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Review

Regio- and stereoselective synthesis of boryl-substituted allylsilanes via transition metal-catalyzed silaboration

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Abstract

Regio- and stereo-controlled synthesis of boryl-substituted allylsilanes via transition metal-catalyzed additions of silylboranes to unsaturated organic compounds is described. Nickel-catalyzed reactions of (dimethylphenylsilyl)pinacolborane with 1,3-dienes, vinylcyclopropanes, and vinylcyclobutanes yielded 4-, 5-, and 6-boryl-substituted allylsilanes, respectively. Palladium-catalyzed addition of the silylborane to allenes took place at the more substituted C=C bond to yield 2-borylallylsilane selectively. The 2-borylallylsilanes served as useful allylation reagents in Lewis acid-mediated reactions with acetals and aldehydes. In addition to the simple allylation reactions, a cascade reaction to form the *trans*-9-boryl-1,2-benzooxadecalin skeleton and a cyclization reaction to form cyclic alkenylboranes were achieved by the use of 2-borylallylsilanes as key reagents. Reactions of methylenecyclopropanes were catalyzed by palladium and platinum catalysts. The reaction course, however, depended upon the substrate structure and the catalyst employed. For instance, cycloalkylidenecyclopropanes yielded 2-cycloalkylidene-3-boryl-1-silylpropanes selectively in the presence of a palladium catalyst, while 3-cycloalkylidene-3-boryl-1-silylpropanes were obtained selectively in the corresponding platinum-catalyzed reactions.

Keywords: Silylation; Borylation; Addition; Allylation

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1. Introduction

Transition metal-catalyzed additions of boron-containing σ-bonds across carbon–carbon multiple bonds have gained increasing attention in organic chemistry [1,2]. The possibility of highly efficient and selective introduction of boron functionalities to organic molecules makes the σ-bond addition reactions highly attractive for the synthesis of organoboron compounds not otherwise readily available. It has so far been reported that additions of B–H [2], B–B [1,3], and B–Sn [4] linkages to carbon–carbon multiple bonds are catalyzed by transition metal complexes.

In 1996, we reported the transition metal-catalyzed addition of a B–Si bond across a carbon–carbon triple bond (Scheme 1(a)) [5]. The addition reaction was effectively catalyzed by palladium and platinum complexes, leading to the selective formation of β-silylalkenylboranes in high yield. In contrast, use of nickel catalysts resulted in the selective formation of 1-silyl-4-boryl-1,4-dienes via successive insertion of alkynes into the Si–B bond (Scheme 1(b)) [6]. The wide variation of the activation catalysts seems to be advantageous over other intermetallic σ-bonds in synthetic applications [7]. In particular, nickel catalysts have been rarely utilized in the intermetallic σ-bond additions with a few exceptions, where additional activation, such as ring strain or neighboring participating group, exists [8].

As expected, wide applicability of silylboranes in transition metal-catalyzed silaboration and silaborative C–C coupling reactions has been demonstrated by us, as well as by other research groups. Our interest has

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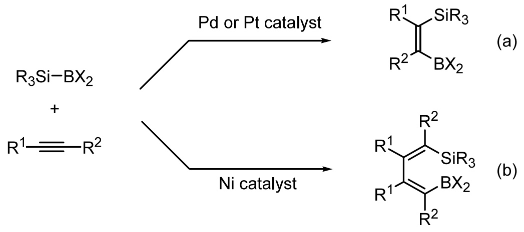
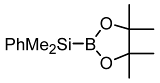


Scheme 1.

focused on the development of new synthetic intermediates that possess reactive silyl and boryl groups. In particular, silaboration reactions that produce boryl-substituted allylsilanes are highly attractive in that they can be utilized for the synthesis of new organoboron compounds by virtue of the well-established allylsilane chemistry [9]. In this paper, we describe the synthesis of boryl-substituted allylsilanes by transition metal-catalyzed silaborations of 1,3-dienes, vinylcyclopropanes, vinylcyclobutanes, allenes, and methylenecyclopropanes. Special emphasis will be placed on the regio- and stereochemical aspects, as well as the wide variation of the catalyst system.

2. Preparation of (triorganosilyl)pinacolboranes

The most frequently used silylborane in silaboration reactions is (dimethylphenylsilyl)pinacolborane (**1**). Although the catechol derivative **2** [10] and bis(diethylamino) derivative **3** [11] were also utilized for silaboration, use of the pinacol derivative **1** in silaborations is advantageous in that hydrolytic as well as thermal stability of the pinacolboryl moiety permits ready isolation of the reaction products.



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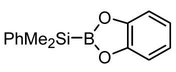

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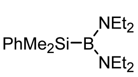
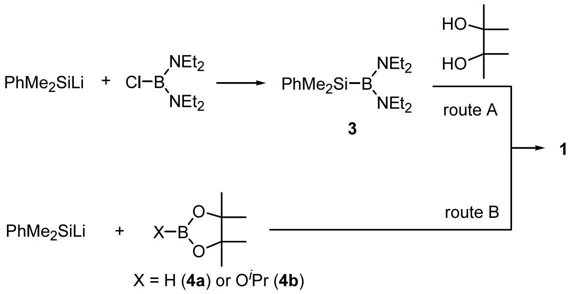


3

The pinacol derivative **1** was originally prepared from the diamino derivative **3** via amino-alkoxy exchange on the boron atom (Scheme 2, route A) [12]. The preparation of **3** from dimethylphenylsilyllithium and chlorobis(diethylamino)borane was established by Biffar et al. [11]. This procedure allows convenient addition of a variety of diol units onto boron using the common silylborane intermediate **3**, although chlorobis(diethylamino)borane is not commercially available.



Scheme 2.

Alternatively, **1** is synthesized by the reaction of pinacolborane (**4a**, pinBH) or pinacol(isopropoxy)borane (**4b**, pinBOPr-*i*) with dimethylphenylsilyllithium (Scheme 2, route B) [13]. The use of two equivalents of the boron precursors was essential to obtain **1** in high yield. The merits of the alternative route involve the ready availability of the boron precursors, either from commercial sources or by preparation. These methods are applicable to the synthesis of some other silylboranes bearing cyclic diol ligands. Furthermore, the synthesis of germylborane was also possible by this method.

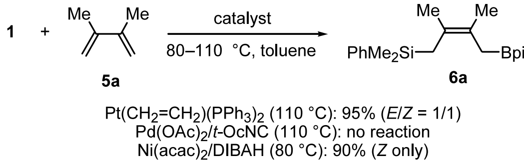
The silylboranes thus prepared are purified by distillation and should be stored under an inert atmosphere to avoid gradual decomposition presumably via oxidation. However, these compounds can be handled in air for a short time. The purity of the silylboranes can be determined by ^{1}H-NMR spectroscopy as well as GC analysis using non-polar capillary columns.

3. Synthesis of boryl-substituted allylsilanes

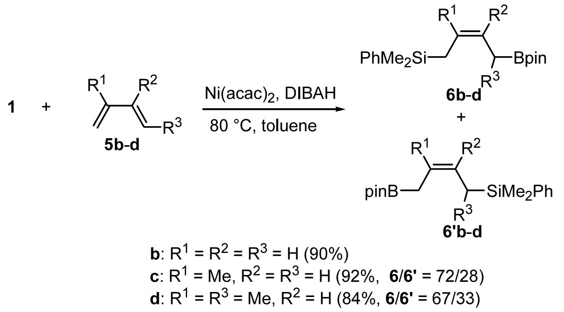
3.1. 4-Borylallylsilanes via nickel-catalyzed silaboration of 1,3-dienes

An attempted reaction of 2,3-dimethyl-1,3-butadiene (**5a**) with **1** did not proceed at all in the presence of a palladium-isocyanide catalyst, which we established as a highly efficient catalyst for silaboration of alkynes (Scheme 3) [5,12]. A platinum catalyst, which was also found to be effective for silaboration of alkenes [14] as well as alkynes, catalyzed the silaboration of the diene in good yield [15]. The silaboration product obtained in the platinum-catalyzed reaction, however, was a 1:1 mixture of *cis*- and *trans*-1-silyl-4-boryl-2-butene (**6a**). Nickel catalysts were then tested for the reaction of **5a** with **1**. A catalyst, which was generated from Ni(acac)$_2$ with two equivalents of diisobutylaluminium hydride (DIBAH) in the presence of the diene, yielded **6a** as a single *cis*-isomer. It should be noted that the diamino derivative **3** did not react with **1** in the presence of the nickel catalyst under the same reaction conditions.

Using the nickel catalyst, silaboration of several 1,3-dienes with **1** was examined. Gaseous butadiene (1 atm)

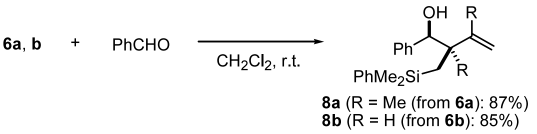


Scheme 3.

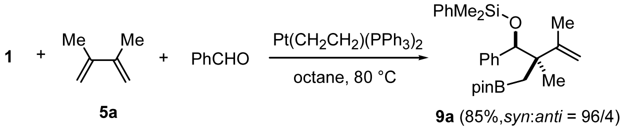


Scheme 4.

afforded **6b** in high yield as a single (*Z*)-stereoisomer (Scheme 4). Unsymmetrical 1,3-dienes **5c** and **5d** afforded the corresponding *Z*-alkenes in good yields as mixtures of regioisomers. Under the same reaction conditions, 1,1- and 1,4-disubstituted 1,3-butadienes, such as 4-methyl-1,3-pentadiene and 2,4-hexadiene, failed to yield the addition products.



Scheme 6.

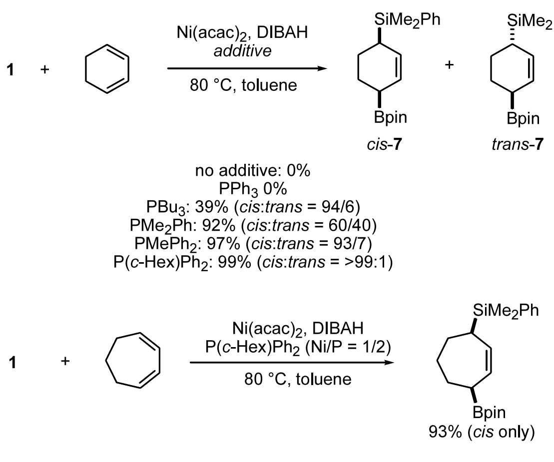


Scheme 7.

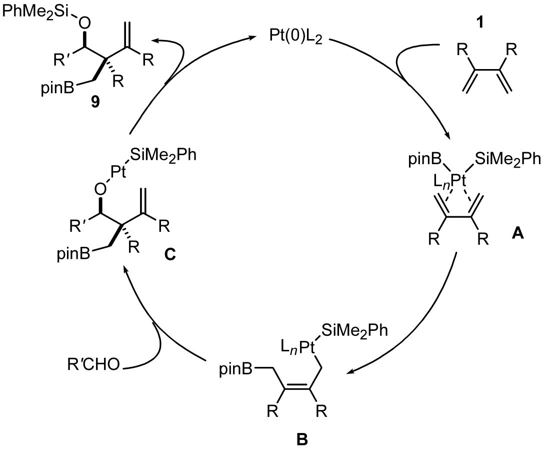
The successful silaboration of the acyclic dienes prompted us to examine cyclic 1,3-dienes. However, 1,3-cyclohexadiene did not undergo the nickel-catalyzed silaboration under the same reaction conditions as those for acyclic dienes (Scheme 5). We then modified the catalytic system by using phosphine ligands such as PPh_3, PBu_3, PMe_2Ph, $PMePh_2$, and $PCyPh_2$. Interestingly, a remarkable effect of the phosphine ligands on the silaboration reactions was observed. Use of PPh_3 failed to give any trace of the desired product, and PBu_3 gave the desired 1,4-addition product only in low yield. Although PMe_2Ph yielded the silaboration product in good yield, a 6:4 mixture of the *cis*- and *trans*-stereoisomers was obtained in the reaction. Remarkably, use of alkyldiphenylphosphines provided the *cis*-silaboration product stereoselectively in high yield. In particular, $PCyPh_2$ was found to be the best ligand for the silaboration of cyclic dienes in terms of stereoselectivity, as well as reaction yield. The optimized reaction conditions were successfully applied to the silaboration of 1,3-cycloheptadiene.

The silaboration products, which possess silyl and boryl groups at their allylic positions, serve as new allylation reagents in the reactions with aldehydes. Thus, reaction of the stereodefined **6** with benzaldehyde afforded *syn*-homoallylic alcohols **8** in high yields through allylboration [15], (Scheme 6).

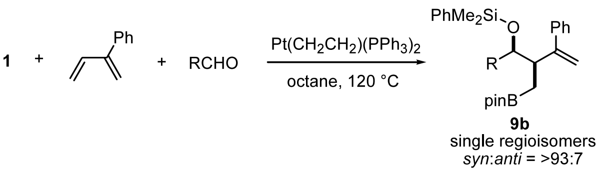
As mentioned earlier, the platinum-catalyzed silaboration gives 1,4-addition products in good yield but with low stereoselectivity. When the platinum-catalyzed silaboration of **5a** was carried out in the presence of benzaldehyde (three equivalents), we found highly stereoselective formation of **9**, which was derived by the coupling of aldehyde, 1,3-diene, and silylborane (Scheme 7) [16]. The product is apparently different from the product **8** obtained via the stepwise silaboration–allylboration sequence (Scheme 6). A reaction mechanism for the catalytic C–C bond formation has been proposed (Scheme 8). The mechanism may involve the formation of an (organosilyl)(allyl)platinum(II) intermediate **B**, which is formed via insertion of the 1,3-diene into the B–Pt bond of the intermediate (silyl)(boryl)platinum complex **A** [17]. The silaborative coupling reaction was applicable to other dienes such as gaseous butadiene and 1,2-dimethylenecyclohexane. It is



Scheme 5.



Scheme 8.



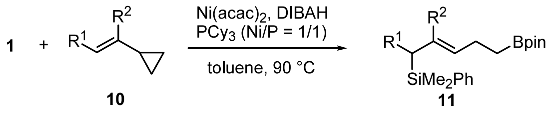
Scheme 9.

interesting to note that the reaction of 2-phenyl-1,3-butadiene proceeded not only stereoselectively, but also regioselectively (Scheme 9). The C–C and B–C bond formations take place at the less substituted C=C bond, giving the silyl ether of *syn*-homoallyl alcohol **9b** in good yield.

3.2. 5- and 6-Borylallylsilanes via nickel-catalyzed silaboration of vinylcyclopropanes and vinylcyclobutanes

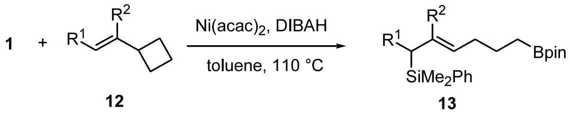
Interesting reactivities of vinylcyclopropanes (VCPs) have been established in the transition metal-catalyzed cycloaddition reactions [18]. They often serve as a homologue of 1,3-butadiene, being utilized as five-carbon synthons in cycloaddition reactions. However, the transition metal-catalyzed σ-bond addition reactions toward VCPs have not been investigated in detail. One pioneering report on the rhodium-catalyzed hydrosilylation of VCPs described the formation of a mixture of hydrosilylation products derived not only from the ring-opening reaction, but also from the direct hydrosilylation reaction with retention of the cyclopropane ring [19]. We expected that the use of silylborane in the reaction with VCPs might lead either to a highly selective silaborative ring-opening reaction or silaboration of the C=C bond that left the cyclopropane ring intact. Both processes seem to be highly attractive for the synthesis of new organometallic synthetic intermediates.

The reaction of (1-phenylvinyl)cyclopropane (**10a**) with **1** was found to be catalyzed by nickel complexes (Scheme 10) [20]. The silaboration reaction of **10a** yielded 5-borylallylsilane (**11a**) via selective cleavage of the proximal C–C bond in the cyclopropane ring. The geometry of the C=C bond was completely controlled to *trans*. Interestingly, the use of tricyclohexylphosphine (PCy_3) in an equimolar amount of nickel was remarkably effective for the silaboration reaction. Use of a smaller or larger amount of the phosphine ligand resulted in a significant decrease in yield. While PBu_3 is a little less effective than PCy_3, other phosphine ligands, such as PPh_3, $PCyPh_2$, $P(t\text{-}Bu)_3$, and PMe_2Ph, resulted in the formation of the silaboration product in less than 10% yield. Under the same reaction conditions using PCy_3, several VCPs including 1-substituted, 2-substituted, and 1,2-disubstituted derivatives underwent the silaborative C–C bond cleavage selectively (Scheme 10) [20].



R^1, R^2, yield = H, *p*-FC_6H_4, 81%; H, Me, 74%; Ph, H, 82%; Bu, H, 87%; Ph, Me, 56%; Ph, Ph, 44%

Scheme 10.



R^1, R^2, yield = H, Ph, 65%; Ph, Me, 69%; Ph, Ph, 77%

Scheme 11.

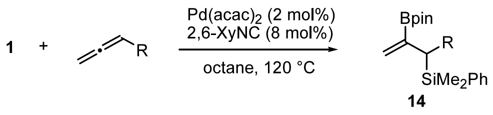
We found that the silaborative C–C bond cleavage protocol was successfully applied to vinylcyclobutanes (**12**, VCBs) (Scheme 11). A nickel catalyst with no phosphine ligand was found to be the most active catalyst for the reaction, giving 6-borylallylsilanes (**13**) in good yields, although higher catalyst loading as well as higher reaction temperature were required. The exclusive formation of the (*E*)-allylsilanes in the reactions suggested that the silaboration of VCBs proceeded via a quite similar mechanism to that of VCPs. Since the transition metal-catalyzed reaction of VCB that is accompanied by C–C bond cleavage has been rarely reported [21], the success in the nickel-catalyzed VCB silaboration may open up the new possibilities of transition metal-catalyzed reaction of VCBs.

3.3. 2-Borylallylsilanes via palladium-catalyzed silaboration of allenes

Bismetallation of allenes has been studied extensively, since allenes exhibit generally higher reactivity in addition reactions than do other typical unsaturated organic molecules such as alkynes and 1,3-dienes [22–24]. For instance, even hexamethyldisilane, which is regarded as one of the least reactive bimetals, reacts with terminal allenes in high yields [22]. Moreover, the bismetallations of allenes provide 2-metallated allylmetals, which may serve as useful synthetic reagents in organic synthesis. It is interesting to note that terminal allenes generally undergo bismetallations at their internal C=C bond despite the steric hindrance. Although palladium-catalyzed silastannation at high temperature affords terminal addition products as major products, it was shown that the internal addition product was kinetically formed and then isomerized to the more thermodynamically favored terminal addition product [23]. In addition to the preference for the internal addition products, when unsymmetrical bimetals are employed, it is interesting to see the regiochemical preference for the addition reaction.

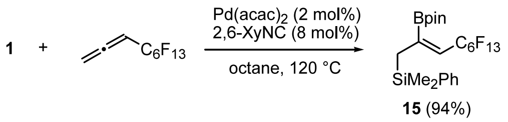
We initially found that the silaboration of terminal allenes was effectively catalyzed by a palladium-isocyanide complex (Scheme 12) [25]. In contrast to the palladium-catalyzed bis-silylation reactions, in which the *tert*-alkyl isocyanides are the catalysts of choice [26], the silaboration was more effectively catalyzed by a 2,6-dimethylphenyl isocyanide-complexed palladium catalyst. A variety of mono-substituted terminal allenes including primary, secondary, and *tert*-alkyl-substituted allenes, aryl-substituted allenes, and methoxyallene underwent silaboration, yielding a series of 2-borylallylsilanes (**14**) in good yield. It is interesting to note that the addition took place selectively at the internal C=C bonds with exclusive boron–carbon bond formation at the central allenyl carbons. Later, we found that the same reactions were successfully catalyzed by palladium complexes bearing ordinary phosphine ligands such as triphenylphosphine [27]. It should be mentioned here that Tanaka's research group independently reported the silaboration of allenes using a palladium complex bearing the tricyclic phosphite ligand, etpo [28].

Some results related to the mechanistic details should be mentioned here. First, perfluorohexylallene underwent reaction exclusively at the *terminal* C=C bond, yielding **15** in high yield (Scheme 13). Second, it was found that the untouched C=C double bond of allene has primary influence on the reaction rate of the silaboration. This was established by a couple of competitive reactions shown in Scheme 14. In one experiment, perfluorohexylallene was more reactive than hepta-1,2-diene, and in another experiment, hepta-1,2-diene underwent the silaboration much more facilely than did nona-4,5-diene. These results strongly suggest that the seemingly unaffected C=C bond may participate in the rate-determining step. We assume the reaction mechanism as follows (Scheme 15). Coordination of an allene followed by oxidative addition of the Si–B to a palladium(0) species may produce a (boryl)(silyl)palladium(II)–allene complex **ii**, whose formation may be in rapid equilibrium. The rate-determining insertion of the *terminal* C=C bond, which is finally unaffected, to the boron–palladium bond takes place, giving a (2-borylallyl)(silyl)palladium(II) intermediate **iii**. Since the σ-allylpalladium(II) intermediate **iii** is not able to undergo reductive elimination due to the *trans*-orientation of the silyl and σ-allyl groups on the palladium, the intermediate may isomerize to the corresponding π-allylpalladium intermediate **iv**. This σ–π isomerization is readily achieved by rotation of the C^1–C^2 bond of the σ-allyl group. The resulting (π-allyl)(silyl)palladium(II) complex is now ready for reductive elimination of the Si–C bond at the internal carbon atom, which is located *cis* to the silyl group. It is important to note that the high regioselectivity for the internal addition product (**14**) may suggest that the reductive elimination of the Si–C bond is much faster than the possible *cis–trans* isomerization of **iv**, which would lead to the formation of a terminal addition product. Although insertion of allenes into the Si–Pd bond of **i** should also be taken into account, some of our mechanistic studies [6] along with the Ozawa's study [17] indicated that the B–M bond (M: Group 10 metals) is more prone to undergo insertion reactions than the Si–M bond is.

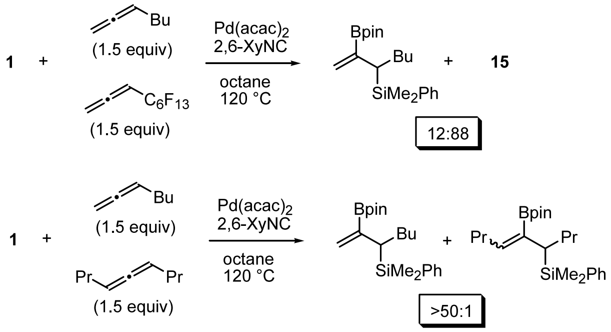


(R = H, Bu, CH_2CH_2Ph, CH_2CO_2Et, *c*-Hex, *t*-Bu, Ph, OMe)

Scheme 12.

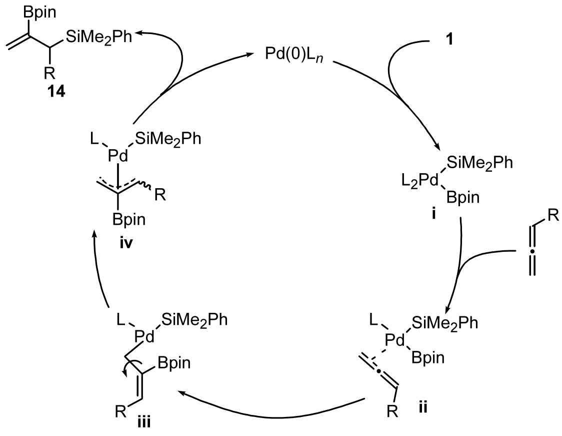


Scheme 13.



Scheme 14.

The 2-borylallylsilane (**14**) seems to be highly attractive in that it carries an allylic silyl group and a vinylic boryl group in the same molecule, both of which find a variety of synthetic transformations in Lewis acid-mediated and transition metal-catalyzed reactions. To



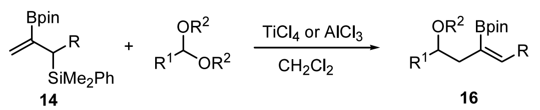
Scheme 15.

establish the utility of 2-borylallylsilane in organic synthesis, we examined the Lewis acid-mediated allylation of electrophiles with **14**.

Reactions of **14** with several acetals turned out to be quite successful (Scheme 16) [29]. In the presence of $TiCl_4$ or $AlCl_3$, the reactions yielded the corresponding 3-borylhomoallyl ethers (**16**) in good yield. It is noteworthy that the stereochemistry of the C=C in the products **16** was found to be 100% *E*. Moreover, the tolerance of the pinacolborane moiety towards Lewis acid-catalyzed reaction conditions is worth mentioning. A reaction of **14a** with propionaldehyde also proceeded in the presence of $TiCl_4$, affording a 3-boryl-substituted homoallylic alcohol **17**, which was isolated as the corresponding acetate **17** (Scheme 17).

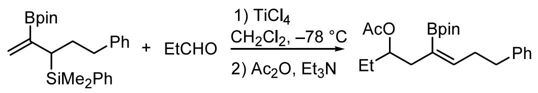
When the reaction of **14a** with propionaldehyde (excess) was carried out in the presence of TMSOTf, we unexpectedly obtained 9-bora-1,2-benzooxadecalin derivative **18**, whose structure was unambiguously determined by a single-crystal X-ray analysis (Scheme 18). Interestingly, the compound was the 1:2 adduct of the 2-borylallylsilane and the aldehyde, and obtained as a single diastereomer. Its formation may be rationalized by a cascade reaction involving allylation, Prins-type cyclization, and subsequent intramolecular Friedel–Crafts reaction as shown later.

Although the one-step construction of the tricyclic molecular framework seemed to be highly interesting, our attempt to incorporate two different aldehydes selectively into the framework failed. Under the reaction conditions using TMSOTf as a Lewis acid, the incorporation of the second aldehyde was faster than that of the first one. Consequently, even the use of just a stoichiometric amount of propionaldehyde resulted in the formation of the tricyclic product **18** bearing two ethyl groups on the framework. We found that the use of $TiCl_4$ as a Lewis acid enabled the stepwise reaction of **14a** with two different aldehydes (Scheme 19). Thus, reaction of **14a** with an equimolar amount of propionaldehyde at −78 °C in the presence of $TiCl_4$ was followed by the addition of acetaldehyde to the reaction mixture kept at −78 °C. A tricyclic product **18′** possessing methyl and ethyl groups selectively at the right positions was isolated in good yield. By this sequential protocol using $TiCl_4$, a variety of tricyclic compounds bearing different R^1 and R^2 became accessible. Apparently, in the presence of $TiCl_4$, the first step, i.e., allylation, became significantly faster than the second step (acetal formation) in the plausible reaction pathway shown in Scheme 19. It should be noted that the 2-boryl group of the allylsilane plays an important role in the stereoselective cyclization. Thus, the corresponding 2-methyl derivative **19a** yielded a stereoisomeric mixture of **20a**, and 2-silyl derivative **19b** gave no tricyclic products under the same reaction conditions as those for **18** (Scheme 20).



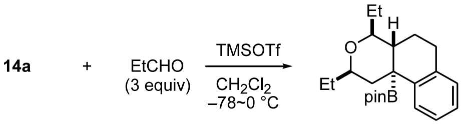
14 **16**

Scheme 16.



14a **17** (69%)

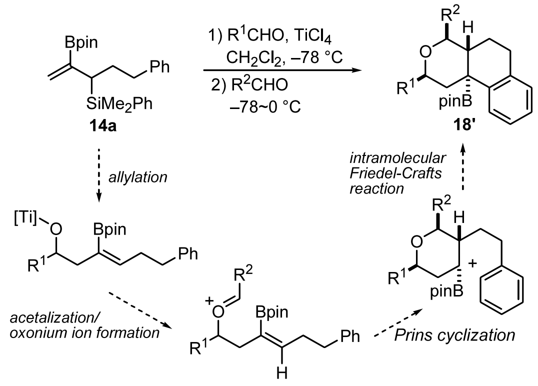
Scheme 17.



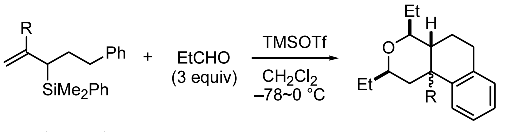
18 (92%)

Scheme 18.

Further synthetic application of the 2-borylallylsilanes relies on the use of functionalized allenes in the silaboration step. Silaboration of siloxy-substituted allenes **21a** and **21b** yielded 2-borylallylsilanes **22a** and **22b**, respectively (Scheme 21) [29]. The allylsilanes were subjected to reaction with aldehydes in the presence of TMSOTf, leading to cyclization reactions via formation of oxonium intermediates followed by intramolecular allylation (Scheme 22). It is noteworthy that the seven-membered ring formation using **22b** was particularly effective, giving the corresponding cyclic alkenylboranes **24** in good yields in reactions with a variety of aldehydes. The six-membered ring formation was similarly effective for the reactions of sterically less demand-



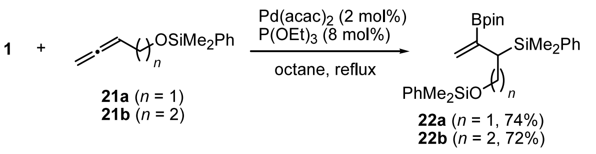
Scheme 19.



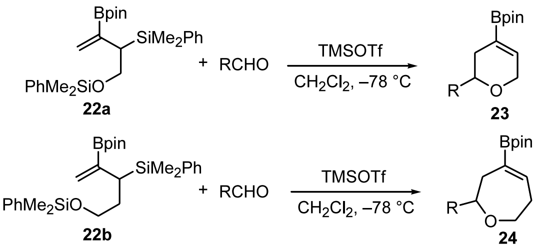
19a (R = Me)
19b (R = Me3Si)

20a (R = Me, 42%, 3:1)
20b (R = SiMe3, not found)

Scheme 20.



Scheme 21.



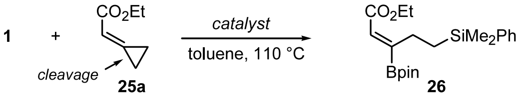
Scheme 22.

ing aliphatic aldehydes, although the corresponding reactions with pivalaldehyde and benzaldehyde resulted in low yields of the desired cyclic alkenylboranes **23** due to Peterson-type elimination of the vicinal silyl and siloxy groups. Nevertheless, the cyclization protocol provided a convenient access to the cyclic alkenylboranes which are otherwise not easily accessible.

3.4. 2-(Borylmethyl)allylsilanes via palladium-catalyzed silaboration of methylenecyclopropanes

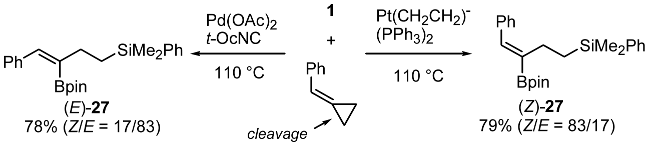
Our interest was then focused on the methylenecyclopropanes (MCPs) as a homologue of allenes. Transition metal-catalyzed reactions of MCPs with some metal-containing σ-bonds have been reported to proceed with cleavage of the carbon–carbon bond in the cyclopropane ring. However, control of the product distribution is often difficult.

We found that the silaboration of MCPs (**25**) was catalyzed by palladium and platinum complexes [30]. In the reaction of ethyl cyclopropylideneacetate (**25a**), both the catalysts gave *Z*-alkenylborane (**26**) as a major product via cleavage of the proximal C–C single bond of the cyclopropane ring (Scheme 23). In other cases, however, complementary synthesis of *E*- or *Z*-alkenylboranes (**27**) was achieved by the use of either the palladium or the platinum catalyst system (Scheme 24). Furthermore, only the platinum catalyst could catalyze the silaboration of α-methylbenzylidenecyclopropane, which gave *Z*-alkenylborane (**28**) exclusively (Scheme 25).

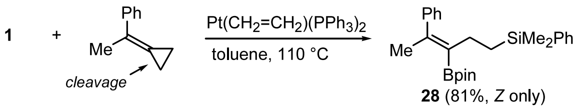


catalyst: Pd(OAc)$_2$/*t*-OcNC (89%, *Z*/*E* = 85/15)
Pt(CH$_2$=CH$_2$)(PPh$_3$)$_2$ (74%, *Z*/*E* = 74/26)

Scheme 23.



Scheme 24.

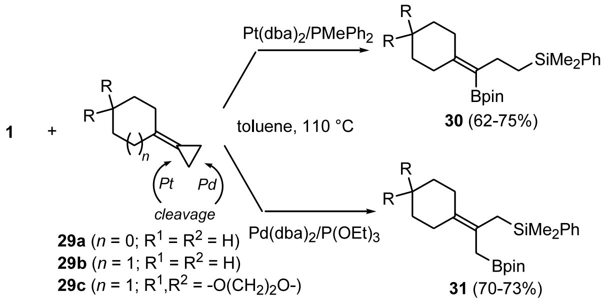


Scheme 25.

It is remarkable that silaboration of cycloalkylidenecyclopropanes could take two distinct reaction pathways by complementary use of the palladium and platinum catalysts (Scheme 26) [30]. Thus, the reactions of cycloalkylidenecyclopropanes **29** in the presence of a Pd(dba)$_2$/P(OEt)$_3$ catalyst provided 2-(borylmethyl)allylsilane (**31**) exclusively via cleavage of the distal C–C bond in the cyclopropane ring, while the corresponding platinum-catalyzed reaction afforded the alkenylborane products **30** exclusively via the proximal C–C bond cleavage. The selective production of the two different organometallic compounds from a single starting material is particularly attractive from the synthetic point of view.

4. Conclusion

The transition metal-catalyzed silaboration reaction has been shown to be an efficient strategy for the synthesis of boron-containing organosilicon compounds. In particular, in cases where the introduced silyl groups are located at the allylic positions, the products, i.e., boryl-substituted allylsilanes, serve as highly efficient reagents for the synthesis of boron-containing organic molecules. By this strategy, 2-, 4-, 5-, and 6-boryl-substituted allylsilanes have so far been synthesized successfully. It is quite likely that the development of their asymmetric versions will signifi-



Scheme 26.

cantly enhance the utility of the silaboration reactions in organic synthesis.

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