphenylallylsilane underwent 1,2-diborylation to give *trans*-1,2-diborylalkenes in high yield with excellent regio- and stereoselectivity. This reaction is applicable to terminal alkenes bearing various functional groups, such as silyl ether, imido, chloro-, and acid anhydride groups, demonstrating high utility as a synthetic reaction.

Scheme 52. PSiP-Pd-Catalyzed Double Dehydrogenative Borylation



This is the first general, direct synthesis of *trans*-1,2-diborylalkenes, which are not accessible by the previous diboration protocols. The reaction is thought to start with generation of a monohydridopalladium complex, **49**, via transmetalation of **47** with $AlEt_3$, followed by *β*-hydride elimination, which reacts with B_2pin_2 to give a monoborylpalladium complex, **50**, and HBpin. The borylpalladium **51** undergoes insertion of alkenes, followed by *β*-hydride elimination, affording borylation products with regeneration of the palladium hydride **49** (Scheme 53). The reactivity of the borylpalladium **50** is greatly enhanced by the strong trans influence of the silicon atom, and therefore, the second borylation of the resulting alkenylboronates **51** proceeds smoothly to give diborylalkenes. This catalytic cycle proceeds without generation of coordinatively unsaturated hydrido(boryl)- or dihydridometal species due to the characteristics of the pincer ligand, realizing an efficient reaction without sacrificial hydroboration or hydrogenation of alkenes. This protocol provides a new, efficient synthetic route to various diborylalkenes, which are highly useful as a module for multiple carbon−carbon bond formation in synthetic organic chemistry.

Scheme 53. Proposed Mechanism



6. SUMMARY AND OUTLOOK

Recent progress on transition metal-catalyzed direct synthesis of bis(boronate) compounds is summarized. The catalytic diboration of C−C (or C−X) multiple bonds with diboron is doubtlessly a powerful tool for the synthesis of bis(boronate) compounds, which are widely employed in organic synthesis. Further development of the enantioselective diboration reaction and site-selective diboration using differentially protected diboron affords highly promising protocols for stereoselective concise synthesis of chiral complex molecules and *π*-conjugated materials. Recent progress on the usage of coinage metals, in particular copper-catalyzed diboration reactions, are noteworthy not only from the viewpoint of avoiding the use of precious group 9 and 10 metals but also from their unique mechanisms, and discovery of new catalyst systems (with or without transition metals) is highly desirable for further development of new types of diboration reactions. We also believe that sequential monoborylation protocols will provide new opportunities of synthesis and application of bis(boronate) compounds that are not available by the concurrent diboration reactions.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: niwasawa@chem.titech.ac.jp.

Notes

The authors declare no competing financial interest.

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