# Catalytic enantioselective diboration, disilation and silaboration: new opportunities for asymmetric synthesis

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This article summarizes recent developments in the area of catalytic enantioselective reactions of unsaturated organic substrates with diboron, silylboron, and disilane reagents. These reactions provide new routes to the functionalization of prochiral substrates and therefore offer new strategies in asymmetric organic synthesis.

## Introduction

Organoboranes and organosilanes are versatile reagents for organic synthesis due, in part, to a combination of accessibility, stability, and reactivity. For instance, while organoboronic esters are stable to air and moisture, under appropriate reaction conditions, they participate in oxidation, amination, sulfination, phosphination, halogenation and a variety of catalyzed and non-catalyzed C–C bond forming reactions.[1] While the range of stereospecific functional group transformations available to the alkyl–Si bond is not as well developed (protiodesilation,[2] oxidation,[3] and cross-coupling[4]) this unit is still a valuable tool for molecular construction. The stereospecificity that usually accompanies reactions of chiral organoboron and silicon reagents bestows an additional element of utility in organic synthesis. Accordingly, significant efforts have been extended towards the invention of catalytic methods for the stereoselective assembly of these molecules. An auspicious recent area of reaction development targets the synthesis of molecules that contain more than one silicon or boron atom. Such transformations may enable the design of novel cascade reaction sequences. Along these lines, the addition of $B_2Cl_4$ to unsaturated substrates has been known for many years and, within the past decade, catalytic versions of this reaction have surfaced.[5] Only recently have catalytic enantioselective methods for the diboration, disilation, and silaboration of unsaturated substrates begun to emerge. The purpose of this review is to highlight these recent exciting advances.

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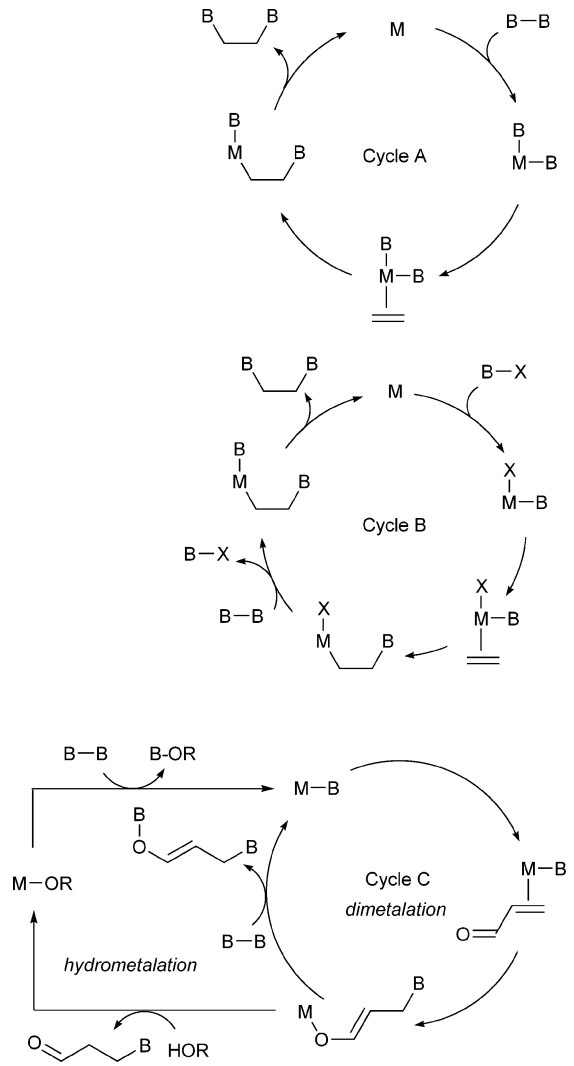
## Background

Three generalized reaction mechanisms account for the majority of catalytic dimetalation reactions, and can be used for selecting appropriate catalytic metal–ligand combinations.[6] The most common mechanism is depicted in cycle A of Scheme 1 and involves oxidative addition of the interelement compound to the transition-metal catalyst.[7] Subsequent to substrate coordination and insertion, reductive elimination releases the product and returns the catalyst to the original oxidation state. Cycle B also accomplishes dimetalation but does so without the requirement for oxidative addition of the interelement reagent. As elegantly revealed by Cheng *et al.*, this cycle can be initiated by oxidative addition of the boron/silicon halide to the catalyst.[8] Substrate insertion is followed by transmetalation with the interelement reagent, which results in regeneration of the boron/silicon halide and provides an intermediate poised for reductive product generation. Lastly, a cycle that employs interelement reagents, but that avoids oxidative addition of any type, may operate with activated alkene substrates (cycle C).[9] In this manifold, substrate insertion into an M–Si or M–B bond, is followed by either transmetalation (dimetalation process) or protonation–transmetalation (hydrometalation process). The later steps release the product and regenerate the M–Si or M–B catalyst.

In considering the above-described catalytic cycles, it becomes clear that if one wishes to employ the wide array of readily available chiral bidentate ligands that have been developed for asymmetric catalysis, then one should avoid the use of group 10 metals in reactions that operate by cycle A or B: in these cases, the metal complex would have a $d^8$ electron count at the metal after oxidative addition, and the




**Scheme 1** Generalized catalytic cycles for dimetalation of unsaturated substrates.

resulting four-coordinate square planar complex would be resistant to coordination of an alkene substrate. Alternatively, group 9 complexes that initiate catalysis from the +1 oxidation state retain a $d^6$ electron count upon oxidative addition and, even with a bidentate ligand, there is still an open coordination site for substrate association. Note that cycle C likely does not preclude the use of bidentate ligands with either group 9 or group 10 metals.

Aside from the catalyst, the nature of the dimetalation reagent is a critical consideration when implementing the catalytic methodologies described below. While studies that examine the impact of silylboron on reactivity are not prevalent, a number of reports have appeared that examine structural effects on disilane and diboron reagents. Generally, the rate of disilation reactions increases as electronegative groups are attached to silicon.[10] Qualitative observations by Marder and Norman on diboron reagents indicate that the oxidative addition of $B_2(cat)_2$ to $(Ph_3P)_2Pt(ethylene)$ is faster than the same reaction employing $B_2(pin)_2$.[7c] This is, perhaps, a surprising observation in light of the fact that the B–B bond length in $B_2(cat)_2$ (1.68 Å) is shorter than the B–B bond length in $B_2(pin)_2$ (1.71 Å).[7d] Studies by Iverson and Smith indicate that the bis(boryl) species derived from oxidative addition of $B_2(cat)_2$ to Pt(0) *may* be more stable than that derived from $B_2(pin)_2$.[11,15b] Collectively, these studies provide a framework to understand the diminished reactivity of $B_2(pin)_2$ relative to $B_2(cat)_2$ in catalytic diboration. These observations also provide insight into the observation that Pt(0) complexes are generally more effective in diboration than Rh(I) and Pd(0)—the increased d-electron energy of Pt(0) facilitates oxidative addition relative to Pd(0) and Rh(I).[7b,12]

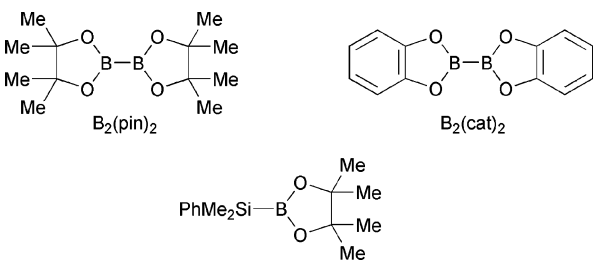
In addition to reactivity, another important issue in reagent selection is availability. While some of the reagents described within must be prepared, many are commercially available (Scheme 2), with some considered commodity chemicals. For instance, bis(pinacolato)diboron, $B_2(pin)_2$, can be purchased on multi-kilogram scale for about US$900 per kg.[13] Bis(catecholato)diboron, $B_2(cat)_2$, is more expensive, a feature which might be attributed to its more difficult preparation and increased sensitivity to moisture. $PhMe_2SiB(pin)$ has recently appeared commercially, and it and its derivatives may be prepared by single step synthesis procedures.[14] While many disilanes are commercially available, those that have been employed in asymmetric dimetalations are not; however, their syntheses are usually accomplished easily and on large scale.

## Unactivated alkene substrates

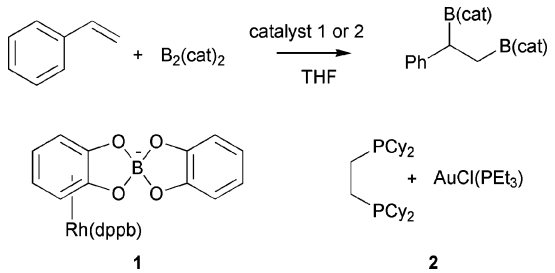
### Diboration of alkenes

Conceptually, unactivated alkenes are the simplest substrate class for dimetalation reactions. These substrates furnish 1,2-bis(metal) species during the reaction and, with appropriate substrate substitution, each olefinic carbon may be rendered prochiral. The first reports concerning the diboration of unsaturated substrates focused on the reaction of alkynes with advances being documented by Suzuki, Miyaura, Marder, and Smith.[7a,7b,15] These initial forays presaged the reaction of alkenes, arguably a process with greater synthetic utility. Following their seminal studies on the oxidative addition of Rh(I) salts to $B_2(cat)_2$, the team of Baker, Marder and Westcott demonstrated the first catalytic diboration of alkene substrates (Scheme 3).[16] Later, "base-free" Pt complexes were shown to exhibit good activity in catalytic alkene diboration,[17] and modest levels of asymmetric induction were observed in alkene diboration with chiral diboron reagents.[18]

In 2002, our lab began investigation of enantioselective alkene diboration reactions. Complexes between Rh(I) salts and (*S*)-Quinap were found to be highly effective for the

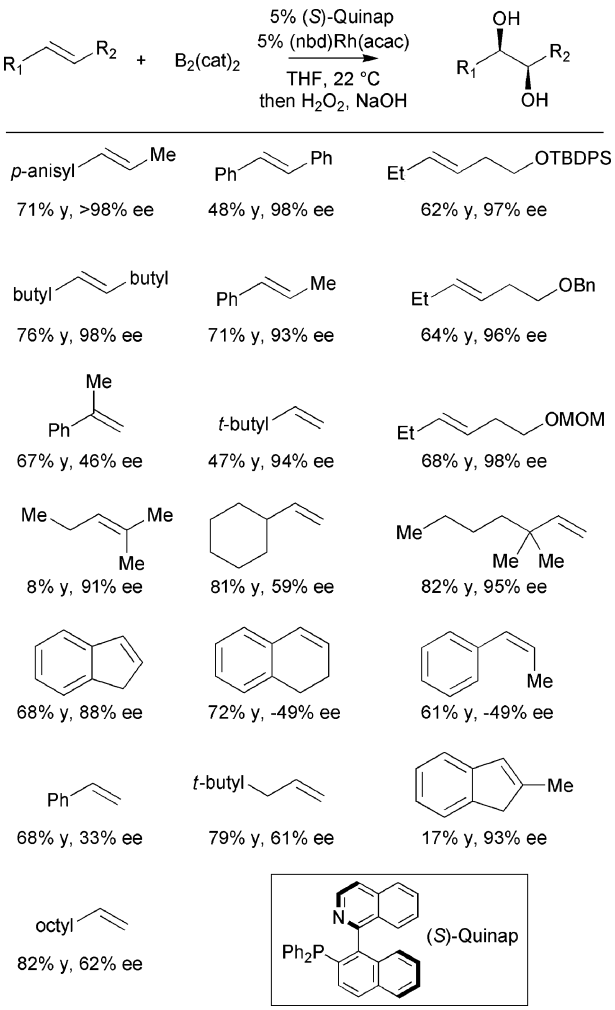



**Scheme 2** Commercially available dimetalation reagents.




**Scheme 3** Catalytic diboration of alkenes as described by Marder, Baker and Westcott.

catalytic diboration of many alkenes with bis(catecholato)-diboron.[19] As depicted in Scheme 4, studies of the substrate scope revealed optimal selectivity for *trans*-alkenes, with *cis*-alkenes providing variable enantioselection. Trisubstituted alkenes react selectively, but the rates of reaction, and corresponding yields, are significantly diminished. While 1-alkenes react quickly, these substrates only provide high levels of asymmetric induction if they are flanked by a quaternary center. Subsequent studies by our group and that of Fernandez have examined the effect of various ligands, Rh sources, and solvents on the reaction outcome;[20] while



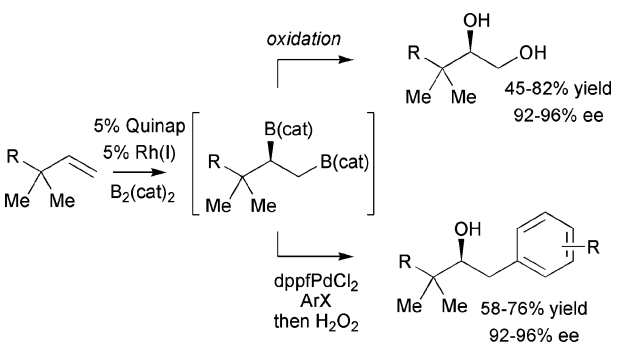

**Scheme 4** Enantioselective catalytic diboration of alkenes.

informative, these studies have not provided a significant improvement compared to originally reported procedures. Recently, Fernandez *et al*. have documented the effectiveness of Pt– and Ag–NHC complexes in alkene diboration, and these studies may offer new opportunities for asymmetric catalysis.[21]

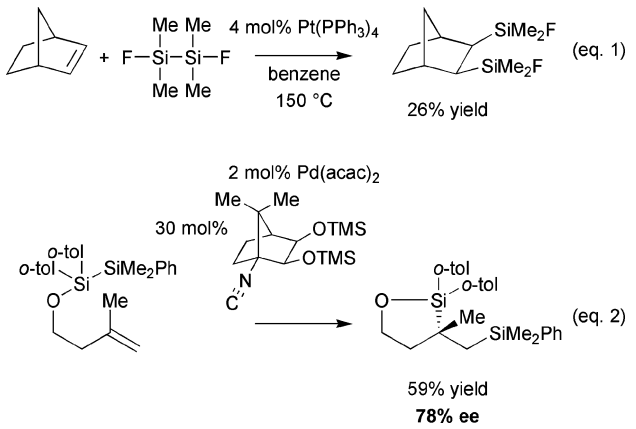
Oxidation of the C–B bonds in alkene diboration products provides synthetically useful chiral 1,2-diols, and this work-up procedure offers a convenient means to assay diboration selectivity. However, the diboration products may also be engaged in other reaction sequences thereby providing efficient routes to alternate compound classes. For example, the net catalytic enantioselective carbohydroxylation of alkenes can be achieved by a sequential single-pot diboration–Suzuki cross-coupling–oxidation process (Scheme 5).[22] In this transformation, a Rh–Quinap catalyzed alkene diboration reaction is first executed. Subsequently, the diboration reaction mixture is diluted with THF–$H_2O$. Then 10 mol% (dppf)$PdCl_2$, four equivalents of $Cs_2CO_3$, and two equivalents of aryl halide are added prior to heating. After subjection to hydrogen peroxide work-up, the carbohydroxylation adduct is obtained in good yield, and in enantioselection that mirrors the diboration–oxidation process.

## Disilation of alkenes

The catalytic intermolecular disilation of alkenes was first reported by Tanaka *et al*. in 1990 (Scheme 6, eq. 1).[23] While $Pt(PPh_3)_4$ can catalyze this transformation, competitive β-hydride elimination generates significant amounts of alkenyl silanes from many substrates, thereby diminishing the yield of the disilation product. Intramolecular disilation of unactivated alkenes is a much cleaner reaction and is most readily accomplished with $Pd(acac)_2$–*tert*-alkyl isocyanide.[24] The isocyanide ligand is a necessary additive—reactions are much slower in its absence—which offers a strategy for asymmetric reaction development. In one of the few examples of asymmetric catalysis with chiral isocyanide ligands, Suginome and Ito documented impressive levels of asymmetric induction in the intramolecular disilation with relatively simple chiral monodentate isocyanide ligands (Scheme 6, eq. 2).[25] Combined with methods for the effective oxidation of C–Si bonds, this development provides an interesting route to non-racemic polyol structures.




**Scheme 5** Enantioselective carbohydroxylation of alkenes by sequential diboration, cross-coupling, and oxidation.




**Scheme 6** Catalytic disilation of alkenes by Tanaka *et al.* and the enantioselective intramolecular reaction developed by Suginome and Ito.

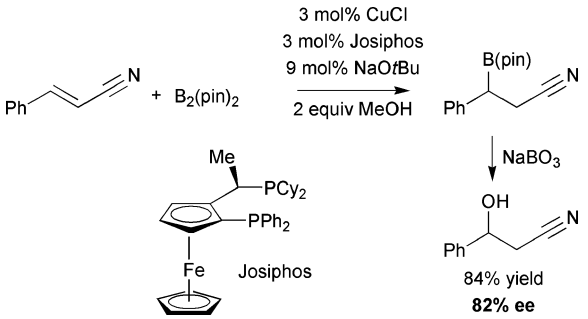
### Silaboration of alkenes

The catalytic silaboration of unactivated alkenes allows differential functionalization of each olefinic carbon atom. In 1997, Ito *et al.* described the intermolecular version of this reaction, which can be accomplished with $Me_2PhSiB(pin)$ and a catalytic amount of $Pt(PPh_3)_4$ or $Pt(ethylene)(PPh_3)_2$.[26] More recently, Suginome *et al.* have studied the intramolecular silaboration of alkenes.[27] While not yet enantioselective, the reported diastereoselective version of this process (Scheme 7) reveals significant ligand effects wherein either diastereomer of product can be generated, depending on ligand choice. This example further demonstrates the considerable utility of this process for asymmetric synthesis; while the intermediate silylboron can be directly oxidized to the 1,2-diol or engaged in Suzuki coupling (not shown), the organoboronic esters can be subject to homologation–oxidation to furnish complementary 1,3,5-triols.

## α,β-Unsaturated ketones and derivatives

### Diboration of enones

Catalytic diboration of unsaturated ketones, nitriles, esters, and phosphonates generally provides the 1,4-addition product, although 1,2-addition to the alkene has been observed.[28] While this transformation has been studied with rhodium and

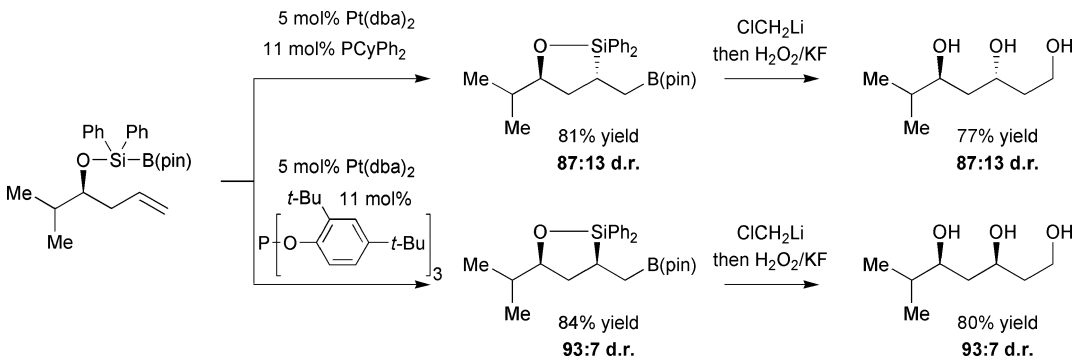



**Scheme 8** Enantioselective diboration on an unsaturated nitrile by Yun *et al.*

platinum catalysts,[28e–f] the reaction has not been rendered enantioselective by the action of these metal salts. However, encouraged by their studies on conjugate reduction with copper catalysts, Yun and co-workers queried whether copper complexes could facilitate catalytic asymmetric conjugate addition of boryl groups to activated enones.[28g] Recent observations by Hosomi, Ito, and Miyaura on copper-catalyzed conjugate borylation,[28a–d] and by Sadighi *et al.* on addition of copper boryls to carbonyls, also augured well for success in this endeavour.[29] As depicted in Scheme 8, a copper–Josiphos complex can provide significant asymmetric induction in conjugate borylation. Effective catalysis requires the addition of methanol, presumably to facilitate protolytic turnover of an intermediate copper enolate (see cycle C, Scheme 1).

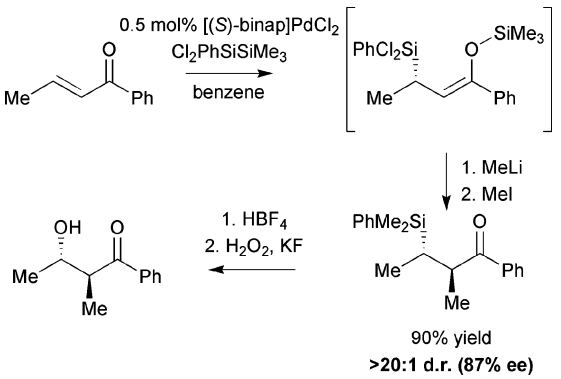
### Disilation of enones

Catalytic asymmetric disilation of enones has been developed by Hayashi and Ito. While both Pd and Cu catalysts have been examined in enone disilation,[6,9b,30] only Pd has been documented as effective for asymmetric catalysis.[31] In a preliminary survey of disilane reagents, Hayashi and Ito established that $Cl_2PhSiSiMe_3$ and $Cl_3SiSiMe_3$ underwent Pd(0)-catalyzed 1,4-addition to enones; symmetric disilanes were unreactive. As depicted in Scheme 9, it was subsequently found that Pd-catalyzed enone disilation could proceed in an enantioselective manner when carried out in the presence of binap. An attractive feature of the 1,4-disilation is that the product enolate may undergo highly diastereoselective alkylation reactions; following the stereoelectronic requirements revealed




**Scheme 7** Diastereoselective intramolecular silaboration of alkenes developed by Suginome *et al.*




**Scheme 9** Hayashi, Ito and co-worker's asymmetric enone disilation.

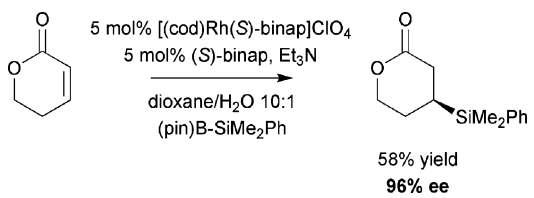
by Fleming and co-workers for alkylation of β-silyl enolates, high 1,2-*anti* stereoinduction is observed.[32]

### Silaboration of enones

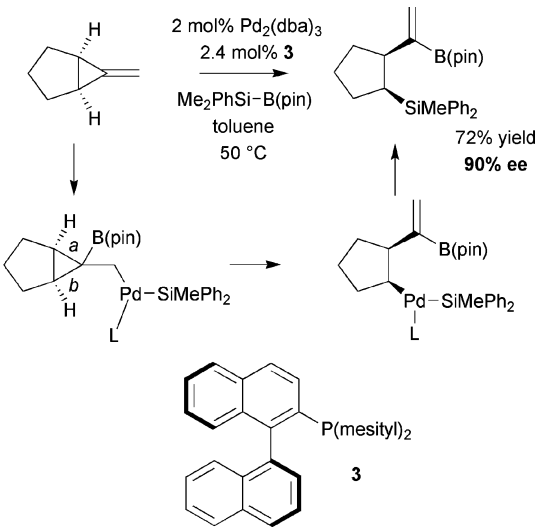
The Rh-catalyzed addition of silylboron reagents was recently introduced by Oestreich *et al*. and is highly selective with cyclic enones (Scheme 10).[33] Considering that the reaction is catalyzed by Rh(I) and requires both a base and water, it suggests that the process most likely occurs by a mechanism similar to that advanced by Hayashi *et al*. for the rhodium-catalyzed conjugate addition reaction (similar to cycle C, Scheme 1).[34] Interestingly, the catalytic reaction requires excess ligand for optimal asymmetric induction, an observation which suggests that background reaction by ligand-free Rh may occur.

## Methylenecyclopropanes

Symmetrically substituted methylenecyclopropanes (MCPs) are *meso* compounds. Suginome and Ito found that when subjected to conditions for catalytic silaboration, the cyclopropane ring is ruptured, and a homoallylic silane is produced.[35] According to the mechanism depicted in Scheme 11, the stereochemistry-determining step of this reaction is the desymmetrizing C–C bond cleavage wherein rupture of either bond *a* or bond *b* dictates the configuration of the favored product enantiomer. Clearly, the ligand may have an effect on the enantiodiscriminating step and a number of chiral monodentate phosphines and phosphoramidite structures were surveyed for their ability to control the stereochemical outcome of the reaction. With $MePh_2SiB(pin)$ as the silylboron reagent and chiral ligand **3**, both cyclic and acyclic methylenecyclopropanes may be converted to the ring-opened products in high enantioselectivity.




**Scheme 10** Oestreich and co-workers' Rh-catalyzed asymmetric silaboration of enones.

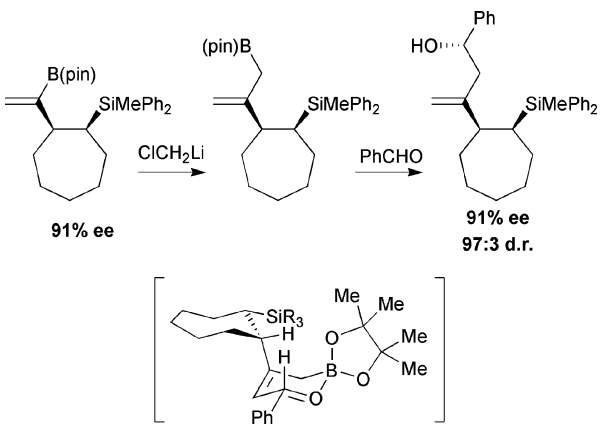



**Scheme 11** Catalytic silaborative desymmetrization of MCPs developed by Suginome *et al*.

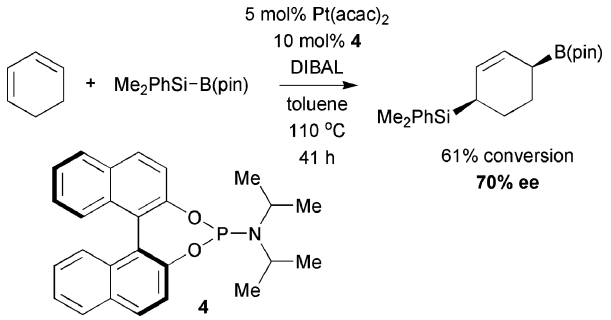
When ring-opened products of methylenecyclopropane silaboration are treated with chloromethyllithium, the Matteson homologation adduct is an allylboronic ester (Scheme 12). In the presence of aldehydes, these compounds undergo highly diastereoselective allylation reactions wherein the adjacent stereocenters impart an impressive level of facial control in the addition reaction. As exhibited in Scheme 12, a transition structure that may account for the stereochemical induction appears to be one that directs the small "H" group at the resident stereocenter towards the apical boronate oxygen, with the large group at the stereocenter directed outside the cyclic transition state array, and the medium-sized $CH_2$ group towards the reacting aldehyde. Clearly, the product of this allylation is a versatile compound in itself. For instance, one might imagine that oxidation of the C–Si bond would furnish a stereodefined, functionalized 1,5-diol from this reaction sequence.

## Dienes

Although many studies have been carried out on the racemic addition of diboron reagents to dienes,[36] the asymmetric




**Scheme 12** Utility of chiral non-racemic MCP silaboration products.



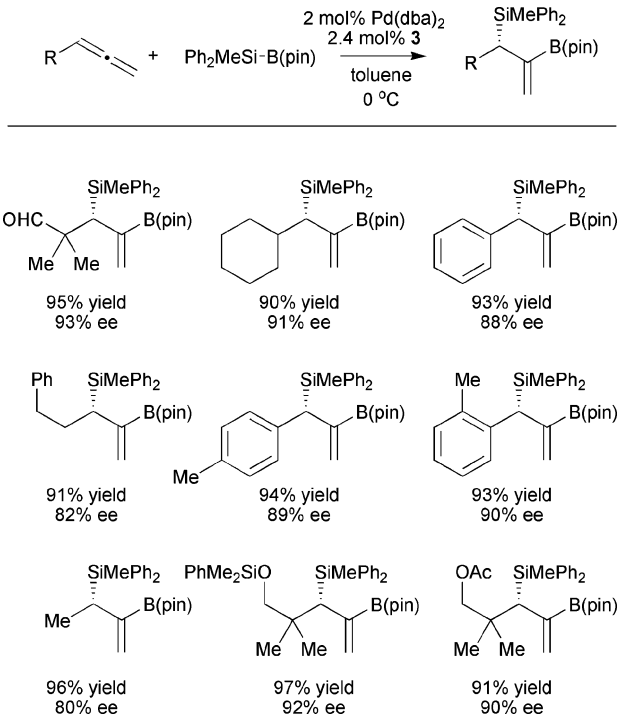

**Scheme 13** Moberg and Gerdin's asymmetric 1,4-silaboration of 1,3-dienes.

variant has been realized with limited success. While one might imagine that chirality transfer from chiral diboron reagents could be an effective tool in delivering enantiomerically enriched bis(allylic)boronate esters, this strategy does not provide high levels of selectivity.[37] For instance, the diboration of unactivated 1,3-dienes with tartrate-derived chiral diboron reagents affords 1,4-bis(boronate)esters in 20% diastereomeric excess, at best. Alternatively, asymmetric catalytic silaboration of unactivated dienes can be accomplished in much higher selectivity. Unlike silaboration of simple alkenes, silaboration of dienes may be accomplished with nickel and platinum catalysis.[38] However, the optimal levels of selectivity have been obtained with platinum catalysis. As the example by Moberg and Gerdin in Scheme 13 depicts, with $Pt(acac)_2$, DIBAL, and a chiral BINOL-derived phosphoramidite ligand, the silaboration of 1,3-cyclohexadiene proceeds in moderate selectivity.[39]

## Allenes

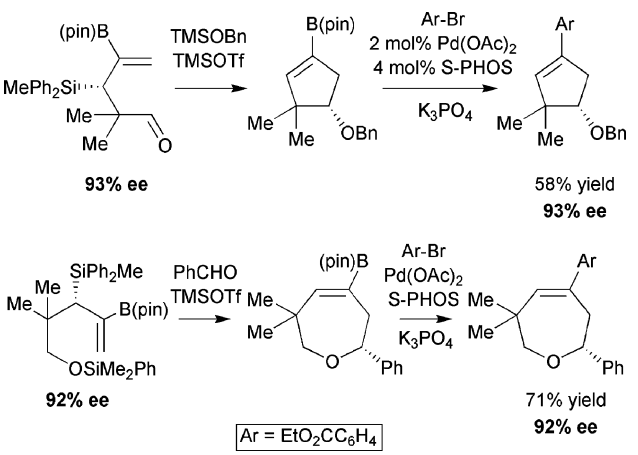
### Silaboration of allenes

The silaboration of 1,2-dienes proceeds effectively with palladium catalysis.[8a,40] Unlike with 1,3-cyclohexadiene, the silaboration of 1,2-dienes presents two additional challenges: control of the reaction site (2,3- *vs.* 1,2-addition to the allene) and regioselection (2-boryl-3-silyl *vs.* 2-silyl-3-boryl). Remarkably, Suginome and Murakami found that both of these elements can be controlled as can the facial selectivity in these reactions. Formative studies in this area focused on the silaboration of allenes with chiral silylboron reagents and chiral catalysts.[41] In these experiments, asymmetric induction from both the catalyst and the reagent work in concert to allow facial selectivity in addition to the allene. These reactions are effective with as little as 1 mol% CpPd(allyl) and 1.2 mol% H-MOP. Subsequent studies by Suginome *et al.* have led to the development of an asymmetric silaboration reaction that employs an achiral silylboron reagent and a readily available Pd source, $Pd(dba)_2$ (Scheme 14).[42] When employing the pinacol-derived silaboron (pin)B–$SiMe_2Ph$ with $Pd(dba)_2$ and H-MOP derivative **3** (see Scheme 11 for ligand structure) as the catalyst, high selectivities were obtained. Highest levels of stereoinduction (93% ee) were achieved with mono-substituted allenes bearing α-quaternary centers, lower enantioselectivities were obtained with primary aliphatic allenes.




**Scheme 14** Suginome and co-workers' asymmetric silaboration of allenes.

Suginome *et al.* have developed a number of useful transformations that employ allene silaboration adducts. As depicted in Scheme 15, they found that aldehyde functionality in the substrate is inert to silaboration conditions and can be employed in a subsequent intramolecular Lewis acid-catalyzed Marko-type allylation.[42] This reaction proceeds with a high level of chirality transfer and furnishes a carbocyclic vinylboronate intermediate that is useful in cross-coupling. A related transformation is available to allene substrates that bear a pendant silyl ether. With these substrates, addition of aldehyde and Lewis acid produces cyclic ether products. These reactions also proceed with a high level of chirality transfer.



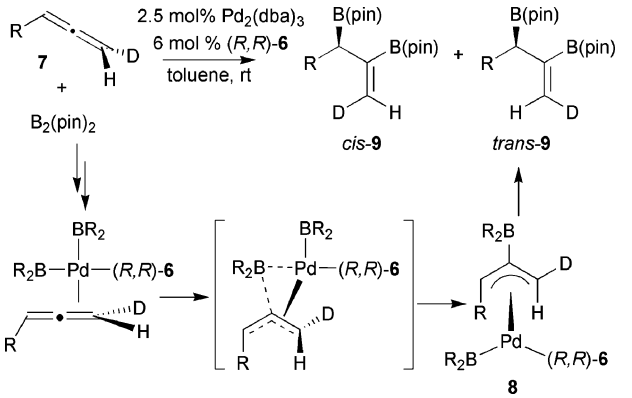

**Scheme 15** Intramolecular allylation reactions with enantiomerically-enriched allene silaboration adducts.

### Diboration of allenes

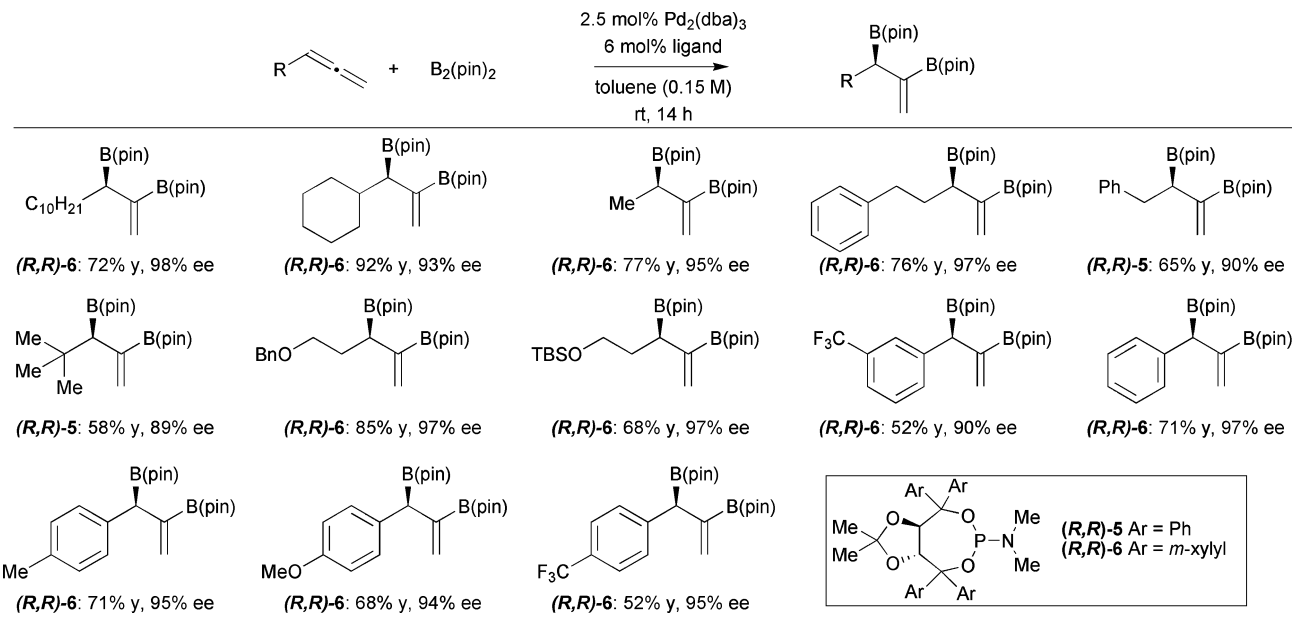
In 1998, Miyaura *et al*. reported the Pt-catalyzed diboration of allenes, a process that holds exceptional promise for asymmetric synthesis.[43] Preliminary studies on an asymmetric version of this process in our laboratory focused on the utility of Rh catalysts and these were unsuccessful. Subsequently, we began to investigate the utility of Pd catalysts; unlike the silaboration of allenes, the only regioselectivity issue this reaction faces lies in favoring the diboration of the internal bond instead of the terminal bond of the allene. In preliminary studies, Lewis basic phosphine ligands were examined and found to accelerate the palladium-catalyzed process and provide the internal addition product exclusively.[44] On the basis of this observation, a number of chiral phosphoramidite ligands were examined in the allene diboration reaction. It was found that when employing the TADDOL-derived phosphoramidite ligand **(*R*,*R*)-5**, the 1,2-bis(boronate) ester products were obtained in high enantioselectivity (87–92% ee, Scheme 16). Modification of the ligand structure led to improvement in the reaction selectivity and, with *m*-xylyl derivative **(*R*,*R*)-6**, enantioselectivity was enhanced for all substrates examined.

Mechanistic studies were undertaken in order to elucidate the mechanism of the Pd-catalyzed allene diboration.[45] Reactions carried out with an equimolar mixture of $B_2(pin)_2$ and $B_2(pin\text{-}d_{12})_2$ show a lack of crossover thereby suggesting that transmetalation reactions (similar to cycles B and C, Scheme 1) are not operative and that a catalytic cycle similar to cycle A operates. An additional revealing observation was provided by a diastereodifferentiation experiment conducted with enantiomerically enriched chiral allene **7** (Scheme 17). Should the mechanism involve initial borylpalladation of the terminal alkene, then reaction in the presence of **(*R*,*R*)-6** should favor formation of *trans*-**9**. Borylpalladation of the internal bond of the allene would favor *cis*-**9**. During the experiment it was clear that *trans*-**9** is the favored product, indicating initial insertion with the terminal alkene. DFT studies suggest that the insertion occurs by an elementary reaction that converts a Pd–allene complex directly to an $\eta^3$-$\pi$-allyl intermediate (**8**).

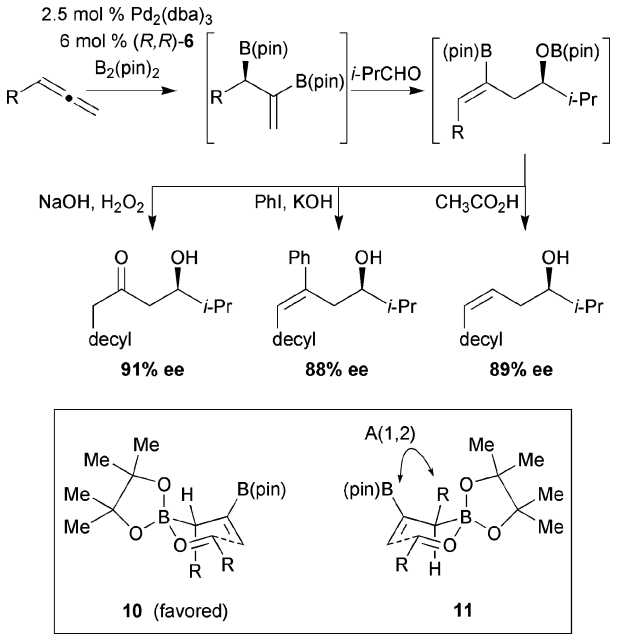



**Scheme 17** Mechanism of the Pd-catalyzed allene diboration.

Enantiomerically enriched allene diboration products hold promise for use in cascade reaction sequences. When treated with aldehydes, these reactive intermediates participate in allylation reactions and provide secondary alcohol derivatives (Scheme 18).[46] A high level of chirality transfer accompanies these allylation reactions, such that the addition product is formed with a high level of enantiomeric excess. A correlation of product chirality with starting material chirality leads to the conclusion that transition structure **10** is responsible for product formation. Apparently, the allylic strain that would exist in transition structure **11** disfavors reaction through this pathway. In terms of synthetic utility, it merits mention that the diboration and allylation may be accomplished in the same reaction flask; simply adding the aldehyde to the diboration reaction mixture leads directly to the allylation product.




**Scheme 16** Pd-catalyzed enantioselective allene diboration reaction.




**Scheme 18** Stereoselective carbonyl allylation with enantiomerically-enriched allene diboration products.

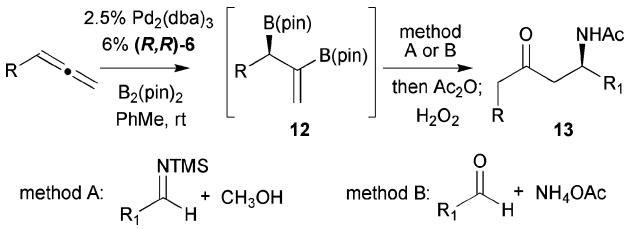
Further, the vinylboronic ester functionality in the allylation product is synthetically versatile and may participate in protodeboronation or oxidation (Scheme 18). Alternatively, metal-mediated cross-coupling may be employed for the installation of an additional carbon–carbon bond in the reaction product. An attractive feature of this last transformation is that the Pd catalyst that catalyzed the diboration is still active for the Suzuki cross-coupling and the conversion of the allene to the derived homoallylic alcohol occurs in a single reaction flask!

In addition to aldehyde allylation, the enantiomerically enriched allene diboration products react with imine electrophiles (Table 1).[47] Kobayashi conditions (method A) for *in situ* primary imine formation are most effective for aromatic aldehydes and allow the formation of enantiomerically-enriched secondary amine derivatives from allenes, in a single reaction vessel. The transition structures that account for the sense and level of chirality transfer in this reaction appear to be analogous to those that operate with aldehyde electrophiles. Notably, the level of chirality transfer is higher with imines, and approaches >99% conservation of enantiomeric excess (% cee). Similar to the aldehyde allylation described above, the intermediate vinylboronic ester may be either oxidized, as shown in Table 1, or it may be subject to protodeboronation or a Suzuki cross-coupling reaction.

## Conclusions

There is still much progress to make in order to fully exploit the utility of diboration, disilation, and silaboration-based asymmetric transformations for the synthesis of chiral materials. However, the evidence obtained to date suggests that these reaction platforms will significantly expand the range of commodity chiral chemicals which may be generated from inexpensive alkene precursors. With the ready availability of disilicon and diboron reagents, these processes promise to provide practical routes to new chiral compounds. Recent developments focused on carbonyl and imine diboration and disilation reveal that many more exciting opportunities are on the horizon.[29,48]

**Table 1** Stereoselective tandem allene diboration–imine allylation




| Entry | R | $R^1$ | Method[a] | % yield | % ee **13** | % cee[b] |
|---|---|---|---|---|---|---|
| 1 | Ph | Ph | A | 68 | 97 | 99 |
| | | | B | 59 | 96 | 98 |
| 2 | Ph | 2-Furyl | A | 68 | 97 | 99 |
| | | | B | 69 | 96 | 98 |
| 3 | Ph | *E*-Hexenyl | A | 70 | 92 | 94 |
| 4 | $PhCH_2CH_2$ | Ph | A | 64 | 93 | 95 |
| | | | B | 59 | 92 | 94 |
| 5 | $PhCH_2CH_2$ | 2-Furyl | A | 69 | 92 | 94 |
| | | | B | 56 | 91 | 93 |
| 6 | $PhCH_2CH_2$ | *E*-Hexenyl | A | 70 | 89 | 91 |
| 7 | Cy | Ph | A | 46 | 91 | 98 |
| | | | B | 30 | 91 | 98 |
| 8 | Cy | 2-Furyl | A | 66 | 92 | 99 |
| | | | B | 39 | 93 | 100 |
| 9 | Cy | *E*-Hexenyl | A | 59 | 87 | 94 |

[a] Method A: imine generated *in situ* from *N*-(TMS)aldimine and MeOH. Method B: imine generated *in situ* from aldehyde and $NH_4OAc$ in MeOH with 4 Å MS. [b] Defined as: (% ee **13** ÷ % ee **12**) × 100.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