

Palladium-Catalyzed Allylation Reaction of Alkynylborates

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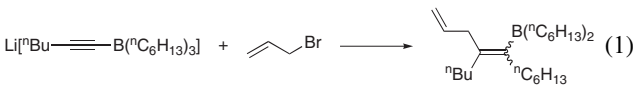
Alkynyl(aryl)(diorganyl)borates, anionic tetrahedral boron compounds, reacted with allylic bromides in the presence of a palladium(0) catalyst to produce (diorganyl)(trisubstituted alkenyl)boranes. Allylation took place at the alkynyl carbon β to boron, inducing 1,2-migration of the aryl group on the anionic boron center to the α-carbon.

Organoboron compounds have received ever-increasing attention because of their interesting photophysical properties[1] as well as facile reactivities as synthetic reagents. In particular, organoboranes having π-conjugation extended through a vacant p-orbital on boron[2] are attractive in terms of optoelectronic materials such as light-emitting diodes,[3] fluorescent sensors,[4] nonlinear optics,[5] and two-photon emitters.[6] Therefore, organic skeletons containing alkenyl–boron linkages have become a synthetic target of current interest. Among the most conventional methods for the synthesis of alkenylboranes are hydroboration reactions of alkynes and substitution reactions of halo- and alkoxyboranes with alkenylmetal reagents.[7] An alternative pathway is available starting from alkynyltriorganylborates,[8] which react with a variety of electrophiles such as a proton,[9] organic halides,[10] carbon dioxide,[11] oxiranes,[12] chlorophosphines,[13] sulfenyl chlorides,[14] metal halides,[15] and π-allylpalladium.[16] An electrophile attacks the alkynyl carbon β to boron, inducing 1,2-migration of an organyl group from boron to the α-carbon. This class of reactions has provided a valuable method to prepare trisubstituted alkenylboranes, which are difficult to synthesize by the other conventional methods mentioned above. For example, a reaction of hexyn-1-yltrihexylborate with allyl bromide affords a 1,4-dienylborane (eq 1). Allyl and hexyl groups are vicinally installed across the boron-substituted carbon–carbon double bond.[10b]

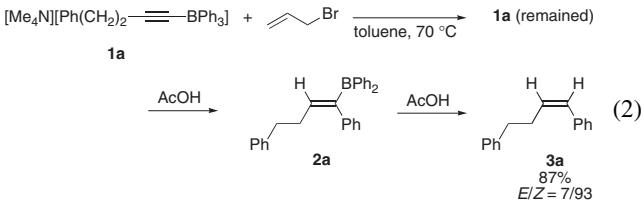


(1)

We have recently developed a palladium-catalyzed reaction of alkynyl(aryl)borates with aryl halides, which furnishes trisubstituted alkenylboranes in a stereo-defined form.[17] A related reaction of alkynyltriarylborates having a tertiary ammonium moiety produced azaboracycles having a boron–nitrogen intramolecular coordination bond.[18] In both reactions, an aryl group on boron migrated to the α-sp^2-carbon of the produced alkenylborane. As a continuation of our investigation on palladium-catalyzed reactions of alkynyltriarylborates, we next examined the use of allyl halides as electrophiles. Although palladium-catalyzed as well as non-catalyzed reactions of alkynyltriorganylborates with allyl acetates, carbonates, and halides have been reported,[10b,16] the migrating organyl groups have been limited to alkyl and alkenyl groups in the previous cases. Herein, we describe our study on the palladium-catalyzed reaction of alkynylborates with allylating reagents, in which an aryl group on boron migrates onto the α-carbon.

Results and Discussion

Optimization of Reaction Conditions. We initially examined a non-catalyzed reaction of alkynyltriphenylborate **1a** with allyl bromide. Alkynyltriphenylborate **1a** was treated with allyl bromide in toluene at 70 °C, and after 15 min, the reaction was quenched by addition of acetic acid (eq 2). Only protonated alkene **3a** was obtained (87% yield), suggesting that allyl bromide was not electrophilic enough to form a carbon–carbon bond with alkynyltriphenylborate **1a**. Instead, the proton of acetic acid employed for quenching acted as the electrophile toward **1a** to promote the 1,2-migration of the phenyl group from boron to the α-carbon.[9] Further protodeborylation of the resulting alkenylborane **2a** afforded alkene **3a**. Thus, alkynyltri*aryl*borates were less reactive than alkynyltri*alkyl*borates in the non-catalyzed reaction with allyl bromide.[10b]



(2)

Next, various palladium catalysts were examined in the allylation reaction of alkynyltriarylborate **1a** (Table 1). The reaction mixture was quenched with acetic acid to obtain a protodeborylated compound. When [Pd(PPh$_3$)$_4$], the active catalyst for the reaction of alkynyltrialkylborates with allyl carbonates,[16a] was employed, 1,4-diene **5a** was obtained in only 11% yield (Entry 1). The use of a palladium catalyst modified with P(*o*-tol)$_3$, which was a suitable catalyst for the reaction with aryl halides,[17] resulted in the formation of a complex mixture (Entry 2). No desired product was observed with DPPE and DPPF (Entries 3 and 4), whereas BINAP afforded **5a** in 42% yield ($E/Z = 29/71$, Entry 5). The bidentate phosphine ligand XANTPHOS, possessing a rigid and planar skeleton with a large bite angle of 108°,[19] furnished **5a** in 91% yield as a mixture of geometric isomers ($E/Z =$

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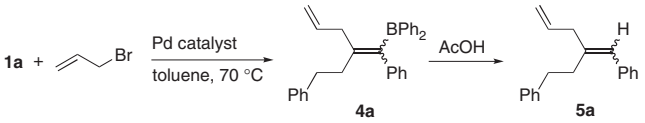
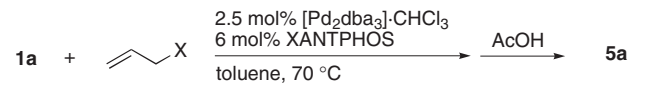
Table 1. Catalyst Screening[a)]



Entry	Catalyst[b)] (mol %)	Yield of **5a**/%[c)]	E/Z[c)]
1	$[Pd(PPh_3)_4]$ (5)	11	72/28
2	$[Pd_2dba_3]\cdot CHCl_3$ (2.5)/P(*o*-tol)$_3$ (6)	complex mixture	—
3	$[Pd_2dba_3]\cdot CHCl_3$ (2.5)/DPPE (6)	<1	—
4	$[Pd_2dba_3]\cdot CHCl_3$ (2.5)/DPPF (6)	2	—
5	$[Pd_2dba_3]\cdot CHCl_3$ (2.5)/BINAP (6)	42	29/71
6	$[Pd_2dba_3]\cdot CHCl_3$ (2.5)/XANTPHOS (6)	91 (91)[d)]	54/46
7	$[Pd_2dba_3]\cdot CHCl_3$ (2.5)/DPEPHOS (6)	6	27/73

a) Reaction conditions: 1.0 equiv of **1a**, 1.2 equiv of allyl bromide, 5 mol % Pd catalyst, toluene, 70 °C, 15 min; then AcOH, rt, 3 h. b) dba: dibenzylideneacetone. c) Determined by GC analysis. d) Isolated yield.

Table 2. Examination on Allylating Reagents[a)]



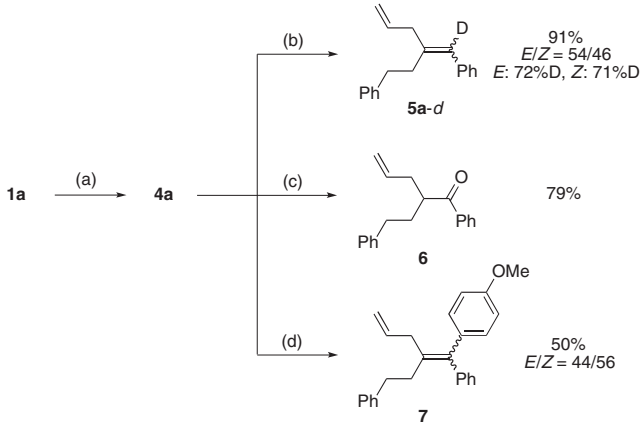
Entry	X	Yield of **5a**/%[b)]	E/Z[b)]
1	Cl	48	43/57
2	OAc	13	56/44
3	OC(O)OMe	3	52/48

a) Reaction conditions: 1.0 equiv of **1a**, 1.2 equiv of allylating reagent, 2.5 mol % $[Pd_2dba_3]\cdot CHCl_3$, 6 mol % XANTPHOS, toluene, 70 °C, 15 min; then AcOH, rt, 3 h. b) Determined by GC analysis.

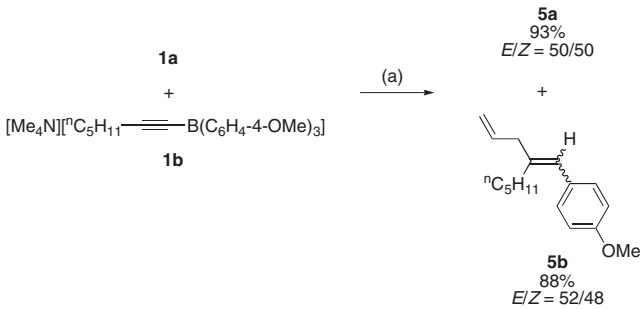
54/46, Entry 6). DPEPHOS, which also has a large bite angle (104°) but is more flexible than XANTPHOS, provided the product in only 6% yield (Entry 7).

Allylating reagents other than allyl bromide were examined (Table 2). Allyl chloride reacted with **1a** under the same reaction conditions, giving allylated product **5a** in 48% yield (Entry 1). Allyl acetate and allyl methyl carbonate were far less reactive, affording only a small amount of the product **5a** (Entries 2 and 3). Thus, allylic bromides were used as the allylating reagent in the following experiments.

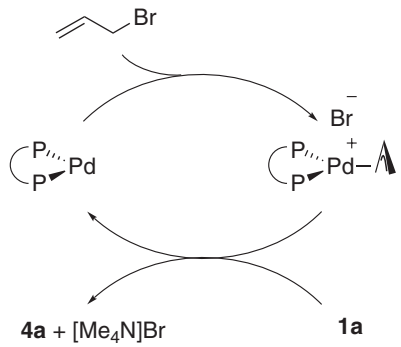
Mechanism. The following experiments were carried out in order to prove the putative formation of the intermediate alkenylborane **4a** (Scheme 1). When AcOD was employed instead of AcOH for quenching by protonolysis, deuterated alkene **5a**-*d* was isolated in 91% yield ($E/Z = 54/46$, 72% incorporation of D for the *E*-isomer, 71% incorporation of D for the *Z*-isomer). On the other hand, treatment of the reaction mixture with trimethylamine *N*-oxide (5 equiv) instead of acetic acid caused oxidation of the carbon–boron bond to afford the ketone **6** in 79% yield. Furthermore, direct addition of *p*-anisyl bromide and NaOH to the solution after the allylation reaction provided the cross-coupling product **7** in 50% yield. Thus, palladium-catalyzed allylation reaction of alkynylborates **1a** resulted in the formation of alkenylborane **4a**.



Scheme 1. Transformation of alkenylborane **4a**. Reaction conditions: (a) 2.5 mol % $[Pd_2dba_3]\cdot CHCl_3$, 6 mol % P(*o*-tol)$_3$, 1.2 equiv allyl bromide, toluene, rt, 3 h. (b) AcOD, rt, 3 h. (c) 5 equiv Me_3NO, rt, 3 h. (d) 3.3 equiv 4-$MeOC_6H_4Br$, 9.0 equiv NaOH, H_2O, rt, 10 h.



Scheme 2. Crossover experiment. Reaction conditions: (a) 5 mol % $[Pd_2dba_3]\cdot CHCl_3$, 12 mol % XANTPHOS, 70 °C, 2.4 equiv allyl bromide, 15 min; then AcOH, rt, 3 h.



Scheme 3. Plausible catalytic cycle.

Next, a crossover experiment was carried out (Scheme 2). When a mixture of **1a** (1.0 equiv) and **1b** (1.0 equiv) was subjected to the palladium-catalyzed reaction with allyl bromide (2.4 equiv), **5a** and **5b** were obtained in 93 and 88% yields, respectively. No crossover products were detected in the reaction mixture by ^1H NMR and GC-MS analysis, suggesting that 1,2-aryl migration occurred in an intramolecular fashion.

A plausible catalytic cycle is depicted in Scheme 3. Initially, allyl bromide oxidatively adds to palladium(0) to yield a π-allylpalladium species ligated by the bidentate ligand

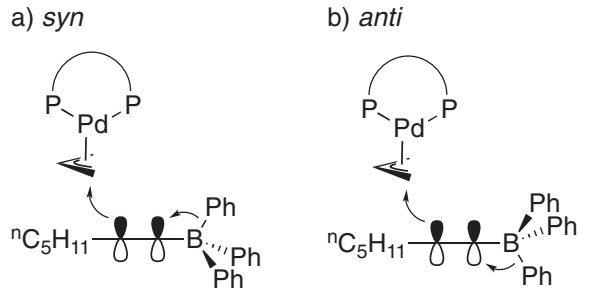


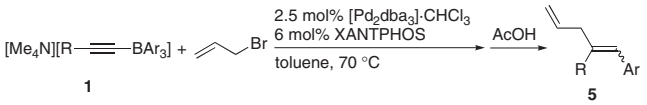
Figure 1. Stereochemical courses of 1,2-migration of the phenyl group on boron.

XANTPHOS. The alkynyl moiety of the borate nucleophilically attacks the π-allylpalladium species, inducing the 1,2-phenyl migration from boron to the α-carbon (vide infra). The alkenylborane **4a** is formed and palladium(0) is regenerated with release of a bromide anion.

No E/Z selectivity was observed with the allylation products. This stereochemical outcome stands in marked contrast to the high stereoselectivity observed in the arylation reaction.[17] Thus, it is inferred that a mechanism different from the previous one is operating in the present reaction. We assume the contrast observed in the stereoselectivities is attributed to the structural difference between π-allylpalladium complex ligated by the bidentate phosphine ligand XANTPHOS and σ-arylpalladium complex ligated by the monodentate phosphine ligand P(o-tol)$_3$. Tetracoordinated [Pd(π-allyl)(xantphos)]$^+$, which would be generated by oxidative addition of allyl bromide, is sterically congested around the palladium center, disfavoring additional direct π-coordination of the alkynyl group to palladium. Instead, the other side of the allyl ligand opposite to palladium is exposed enough to be intermolecularly attacked by the alkynyl group of the borate. Carbon–carbon bond formation between the allyl group and the β-carbon of the alkynylborate thus takes place at the opposite side of palladium.[20] Another carbon–carbon bond is concomitantly formed by 1,2-phenyl migration (Figure 1). It can proceed in both *syn*- and *anti*-periplanar relationships to π-allylpalladium, giving a mixture of the stereoisomers. On the other hand, tricoordinated [(o-tol)$_3$P][Pd(aryl)Br], which is generated by oxidative addition of an aryl halide to palladium(0), has a vacant site on palladium, allowing the alkynylborate to coordinate.[21] Consequently, it undergoes carbopalladation across the carbon–carbon triple bond in a *syn* fashion, leading to the stereoselective formation of the arylation product.

Reaction Scope. Various alkynylborates were subjected to the palladium-catalyzed allylation reaction under the optimized conditions (alkynyltriarylborate **1** (1.0 equiv), allyl bromide (1.2 equiv), [Pd$_2$dba$_3$]·CHCl$_3$ (2.5 mol %), XANTPHOS (6 mol %), toluene, 70 °C, 15 min; then AcOH, rt, 3 h). The results are summarized in Table 3. Alkynylborates with a primary alkyl substituent yielded the corresponding 1,4-dienes in high yield (Entries 1 and 2). In the case of a secondary alkyl substituent, the yield was moderate (72%, Entry 3). Triphenyl(phenylethynyl)borate (**1f**) was less reactive and the yield decreased to 24% (Entry 4). As the aryl group on boron, both electron-donating and -accepting aryl groups could participate in the reaction (Entries 5–7 and Scheme 2). The reaction of

Table 3. Allylation of Various Alkynyltriarylborates[a)]



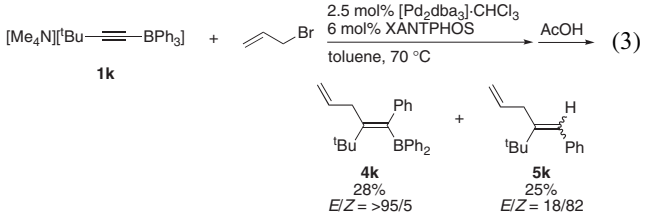
1 **5**

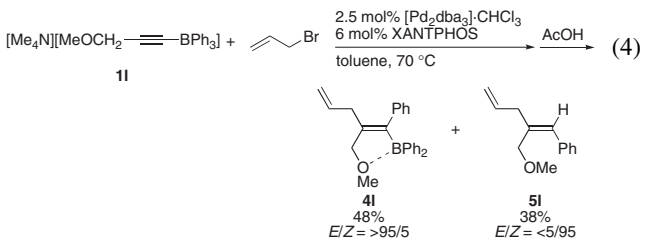
Entry	Alkynyltriarylborate	R	Ar	Yield /%[b)]	E/Z[c)]
1	**1c**	^{n}C$_5$H$_{11}$	Ph	91	54/46
2	**1d**	^{i}Bu	Ph	89	55/45
3	**1e**	^{i}Pr	Ph	72	57/43
4	**1f**	Ph	Ph	24	50/50
5	**1g**	^{n}C$_5$H$_{11}$	4-MeC$_6$H$_4$	89	47/53
6	**1h**	^{n}C$_5$H$_{11}$	3-MeC$_6$H$_4$	91	48/52
7[d)]	**1i**	^{n}C$_5$H$_{11}$	4-FC$_6$H$_4$	83	53/47
8	**1j**	^{n}C$_5$H$_{11}$	2-thienyl	79	71/29

a) Reaction conditions: 1.0 equiv of **1**, 1.2 equiv of allyl bromide, 2.5 mol % [Pd$_2$dba$_3$]·CHCl$_3$, 6 mol % XANTPHOS, toluene, 70 °C, 15 min; then AcOH, rt, 3 h. b) Isolated yield. c) Determined by ^{1}H NMR analysis. d) Reaction time: 30 min.

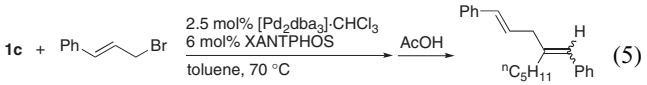
alkynyltriarylborate **1i** (Ar = 4-fluorophenyl) was slower than those of **1c** and **1g**, requiring 30 min to complete (Entry 7). A 2-thienyl group also migrated to give the corresponding product in 79% yield (Entry 8).

The allylation reaction of *tert*-butyl-substituted alkynylborate **1k** afforded 1-boryl-1,4-diene **4k** in 28% yield (E/Z = >95/5) and 1,4-diene **5k** in 25% yield (E/Z = 18/82) after quenching with acetic acid (eq 3). It was likely that a mixture of (*E*)- and (*Z*)-isomers of **4k** was formed initially. The boron–carbon bond of the (*E*)-isomer was less labile to protodeborylation with acetic acid owing to the steric protection by the neighboring *tert*-butyl group, which allowed partial isolation of (*E*)-**4k**. The other isomer (*Z*)-**4k** together with some portion of (*E*)-**4k** underwent protodeborylation to afford a mixture of 1,4-diene **5k** with the (*Z*)-isomer predominating. The reaction of alkynylborate **1l** equipped with a methoxymethyl substituent gave a mixture of (*E*)-alkenylborane **4l** (48% yield) and (*Z*)-alkene **5l** (38% yield) after addition of acetic acid (eq 4). The (*E*)-alkenylborane **4l** was stabilized by the intramolecular coordination of the oxygen atom to remain as such, whereas the other (*Z*)-isomer initially formed was facilely protodeborylated to **5l**. The coordination of oxygen to the boron center in (*E*)-**4l** was supported by up-field shift of the ^{11}B NMR signal (δ 18.5).

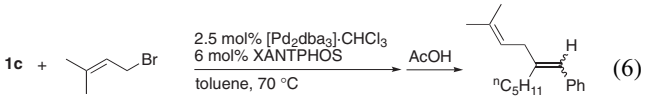




We also conducted the allylation reaction with substituted allylic bromides. The reaction of **1c** with cinnamyl bromide afforded the 1,4-diene **8** in 93% yield ($E/Z = 42/58$, eq 5). A prenyl group was also incorporated into the product to give **9** in 71% yield ($E/Z = 53/47$, eq 6). In both cases, a carbon–carbon bond was formed at the less-substituted allylic position.

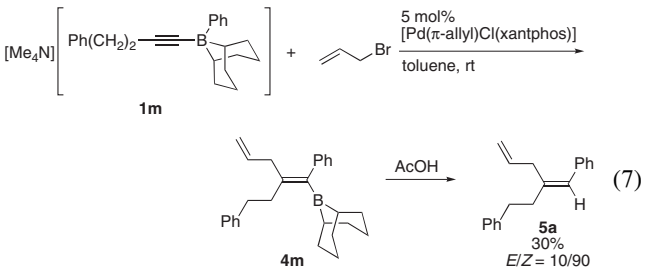


8
93%
E/Z = 42/58 (5)



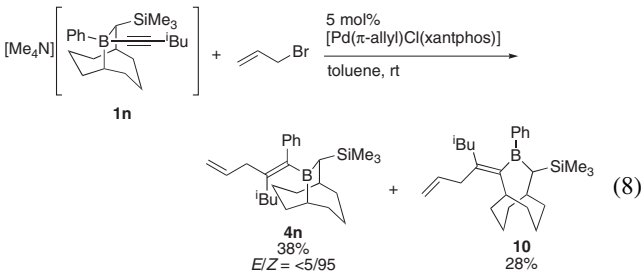
9
71%
E/Z = 53/47 (6)

We then examined the use of *dialkyl*(alkynyl)(aryl)borates in the Pd/XANTPHOS-catalyzed reaction with allyl bromide. The 9-BBN derivative **1m** was reactive enough at room temperature to provide trisubstituted alkene **5a** in 30% yield after hydrolysis (eq 7).[22] The low yield is ascribed to the formation of many other unidentified products. Better stereoselectivity was observed with **5a** ($E/Z = 10/90$) than that of the reaction of the corresponding alkynyltriphenylborate **1a**. An attempt to isolate the alkenyl-9-BBN **4m** failed due to instability toward air.



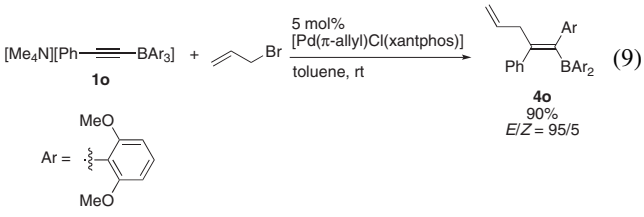
(7)

Next, alkynylarylborate **1n** having a 9-borabicyclo[3.3.2]-decane (9-BBD) framework[23,24] was tested (eq 8). The borate **1n** was treated with allyl bromide in the presence of [Pd(π-allyl)Cl(xantphos)], and the reaction mixture was directly subjected to column chromatography on silica gel to afford a mixture of alkenylboranes **4n** (38% yield) and **10** (28% yield). Thus, the produced alkenylboranes **4n** and **10** were stable enough to be isolated by column chromatography. The structures of **4n** and **10** were determined by NMR analyses (COSY, NOESY, HSQC, and HMBC).[25] The better stability of **4n** and **10** than **4m** is probably due to the steric hindrance around the boron center caused by the bulky trimethylsilyl group. Alkenyl-9-BBD **4n** was formed through allylation at the β-alkynyl carbon and 1,2-phenyl migration from boron to the α-carbon as described above. Not only the phenyl group but also the bridgehead sp^3 carbon of the rigid 9-BBD framework migrated, resulting in the formation of **10** with the enlarged bicyclic skeleton appended by an *exo*-alkylidene moiety. Thus, comparable migrating abilities of the aryl group and the alkyl group of **1n** under the reaction conditions were demonstrated.



(8)

Then, we tried to synthesize air-stable (α-arylalkenyl)diarylboranes by increasing the steric bulkiness of the aryl groups. The alkynylborates **1o** and **1p** prepared from tris(2,6-dimethoxyphenyl)borane were considerably more reactive than triphenyl(phenylethynyl)borate (**1f**), so that the palladium-catalyzed reaction with allyl bromide proceeded even at room temperature. The phenylethynylborate **1o** gave isolable alkenylborane **4o** in 90% yield in a stereoselective manner ($E/Z = 95/5$, eq 9). The stereochemistry of the major isomer was determined as *E* by NOE analysis. The (cyclohexenylethynyl)borate **1p** also provided the corresponding alkenylborane **4p** in 93% yield (eq 10). The higher reactivity could be attributed to the electron-rich nature of the 2,6-dimethoxyphenyl group. This accelerating electronic effect is in line with the slower reaction rate observed with tris(4-fluorophenyl)-borate **1i** (Table 3, Entry 7). The high stereoselectivity might be due to the sterics of the methoxy groups on *ortho*-positions because the methoxy group on the *para*-position did not affect the stereoselectivity (Scheme 2). Concerning the stability of the produced alkenylboranes **4o** and **4p**, no decomposition was observed during isolation by column chromatography on silica gel. The stability is to be ascribed to steric hindrance of the 2,6-dimethoxyphenyl groups rather than to intramolecular coordination of the methoxy group to boron. In the ^{1}H NMR spectra of **4o** and **4p**, the two methoxy signals on each aryl group were observed as equivalent. In the ^{11}B NMR spectra, no up-field shift was observed (δ 68.6 for **4o**, δ 67.1 for **4p**). Thus, intramolecular coordination is unlikely.



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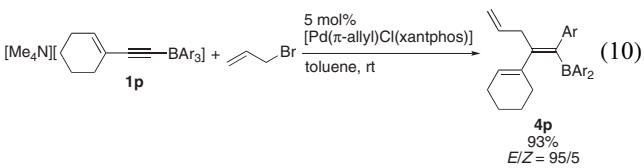
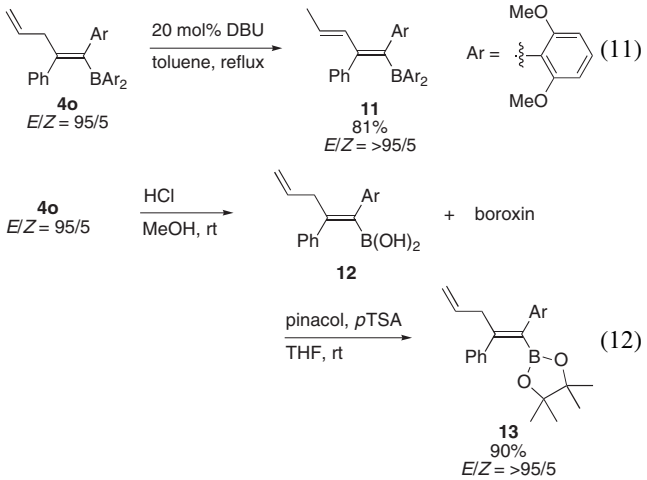


(10)

Finally, we examined the reactivity of alkenylborane **4o**. Treatment of 1,4-dienylborane **4o** with DBU (20 mol %) caused a shift of the carbon–carbon double bond to afford 1,3-dienylborane **11** as a single stereoisomer in 81% yield (eq 11). The steric hindrance around the boron atom would suppress the complexation with DBU and the π-accepting ability of the vacant p-orbital of boron facilitates deprotonation, invoking isomerization to the conjugate system with control of stereo-

chemistry.[26] Treatment of **4o** with 1.0 M HCl in methanol caused site-selective protonolysis of the 2,6-dimethoxyphenyl–boron linkages without cleavage of the alkenyl–boron linkage, giving alkenylboronic acid **12** together with the corresponding boroxin.[27] After esterification with pinacol, boronic ester **13** was obtained in 90% yield with retention of the stereochemistry ($E/Z = >95/5$, eq 12).



Conclusion

In this paper, we described the palladium-catalyzed allylation reaction of alkynyl(aryl)(diorganyl)borates. A palladium(0) complex ligated by XANTPHOS was an active catalyst for the allylation reaction to give alkenylboranes as a mixture of stereoisomers. When a bulky 2,6-dimethoxyphenyl group was employed as the substituent on boron, the palladium-catalyzed allylation reaction proceeded stereoselectively to give air-stable 1,4-dienylboranes, which were selectively hydrolyzed by acid to give the corresponding boronic acids.

Experimental

Palladium-Catalyzed Allylation of Alkynyltriarylborate 1a. A Typical Procedure. Under an argon atmosphere, a toluene solution (0.5 mL) of tetramethylammonium alkynyltriarylborate **1a** (89.0 mg, 0.20 mmol), $[Pd_2dba_3]\cdot CHCl_3$ (5.2 mg, 5 μmol), and XANTPHOS (6.9 mg, 12 μmol) was stirred for 30 min at room temperature. To the solution was added allyl bromide (28.8 mg, 0.24 mmol) in toluene (0.5 mL). After being stirred at 70 °C for 15 min, AcOH (1 mL) was added at room temperature. After 3 h, the reaction mixture was neutralized with Na_2CO_3 solution. The aqueous layer was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over $MgSO_4$ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane) to afford the trisubstituted alkene **5a** (44.5 mg, 0.18 mmol, 91% yield, $E/Z = 54/46$).

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Supporting Information

Other experimental procedures and spectral data of new compounds are described in the Supporting Information. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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