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The Reaction of Alkenylboranes with Palladium Acetate. Stereoselective Synthesis of Olefinic Derivatives†,[1]

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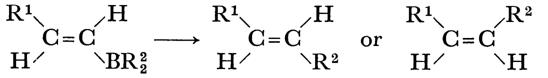
The reactions of alkenylboranes with palladium acetate were investigated. Alkenyldialkylboranes, derived from terminal alkynes, underwent intramolecular migration reaction in the presence of an equimolar amount of palladium acetate and triethylamine to give (*E*)-olefins. On the other hand, under the same conditions as above or even in the presence of catalytic amounts of palladium acetate, alkenyldialkylboranes derived from internal alkynes underwent protonolysis reaction to produce (*Z*)-olefins. An alkenylpalladium intermediate which was presumably involved in the latter reaction was trapped by allylic chloride to give 1,4-dienes.

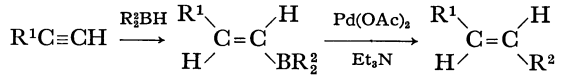
Organic syntheses *via* boranes have been broadening the synthetic applicability of olefinic or acetylenic derivatives, since organoboranes are easily obtainable *via* hydroboration. Especially, application of alkenylboranes toward organic syntheses may enchant synthetic chemists in view of introduction of alkenyl groups with *trans* configuration into organic molecules. Indeed, various synthetic methods using alkenylboranes have been developed.[2] As for the C–C bond formation which is accomplished by the intramolecular migration reaction as shown in Eq. 1,[3] there lies a limitation


(1)

concerning to the R^2 group; R^2 is limited to the secondary. The methodology of transmetallation from less reactive B–C bond to a reactive other metal-carbon bond seems to exclude this limination and provide a possibility of versatile intermolecular C–C bond formations.[4] It was reported in previous papers that such a transmetallation was realized in the case of copper by the reaction between methylcopper and alkenylboranes.[4a] This result prompted to investigate other transition metal such as palladium,[5,7] which was of potentially wide applicability to organic synthesis.[6] In this paper the reactions of alkenylboranes with various palladium complexes are examined and three types of reactions, 1) intramolecular migration reaction,[1a] 2) protonolysis reaction,[1b] and 3) cross-coupling reaction are reported.

Results and Discussion

Intramolecular Migration Reaction Promoted by Palladium Acetate. First, alkenyldialkylboranes (**1**) derived from terminal alkynes were tried to react with an equimolar amount of various palladium complexes such as $PdCl_2$, $Pd(AcAc)_2$, $Pd_2(DBA)_3$, $Pd(PPh_3)_4$[7] and $Pd(OAc)_2$. Quite interestingly, only palladium acetate reacted smoothly at room temperature with **1** to produce (*E*)-olefins (**2**) as the coupling product between alkenyl and alkyl groups. (Eq. 2).


(2)

1a: R^1=Ph, R^2=Sia   **2a**: R^1=Ph, R^2=Sia

b: R^1=*n*-Bu, R^2=Sia   **b**: R^1=*n*-Bu, R^2=Sia

Sia=$CHMeCHMe_2$

This reaction essentially needed triethylamine and the yield of **2** depended upon the amount of triethylamine. When catalytic amounts of triethylamine (7 mol %) were used in the reaction of (*E*)-styryldisiamylborane (**1a**), **2a** was obtained in the highest yield. In contrast to this, when R^1 was alkyl such as (*E*)-1-hexenyldisiamylborane (**1b**), an equimolar amount of triethylamine gave the best result. (see, Table 1).

Table 1. Reaction of **1** with $Pd(OAc)_2$ in the presence of various amounts of amine[a)]

1 (**1a** or **1b**)	Product (**2a** or **2b**)	Et_3N mmol	Yield of **2**[b)] %
1a	**2a**	2	64
		1	68
		0.35	79
		0.07	98
		0	60
1b	**2b**	2	55
		1	74
		0.05	33
		0	10

a) **1** (1 mmol), $Pd(OAc)_2$ (1 mmol).
b) By GLPC yield.

Taking account of these results, various types of (*E*)-olefins (**2**) were synthesized from alkynes (Table 2). The stereochemistry of the products in each case was over 96% *trans* as determined by the strong absorption at 965 cm^{-1} region in IR spectra and GLPC examination in comparison with the corresponding *Z*-isomer.

Previously, Zweifel and his co-workers reported the stereoselective synthesis of (*E*)-olefins from alkenylboranes using BrCN.[3a] Attempts to apply this procedure to styrylboranes (Table 2 entries 1, 3, and 4) resulted in failure; reaction of **1a** with BrCN gave

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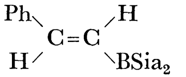
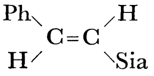
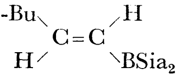
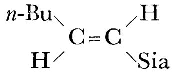
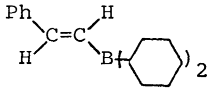
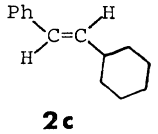
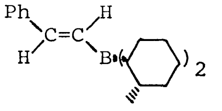
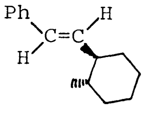
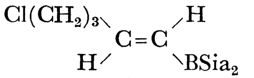
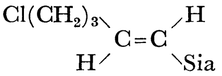
† Thesis submitted by the author (H. Y.) to Kyoto University in partial fulfillment of the requirements for the degree of Rigaku-Hakushi (Ph. D.).

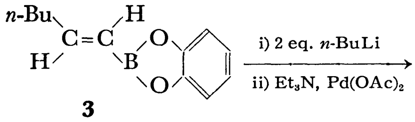
TABLE 2. REACTION OF **1** WITH $Pd(OAc)_2$–Et_3N[a)]

Entry	Acetylene	Borane[c)]	Product[d)]	Yield[e)] (Isoln)[b)]
1[f)]	PhC≡CH	 **1a**	 **2a**	94(86)
2[g)]	n-BuC≡CH	 **1b**	 **2b**	74(58)
3[f)]	PhC≡CH	 **1c**	 **2c**	58(35)
4[f)]	PhC≡CH	 **1d**	 **2d**	(86)
5[g)]	$Cl(CH_2)_3C$≡CH	 **1e**	 **2e**	(62)

a) All reactions were performed on a 1 mmol scale. b) Isolation was carried out on a 5 mmol scale. c) Sia=$CHMeCHMe_2$. d) Identified by IR and NMR spectroscopies, elemental analyses, and/or comparison with authentic materials. e) By GLPC based on the acetylenes. f) Catalytic amounts of Et_3N (7 mol %) were used. g) Stoichiometric amounts of Et_3N were used.

styrene instead of **2a**. Consequently, the present reaction offers a noteworthy improvement in the existing methodology of intramolecular migration reaction.

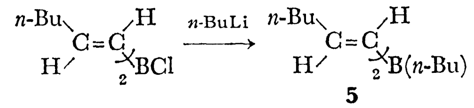
By the hydroboration method for the preparation of alkenyldialkylboranes, the alkyl groups are limited to secondary groups. Thus, the introduction of the primary alkyl group was achieved by the two methods as shown in Eqs. 3 and 4. Although the desired (E)-5-decene (**4**) was obtained by both methods, yields were low and the reaction in Eq. 4 gave 1,3-diene (**6**) as a by-product.



3

$$n\text{-BuCH=CH}(n\text{-Bu}) \qquad (3)$$

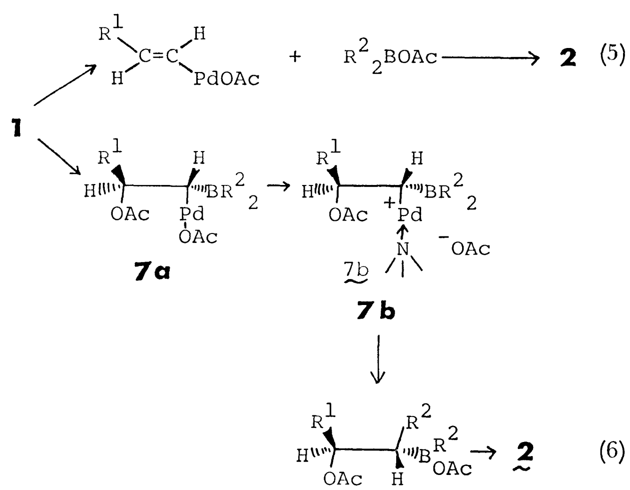
4



5

$$\xrightarrow[Et_3N]{Pd(OAc)_2} \underset{31\%}{\mathbf{4}} + \underset{\underset{57\%}{\mathbf{6}}}{(n\text{-BuCH=CH})_2} \qquad (4)$$

Two mechanisms appear reasonable to consider for this transformation; a) intermolecular coupling process *via* the alkenylpalladium acetate on the analogy of transmetallation to Hg[4c)] and Pd[5)] (Eq. 5), and b) intramolecular process *via* acetoxypalladation-migration-elimination (Eq. 6). Although a mixture of **1a** and dicyclohexylacyloxyborane was treated with $Pd(OAc)_2$–Et_3N, cross-coupling product (β-cyclohexylstyrene) could not be obtained thus excluding the intermolecular mechanism. Therefore, intramolecular migration is reasonable. There remain the following two possibilities; 1) *cis* acetoxypalladation-migration[3)] from boron to the α-carbon with inversion at the migration terminus syn elimination[3a,8,9)] or 2) *trans* acetoxypalladation-inversion anti elimination.[3b,8a)] The hitherto known migrations proceed with inversion of configuration and the anti β-elimination is restricted to the reaction in the presence of strong base. Consequently, intramolecular process 1) demanding the *cis*-acetoxypalladation is favorable.[10)]



The orientation of the acetoxypalladation may be explained as follows. The vacant p orbital of boron atom interacts with π-electrons of the double bond[11)] to make the β-carbon of alkenylborane electropositive.

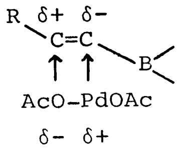


Fig. 1.

Therefore the nucleophilic acetoxyl group can attack this β-carbon to give **7** (Fig. 1).[12]

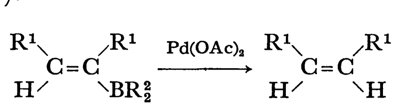
The investigation of effect of various amines showed that the yield of **2b** had a relation with coordination ability of amines with trimethylborane (Table 3). That is, the present reaction can proceed smoothly under the conditions in which amine coordinates with palladium rather than boron. Et_3N could satisfy these conditions and coordinate with palladium to give cationic palladium complex (**7b**) which may induce alkyl migration more easily.[13]

Table 3. Reaction of **1b** with $Pd(OAc)_2$ in the presence of amine[a]

Amine	Yield of **2b** (%)	Amine: BMe_3 dissociation const.[b]
	32	0.301
Me_3CNH_2	49	9.46
Et_3N	74	—[c]

a) **1b** (1 mmol), $Pd(OAc)_2$ (1 mmol), amine (1 mmol). b) H. C. Brown, "Boranes in Organic Chemistry," Cornel Univ. Press **1972**, p. 59. c) Too highly dissociated to be measured.

Application of this type of reaction to alkenyldialkylboranes (**8**), derived from internal alkynes, resulted in failure giving (*Z*)-olefins (**9**) instead which were formed *via* retentive protonalysis of the alkenylgroup of **8** (Eq. 7).



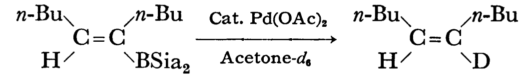
$$\begin{array}{c}R^1\quad\;\; R^1\\ C{=}C\\ H\quad\;\; BR^2_2\end{array} \xrightarrow{Pd(OAc)_2} \begin{array}{c}R^1\quad\;\; R^1\\ C{=}C\\ H\quad\;\; H\end{array} \qquad (7)$$

8a: R^1=*n*-Bu
R^2=Sia

9a: R^1=*n*-Bu

Protonolysis of Alkenyldialkylboranes (8) Catalyzed by Palladium Acetate. As mentioned above, treatment of (*E*)-5-decenyldisiamylborane (**8a**) with an equimolar amount of palladium acetate and triethylamine produced **9a** in a yield of 71%. Quite interestingly, this protonolysis reaction proceeded successfully even in the presence of catalytic amounts of palladium acetate (5—10 mol%). The results are summarized in Table 4. Judging from Table 4, applicability of this method appears to be general for internal alkynes. However, similar treatment of alkenylborane derived from terminal alkyne gave unsatisfactory result.

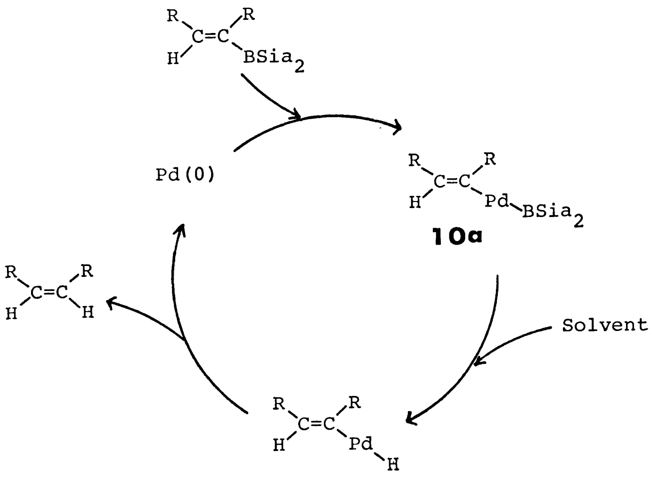
Previous methods for the protonation of alkenylboranes under acidic[14] or basic[15] conditions have several disadvantages; *e.g* incompatibility with various acid or base sensitive functional groups. The present procedure under a neutral and mild conditions can give a solution to this problem.



$$\begin{array}{c}n\text{-Bu}\quad\;\; n\text{-Bu}\\ C{=}C\\ H\quad\;\; BSia_2\end{array} \xrightarrow[\text{Acetone-}d_6]{\text{Cat. Pd(OAc)}_2} \begin{array}{c}n\text{-Bu}\quad\;\; n\text{-Bu}\\ C{=}C\\ H\quad\;\; D\end{array} \qquad (8)$$

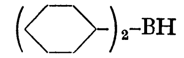
8a *d*-Content 88%

The experiment using acetone-d_6 as a solvent gave deuterium incorporated olefin[16] (Eq. 8). Accordingly, the proton source was confirmed to be the solvent. A mechanistic rationale which readily accounts for the observed catalytic process and deuterium labelling in



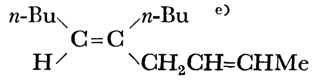
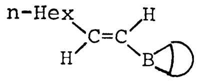
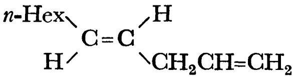
Scheme 1.

Table 4. Protonolysis of **8** with catalytic amounts of $Pd(OAc)_2$[a]

Acetylene	Hydroborating reagent[b]	Product	Yield/% (Isoln)[d]
n-BuC≡C*n*-Bu	Sia_2BH	(*Z*)-5-Decene	95
n-BuC≡C*n*-Bu		(*Z*)-5-Decene	94
n-HexC≡CEt	Sia_2BH	(*Z*)-3-Decene	(70)
PhC≡CPh	Sia_2BH	(*Z*)-Stilbene	69[e]
n-OctC≡C$(CH_2)_7$COOMe	Sia_2BH	Methyl oleate	91
n-BuC≡CH	Sia_2BH	1-Hexene	30[f]

a) All reactions were carried out at room temperature overnight. b) Sia=CHMeCHMe$_2$. c) All products were identified by NMR, IR, and comparison with the authentic materials. d) By GLPC yield. Yields were based on alkynes. e) Starting material was recovered in 24% yield, owing to incomplete hydroboration. f) The starting borane was recovered in 70% yield.

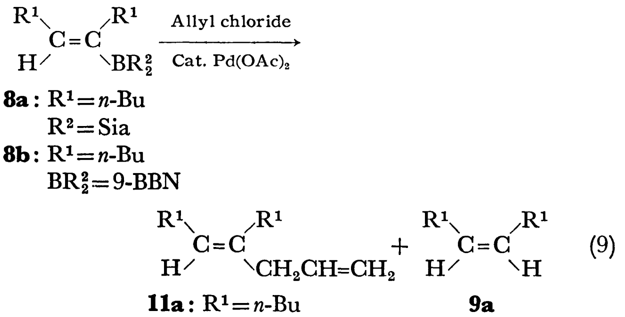
Table 5. Cross-coupling of **8** with allylic chloride[a)]

Entry	Alkenylborane	Halide	Product[c)]	Yield[d)] (Isoln)[b)] 11	9
1	**8a**	$CH_2{=}CHCH_2Cl$	**11a**	23	65
2	**8b**	$CH_2{=}CHCH_2Cl$	**11a**	70	13
3	**8b**	$CH_2{=}CHCHMeCl$	 $(n\text{-Bu})(H)C{=}C(n\text{-Bu})(CH_2CH{=}CHMe)$ [e)] **11b**	60	20
4	**8b**	$MeCH{=}CHCH_2Cl$		—	47
5	**8c** $R^1{=}Cl(CH_2)_3$ $BR^2_2{=}$9-BBN	$CH_2{=}CHCH_2Cl$	**11c** $R^1{=}Cl(CH_2)_3$	(30)	
6		$CH_2{=}CHCH_2Cl$	 $(n\text{-Hex})(H)C{=}C(H)(CH_2CH{=}CH_2)$	trace	30

a) All reactions were performed on a 1 mmol scale. b) Isolation was carried out on a 5 mmol scale. c) Identified by IR, NMR, and/or comparison with the authentic materials. d) By GLPC, based on alkenylboranes. e) Mixture of 2*E* and 2*Z*-isomers.

acetone-d_6 is shown in Scheme 1; a) oxidative insertion of Pd(0) into the C–B bond followed by b) H-abstraction from the solvent and c) reductive elimination. Supposedly, in contrast to the alkenylboranes derived from terminal alkynes, migration of the alkyl group of **8** to the α-carbon must proceed quite sluggishly due to bulky alkenyl group of **8** compared to that of **1**.

Cross-coupling of Alkenylboranes Catalyzed by Palladium Acetate. The mechanistic consideration of the protonolysis reaction as suggested above indicates that this reaction might proceed *via* an alkenylpalladium intermediate such as **10**. It appears possible that such an intermediate may be trapped by an appropriate olefin. Actually, allyl chloride reacted with the intermediate to give (*E*)-1,4-dienes (**11**) stereoselectively. The protonolysis reaction, however, competed with the cross-coupling reaction (Eq. 9). This problem was solved by using alkenyl-9-borabicyclo[3.3.1]nonane (alkenyl-9-BBN) as a starting material. (see, Table 5).



$$(R^1)(H)C{=}C(R^1)(BR^2_2) \xrightarrow[\text{Cat. Pd(OAc)}_2]{\text{Allyl chloride}} (R^1)(H)C{=}C(R^1)(CH_2CH{=}CH_2) + (R^1)(H)C{=}C(R^1)(H) \qquad (9)$$

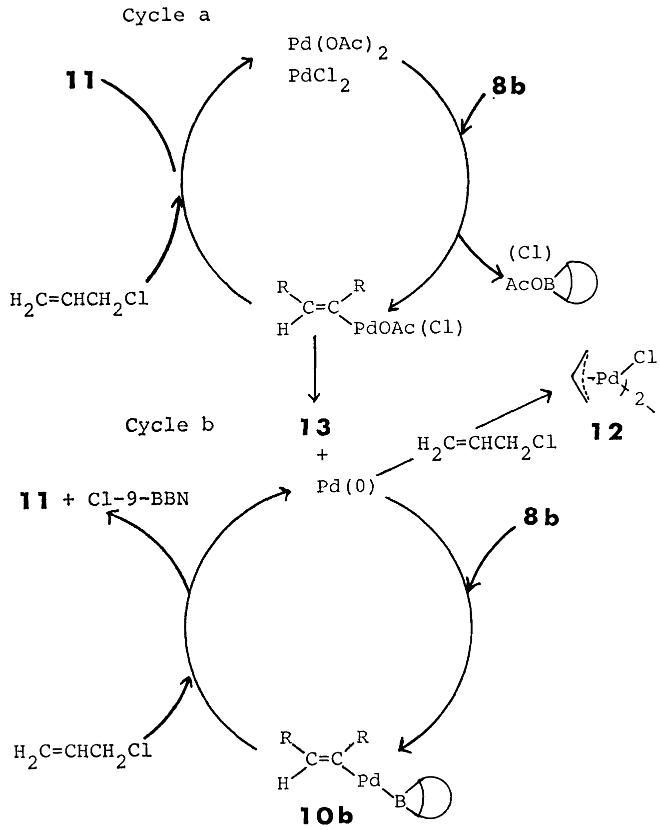
8a: $R^1{=}n$-Bu
$R^2{=}$Sia
8b: $R^1{=}n$-Bu
$BR^2_2{=}$9-BBN

11a: $R^1{=}n$-Bu **9a**

	11a	9a
From **8a**:	23%	65%
8b:	70%	13%

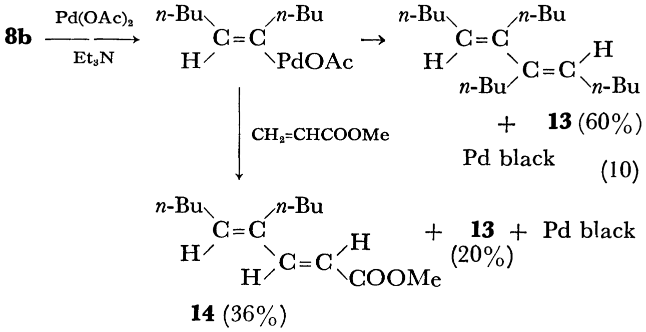
Allyl chloride and 3-chloro-1-butene underwent the effective cross-coupling (entries 2, 3, and 5), while crotyl chloride gave a poor result (entry 4). The cross-coupling reaction proceeded completely as S_N2' process and with retention of configuration of the double bond of alkenylboranes. Unfortunately the reaction of 1-alkenyl-9-BBN derived from terminal alkynes with allyl chloride gave only trace amounts of desired diene.

This reaction nearly completed within 30 min at room temperature, and at this time di-π-allyl-μ,μ′-dichlorodipalladium (**12**) was formed. Since it was confirmed that **12** did not react with **8a** or **8b**, **12** was not a real catalyst. Two catalytic cycles are possible for the reaction (Scheme 2); a) direct transmetallation of the B–C bond followed by insertion and elimination which is a process similar to Heck's[17)] and Larock's[18)] reaction, might be involved; b) oxidative addition of alkenyl boranes to Pd(0) produces **10**, which is considered to be an intermediate in the protonolysis reaction, and the subsequent insertion of allylic chloride and elimination give the product. The reaction of stoichiometric



Scheme 2.

amounts of palladium acetate with **8b** gave the dimeric product (**13**), presumably *via* alkenylpalladium acetate. In the presence of methyl acrylate[5] the cross-coupling product (**14**) was also obtained (Eq. 10). Therefore, there might be a possibility for the cycle a. However, cycle b can not be discarded on the basis of the following results; the addition of allyl chloride, after stirring the mixture of **8b** and catalytic amounts of palladium acetate for 1 h, also produced **11a** in a yield of 45%. In this system catalytic species is considered to be Pd(0) since palladium acetate must be reduced by the initial reaction[20] *via* the transmetallation and dimerization as shown in Eq. 10[21] Accordingly it is favorable to consider that b is a main cycle for this reaction and formation of **12** extinguishes Pd(0) species. In the reaction with crotyl chloride, the formation of **12** might prevail over the insertion of crotyl chloride into **10b** owing to its steric effect.[22]



Experimental

NMR spectra were recorded on a JEOL-PS-100 spectrometer; chemical shifts in CCl_4 are expressed in parts per Million relative to Me_4Si. IR spectra were recorded on a JASCO-IR A-1 and GLPC analyses were performed on a JEOL-JGC-20K instrument, using a 2m column packed with SE-30 or Silicone DC-550 on Celite 545 AW. GC-MS were measured on a HITACHI-MR-1 using a 1 m column (SE-30). Elemental analyses were performed by the Microanalytical Laboratory of Kyoto University, Kyoto, Japan. Air sensitive materials were handled *via* the standard techniques described in Chapter 9 of Ref. 14. The reaction flasks were fitted with a side arm capped with a rubber septum. All reactions were carried out under a static pressure of nitrogen.

Reagent-grade solvents were purified by standard techniques and kept over a drying reagent. BH_3: THF and 9-borabicyclo[3.3.1]nonane (9-BBN) were prepared according to Ref. 14. Alkenylboranes[14] were prepared *in situ* without distillation. (*E*)-5-Decenyl-9-BBN,[23] di[(*E*)-1-hexenyl]chloroborane,[24] and 2-[(*E*)-1-hexenyl][1,3,2]benzodioxaborole[13] were distilled and their physical data are listed in Ref. 25. Commercially available *n*-BuLi was titrated by Eastham's method.[26] $Pd(OAc)_2$,[27] $Pd_2(DBA)_3$,[28] $Pd(PPh_3)_4$,[29] and $Pd(AcAc)_2$[30] were prepared according to the known procedures. Spectral data of products are listed in Table 6.

General Procedure for Synthesis of 2. Syntheses of **2a**, **2c**, and **2d** were as follows. To a solution of $Pd(OAc)_2$ (5 mmol) and triethylamine (0.35 mmol) in THF (20 ml), **1** (5 mmol) was added. Palladium black soon precipitated from the resulting mixture. After stirring overnight at room

TABLE 6. SPECTRAL DATA OF PRODUCTS

Product	NMR	(IR cm^{-1})	Anal. (%) or MS
(*E*)-3,4-Dimethyl-1-phenylpentene (**2a**)	7.38—7.05 (5H, m), 6.35 (1H, d, J=15 Hz), 6.09 (1H, d-d, J=15, 7.5 Hz), 2.31—1.95 (1H, m), 1.80—1.35 (1H, m), 1.05 (3H, d, J=7 Hz), 0.93 (6H, d, 7 Hz)	965	Found: C, 89.88; H, 10.47 Calcd: C, 89.59; H, 10.41
(*E*)-2,3-Dimethyl-4-nonene (**2b**)	5.45—5.20 (2H, m), 2.20—1.70 (3H, m), 1.70—1.13 (5H, m), 1.13—0.95 (9H, m)	965	a)
(*E*)-1-Cyclohexyl-2-phenylethylene (**2c**)	7.41—7.08 (5H, m), 6.33 (1H, d, J=15 Hz), 6.03 (1H, d-d, J=15, 7 Hz), 2.37—2.01 (1H, m), 2.01—1.53 (6H, m), 1.53—1.02 (4H, m)	965	Found: H, 90.33; H, 9.71 Calcd: C, 90.26; H, 9.74
(*E*)-1-(*trans*-2-Methylcyclohexyl)-2-phenylethylene (**2d**)	7.41—7.05 (5H, m), 6.33 (1H, d, J=15.5 Hz), 5.94 (1H, d-d, J=15.5, 7.5 Hz), 1.98—1.53 (5H, m), 1.53—0.99 (5H, m), 0.92 (3H, d, J=6 Hz)	965	Found: C, 89.95; H, 10.19 Calcd: C, 89.94; H, 10.06
(*E*)-8-Chloro-2,3-dimethyl-4-octene (**2**)	5.40—5.16 (2H, m), 3.48 (2H, t, J=6 Hz), 2.34—1.98 (2H, m), 2.04—1.20 (4H, m), 1.05—0.75 (9H, m)	965	a)
(5*E*)-5-Butyl-2,5-decadiene (**11b**)	5.40—5.20 (2H, m), 5.02 (1H, bt, J=6 Hz), 2.70—2.50 (2H, m), 2.10—1.80 (4H, m), 1.62 (*E*-Me, d, J=4 Hz), 1.56 (*Z*-Me, d, J=4 Hz), 1.40—1.20 (8H, m), 0.90 (6H, bt, J=6 Hz)	965	M^+ (196)
(*E*)-8-Chloro-4-(chloropropyl)-1,4-octadiene (**11c**)	5.90—5.50 (1H, m), 5.20—4.80 (3H, m), 3.60—3.30 (4H, m), 2.70 (2H, d, J=6 Hz), 2.30—2.10 (4H, m), 1.80—1.70 (4H, m)	1635 990 910	M^+ (220) $M^+ - Cl$ (185)

a) Comparison with an authentic material prepared by Zweifel method.[3a)] temperature the mixture was concentrated under reduced pressure. Essentially pure products were obtained simply by passing this residue through an alumina column. **2b** and **2e** were isolated by the same method using 5 mmol of triethylamine. The investigation of the effect of amine was performed on 1 mmol scale and the reaction mixture was analyzed by GLPC. IR and NMR spectra of **2b** and **2e** were identified with those of authentic materials, prepared by the Zweifel method.[3a)] Other products exhibited the expected spectroscopic characteristics.

*Isomeric Purity of **2**.* In every case, the corresponding *Z*-isomers were synthesized by the Zweifel method; iodine-promoted intramolecular migration reaction.[3b)] The GLPC examination (DC-550) revealed that each of **2a**, **2c**, and **2d** had longer retention time than that of corresponding *Z*-isomer. On the other hand, each of **2b** and **2e** had almost the same retention time as that of the corresponding *Z*-isomer, making the analysis difficult. It was found, however, that the corresponding epoxides of these compounds were easily separated by GLPC (DC-550).[31)] Each Epoxide of *E*-isomers had shorter retention time than that of *Z*-isomers.

*Synthesis of **4**.* *a*): *n*-BuLi in hexane (2 mmol) was added to **3** (1 mmol) in THF (2 ml) at 0 °C. The resulting mixture was stirred for 30 min at 0 °C and then triethylamine (1 mmol) and $Pd(OAc)_2$ (1 mmol) were added. The mixture was stirred overnight. The formation of **4** was confirmed by GC-MS in comparison with an authentic material and GLPC examination by internal standard method revealed this solution contained **4** in 27% yield.

b): **6** (1 mmol) was prepared in situ by the slow addition of *n*-BuLi (1 mmol) to di[(*E*)-1-hexenyl]chloroborane (1 mmol) in THF at −78 °C. To this solution, $Pd(OAc)_2$ (1 mmol) and triethylamine (1 mmol) were added at room temperature. GLPC examination by the same method as above revealed that this solution contained **4** in 31% yield accompanied by **6** in 57% yield.

*General Procedure for the Synthesis of **9**.* Alkynes (5 mmol) were hydroborated by disiamylborane (5 mmol) to form alkenyldisiamylboranes (**8**). To this solution, $Pd(OAc)_2$ (0.5—0.1 mmol) was added under a static pressure of nitrogen at room temperature and the resulting mixture was stirred overnight. THF was removed under reduced pressure. The products were isolated through an alumina column. All products were identified by comparison with authentic materials which were obtained commercially or by the reduction of the corresponding alkynes.[32)] IR spectra of all products showed no absorption at 965 cm^{-1}.

Deuterium Labelling Study. 5-Decyne was hydroborated by disiamylborane (1 mmol). THF was removed under reduced pressure. To remove THF completely, BCl_3 (2 mmol) in hexane was added to this residue and precipitated THF: BCl_3 was filtrated. The solvent and excess BCl_3 were removed under reduced pressure and the residue was utilized for the protonolysis reaction in acetone-d_6 (2 ml) catalyzed by $Pd(OAc)_2$ (0.1 mmol). The deuterium content was determined by GC-MS and NMR to be 88%.

*General Procedure for (E)-1,4-Dienes (**11**).* To a solution of alkenyl-9-BBN (5 mmol) and allyl chloride (5 mmol), $Pd(OAc)_2$ (0.5—0.1 mmol) was added and the resulting mixture was stirred overnight at room temperature. The products were isolated through an alumina column. Stereochemistry of **11a** was determined as follows. An authentic sample of **11a** was prepared according to Eisch method;[33a)] NMR (δ, CCl_4) 5.65 (d-d, J=18, 10 Hz, 1H), 5.00 (t, J=6 Hz, 1H), 4.98—4.76 (m, 2H), 2.66 (d, J=6 Hz, 2H), 2.10—1.80 (m, 4H), 1.52—1.08 (m, 8H), 0.90 (t, J=6 Hz, 6H). IR (cm^{-1}), 990, 910. (*Z*)-4-Butyl-1,4-nonadiene, stereoisomer of **11a**, was prepared by the Zweifel method;[33b)] 5-decyne (5 mmol) was hydroaluminated by $(i\text{-Bu})_2$-AlHMeLi, prepared from $(i\text{-Bu})_2AlH$ and MeLi. Then allyl bromide (10 mmol) in THF was added and resulting mixture was refluxed for 2 h. After addition of aq H_2SO_4 (0.5 M), the resulting mixture was extracted several times with hexane. The hexane solution was washed with aq $NaHCO_3$ and sat. solution of NaCl. Hexane was evaporated and the residue was chromatographed over alumina by using petroleum ether. Kuhgel rohr distillation gave (*Z*)-4-butyl-1,4-nonadiene; bp 140—160 °C/20 mmHg (40% yield), NMR (δ, CCl_4), 5.65 (d-d, J=10 Hz, 1H), 5.10 (t, J=6 Hz, 1H), 5.06—4.80 (m, 2H), 2.73 (d, J=6 Hz, 2H), 2.16—1.80 (m, 4H), 1.52—1.14 (m, 8H), 0.88 (bt, J=6 Hz, 6H), IR (cm^{-1}) 1630, 990, 905. Consequently, these isomers could be clearly discriminated by the chemical shift at the region between 2.66 and 2.73 ppm and NMR spectrum of the reaction product completely accorded with that of 4*E*-isomer. Furthermore, these isomers could be separated by GLPC (3m, 30% of Apiezon on Celite 545 AW). The retention time of 4*Z*-isomer was shorter than that of 4*E*-isomer, and the GLPC analysis of the reaction product showed a single sharp peak, whose retention time accorded with that of 4*E*-isomer. Accordingly, the reaction product can be assigned to pure 4*E*-isomer. This result indicates that the cross-coupling products retain the stereochemistry of the starting alkenyl-9-BBN. The stereochemical result could apply to other cross-coupling reaction. **11b** was assigned to a mixture of 2*E* and 2*Z*-isomers, since the IR spectrum showed a weak absorption at 965 cm^{-1} region.

*Synthesis of **13**.* To a THF solution (4 ml) of Et_3N (1 mmol) and $Pd(OAc)_2$ (1 mmol), **8b** (1 mmol) was added. After stirring for 1 h at room temperature, palladium black was precipitated. GLPC examination revealed that **13** was formed in 60% yield, the structure of which was confirmed by GC-MS in comparison with an authentic material.[34)]

*Synthesis of **14**.* To a THF solution (4 ml) in which $Pd(OAc)_2$ (1 mmol), Et_3N (1 mmol), and methyl acrylate (2 mmol) were dissolved, **8b** (1 mmol) was added at room temperature. After stirring for 1 h, GLPC examination revealed that **14** and **13** were formed in 36 and 20% respectively. **14** was isolated through an alumina column by using hexane; NMR (δ, CCl_4), 7.10 (d, J=16 Hz, 1H), 5.80 (t, J=6 Hz, 1H), 5.68 (d, J=16 Hz, 1H), 3.64 (s, 3H), 2.30—2.00 (m, 4H), 1.60—1.20 (m, 8H), 1.00—0.80 (m, 6H). MS; 223 (M^+).

Mechanistic Study. THF solution (2 ml) of $Pd(OAc)_2$ (10 mg) showed an absorption at 400 nm (ε=30). By the addition of **8a** or **8b** (1 mmol) this absorption disappeared, and then the solution was stirred for 1 h. After addition of allyl chloride (1 mmol), a new absorption at 350 nm appeared in UV spectrum. This absorption corresponded with that of di-π-allyl-μ,μ'-dichlorodipalladium (**12**) in THF. In the stoichiometric reaction (1 mmol scale), **12** was isolated in 10% yield by column chromatography (alumina–hexane). GLPC examination revealed that the cross-coupling took place within 30 min and yield was 45%.

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