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J. Am. Chem. Soc., **2005**, 127 (1), 126-131• DOI: 10.1021/ja044662q • Publication Date (Web): 03 December 2004

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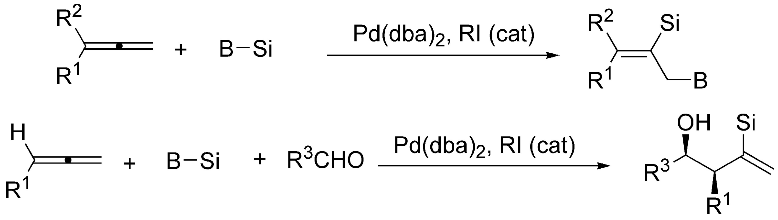

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Unusual Palladium-Catalyzed Silaboration of Allenes Using Organic Iodides as Initiators: Mechanism and Application

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Abstract: A highly regio- and stereoselective method for the synthesis of various 2-silylallylboronates **7** from allenes **1** and 2-(dimethylphenylsilanyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**5**) catalyzed by palladium complexes and initiated by organic iodides is described. Treatment of monosubstituted aryl and alkylallenes $RCH{=}C{=}CH_2$ (**1a**−**m**) and 1,1-dimethylallene (**1n**) with borylsilane **5** in the presence of Pd(dba)$_2$ (5 mol %) and organic iodide **3a** (10 mol %) afforded the corresponding silaboration products **7a**−**n** in moderate to excellent yields. This catalytic silaboration is totally regioselective with the silyl group of **5** adding to the central carbon and the boryl group to the unsubstituted terminal carbon of allene. Furthermore, the reactions show very high *E* stereoselectivity with the *Z*/*E* ratios lying in the range from 1/99 to 7/93. In the absence of an organic iodide, silaboration of **1** with **5** still proceeds, but gives products having completely different regiochemistry as that of **7**. The silaboration chemistry can be applied to the synthesis of homoallylic alcohols. Treatment of allenes (**1**) with borylsilane **5** and aldehydes **14** in the presence of Pd(dba)$_2$ (5 mol %) and **3a** (10 mol %) at 80 °C in ethyl acetate for 5 h afforded homoallylic alcohols **15a**−**p** in one pot in good to excellent yields, with exceedingly high syn selectivity ($>$93%). Mechanistic pathways involving an unusual palladium-catalyzed three-component assembling reaction of dimethylphenylsilyl iodide, allene **1**, and borylsilane **5** were proposed to account for these catalytic reactions.

1. Introduction

Addition of metal−metal bonds of the main group elements to alkenes and alkynes catalyzed by transition-metal complexes has attracted great attention in recent years.[1] These reactions provide a convenient route for synthesizing organometallic compounds having vinylic and allylic metal moieties that are useful intermediates for organic synthesis.[2] In most cases, the catalytic reaction proceeds via oxidative addition of the bimetallic substrate to the transition-metal catalyst as a key step.[1] Transition-metal-catalyzed addition of diboron to unsaturated carbon−carbon bonds[3,4] provides an efficient route to diboronic compounds, which are versatile intermediates in organic synthesis.[5] Platinum complexes are known to readily catalyze the addition of diboron to unsaturated carbon−carbon bonds to provide diboronic compounds, whereas the palladium complexes, which are the best catalysts for silyl-[6] and stannylation,[7] are not active for the diboration of alkynes and alkenes. The difference in the reactivity of Pt and Pd lies in the ability to undergo oxidative addition of the B−B bond to these metal (0) species.[8] While stable oxidative adducts of diboron to Pt species are reported, no oxidative addition of diboron to Pd are known.[9] In a preliminary communication, we showed an unusual organic

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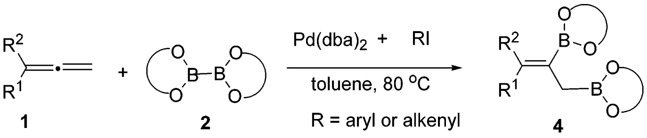
10.1021/ja044662q CCC: $30.25 © 2005 American Chemical Society

iodide-initiated and palladium-catalyzed diboration of allenes (Scheme 1).[10] This catalytic reaction is completely regioselective, with one boryl group adding to the middle carbon and the other to the nonsubstituted terminal carbon of the allene moiety. A new mechanistic pathway involving a three-component assembling reaction[11,12] was proposed to account for this diboration.

Scheme 1

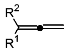
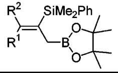


Herein, we wish to report the extension of this chemistry to the addition of borylsilane to allenes to give 2-silylallylboronates. This new silaboration shows remarkably high regio- and stereoselectivity, with the regiochemistry of the silaboration product being totally different from that reported previously.[13] The products generated in situ can further be used as allylation reagents for aldehydes. This method offers a mild and convenient route for the synthesis of homoallylic alcohols[14] in one pot from allenes, borylsilane, and aldehydes, with excellent regio- and syn selectivity in good to excellent yields.

2. Results and Discussion

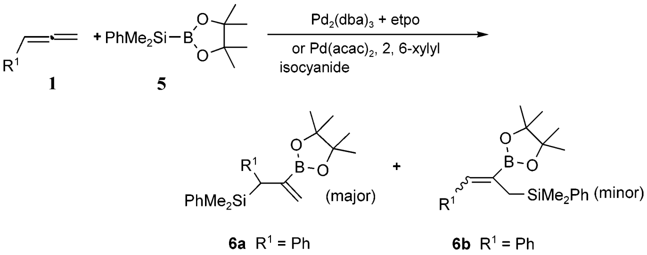
2.1. Palladium-Catalyzed Silaboration of Allenes. Silaboration of unsaturated carbon−carbon bonds via the oxidative addition of a Si−B bond to transition-metal catalysts as a key step is known.[13,15] The silaboration of allenes catalyzed by palladium complexes gave two regioisomers, both having the boryl group attached to the central carbon of the allene moiety (Scheme 2).[13] The prior unusual organic iodide-initiated and palladium-catalyzed diboration of allenes prompted us to investigate the addition of borylsilane to allenes under similar reaction conditions.

Table 1. Results of Addition of Borylsilane **5** to Allenes **1**[a]

entry	allene				product		Z/E	yield
			R^1	R^2				(%)[b]
1	**1a**		Ph	H	**7a**		<1/99	82 (87)
2	**1b**		1-naphthyl	H	**7b**		<1/99	79 (85)
3[c]	**1c**		*p*-MeOC_6H_4	H	**7c**		<1/99	93 (99)
4[c]	**1d**		*m*-MeOC_6H_4	H	**7d**		<1/99	86 (92)
5[c]	**1e**		*o*-MeOC_6H_4	H	**7e**		<1/99	44 (50)
6[d]	**1f**		*p*-ClC_6H_4	H	**7f**		<1/99	81 (87)
7[d]	**1g**		*p*-BrC_6H_4	H	**7g**		<1/99	79 (85)
8[d]	**1h**		*m*-BrC_6H_4	H	**7h**		<1/99	76 (83)
9	**1i**		*p*-MeOCC_6H_4	H	**7i**		<1/99	85 (89)
10[d]	**1j**		*p*-EtO_2CC_6H_4	H	**7j**		<1/99	84 (88)
11	**1k**		*n*-Bu	H	**7k**		5/95	84 (89)
12	**1l**		cyclopentyl	H	**7l**		7/93	82 (87)
13	**1m**		cyclooctyl	H	**7m**		7/93	70 (75)
14[c]	**1n**		Me	Me	**7n**			62 (70)

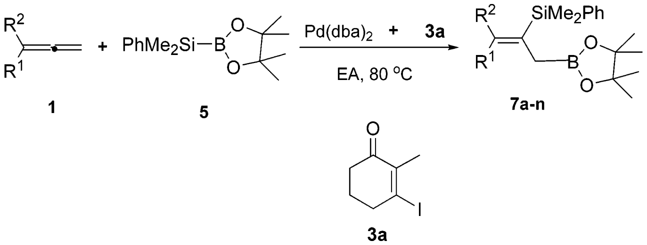
[a] Unless stated otherwise, all reactions were carried out using alkenyl iodide **3a** (0.0500 mmol, 10 mol %), Pd(dba)$_2$ (0.0250 mmol, 5 mol %), borylsilane **5** (0.500 mmol), and allene **1** (1.00 mmol) in ethyl acetate (0.50 mL) at 80 °C under nitrogen for 5 h. [b] Isolated yields; yields in parentheses were determined by ^{1}H NMR integration method using DMF as an internal standard. [c] Reaction was carried out at room temperature. [d] CH_3CN is used as the solvent.

Scheme 2



In the presence of Pd(dba)$_2$ (5.0 mol %) and 3-iodo-2-methyl-2-cyclohexen-1-one (**3a**) (10 mol %), phenylallene (**1a**) reacts with borylsilane **5**[16] at 80 °C in ethyl acetate to give 2-silylallylboronate **7a** in 87% yield (Scheme 3 and Table 1). This catalytic silaboration is completely regioselective, with the silyl group of **5** adding to the central carbon and the boryl group to

Scheme 3



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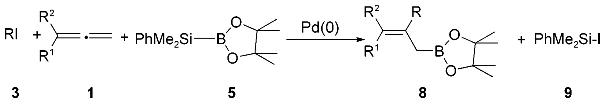
the unsubstituted terminal carbon of allene **1a**. Furthermore, the reaction shows completely stereoselectivity giving only the corresponding *E* isomer within the NMR detecting limit. Product **7a** was characterized by its ^{1}H and ^{13}C NMR and mass spectral data.

No silaboration product was formed in the absence of Pd(dba)$_2$. However, without alkenyl iodide **3a**, silaboration of phenylallene **1a** by **5** still proceeded to give products **6a** and **6b** in a 3:1 ratio and in a combined yield of 40% (Scheme 2).[13] It is noteworthy that these two products with the boryl group attached to the central carbon of the allene moiety are completely different in regiochemistry from **7a**. The use of 2−4 mol % **3a** and 5.0 % Pd(dba)$_2$ relative to borylsilane **5** led to the formation of a mixture of products **6a**, **6b**, and **7a**. Products **6a** and **6b** were completely inhibited as **3a** employed in the reaction solution was increased to 8%. Further increase of **3a** did not significantly change the yield of **7a**, but a substantial amount of **3a** was left unreacted in the solution.

The reaction of **1a** with **5** in the presence of **3a** depends greatly on the catalyst used. In addition to Pd(dba)$_2$, other phosphine-free Pd complexes, Pd(OAc)$_2$ and Pd(CH$_3$CN)$_2$Cl$_2$, tested also show activities for the addition reaction, but with lower yields (72 and 66%) of product **7a**. The reaction using Pd(dba)$_2$ as the catalyst is strongly inhibited by the phosphine present in the solution. Addition of 1, 2, and 4 equiv of PPh$_3$ to the Pd(dba)$_2$-catalyzed reaction solution reduces the yield of **7a** to 53, 23, and 0% yields, respectively. In agreement with the foregoing observation, Pd(PPh$_3$)$_2$Cl$_2$ and Pd(dppe)Cl$_2$ show low catalytic activity, giving **7a** in 5 and 46% yields, respectively. The selection of solvent is crucial for achieving a high yield of product **7a**. Ethyl acetate and acetonitrile appear to be the best solvents tested, giving **7a** in 87 and 85% yields, respectively. Toluene and DMF are less effective, affording **7a** in 67 and 10% yields, respectively. The observed low yield of **7a** in DMF is due to incomplete reaction, probably caused by the decomposition of the palladium complex that gave black precipitate in the reaction.

While the presence of **3a** is essential for the catalytic reaction (see Scheme 4) to proceed, **3a** can be replaced by other organic iodides. Aryl iodides, such as *p*-iodoanisole and *p*-iodoacetophenone, are also efficient initiators for the catalysis, giving **7a** in 85 and 87% yields, respectively. Interestingly, I$_2$ and Me$_3$SiI also promote the silaboration of **1a** successfully to afford **7a** in 85 and 75% yields, respectively. On the other hand, the use of 4-bromoacetophenone gave only a trace of the desired product.

Scheme 4

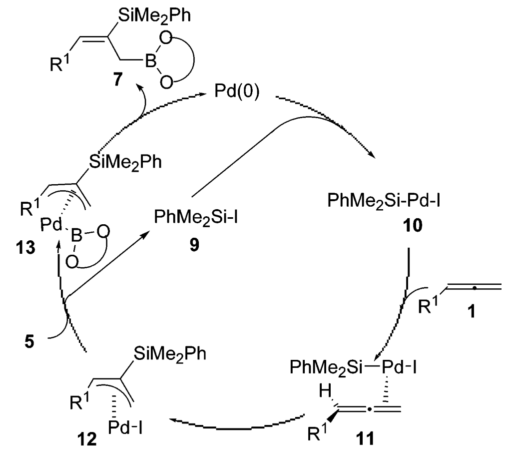


Under similar reaction conditions, various monosubstituted aryl and alkylallenes RCH═C═CH$_2$ (**1b**−**m**) and 1,1-dimethylallene (**1n**) underwent silaboration with **5** in the presence of Pd(dba)$_2$ and **3a** to give the corresponding silaboration products **7b**−**n** in moderate to excellent yields. As revealed in Scheme 3 and Table 1, the addition reaction is compatible with various functional groups on the allenes (entries 3−10). Again, all of these reactions are completely regioselective. A key evidence for the proposed regiochemistry with the boryl moiety adding to the unsubstituted terminal carbon of the allene moiety is the presence of a broad methylene carbon signal at 14−17 ppm in their ^{13}C NMR spectra due to the interaction of the methylene carbon and boron nuclei in products **7a**−**n**.[15f,g] The stereochemistry of the products derived from monosubstituted allenes **1** was determined by typical ^{1}H NMR NOE experiments. For aryl allenes, the corresponding *E* isomers are the sole products observed (entries 1−10). For alkyl-substituted allenes, the reactions gave *E* isomers as the major species with *Z*/*E* ratios between 7/93 and 5/95 (entries 11−13). It is noteworthy that the regiochemistry of products **7a**−**m** is entirely different from that observed previously using Pd(acac)$_2$/2,6-xylyl isocyanide[13a] or Pd$_2$(dba)$_3$/etpo[13b] as the catalyst systems (Scheme 2).

3. Mechanistic Consideration

3.1. Mechanism for Silaboration of Allenes. The observation that an aryl iodide, alkenyl iodide, I$_2$, or Me$_3$SiI was required for the catalytic reaction and that the use of organic iodide changes completely the regiochemistry of the catalytic reaction is crucial to the understanding of the catalytic mechanism. To account for the present palladium-catalyzed and organic halide-initiated silaboration of allenes, possible pathways, as depicted in Schemes 4 and 5, are proposed. The organic iodide likely acts as an initiator undergoing oxidative addition with Pd(0) to give a palladium(II) intermediate that reacts with allene **1** and borylsilane **5** to afford product **8** and a common product silyl iodide **9** (Scheme 4), respectively. Compound **9** then reacts with Pd(0) to begin the catalytic reaction (Scheme 5). Oxidative addition of **9** to Pd(0) species affording Pd(II) intermediate **10** is followed by coordination and insertion of allene **1** to give Pd−allyl species **12**, with the silyl group attached to the central carbon of the allyl group. Transmetalation of **12** with borylsilane **5** regenerates **9** and affords Pd−allyl species **13**. Reductive elimination of **13** yields the final product **7** and regenerates the Pd(0) catalyst. The formation of **8** is evidenced by the observation of **8b** (R^{1} = R^{2} = Me; R = *p*-MeCOC$_6$H$_4$) in GC−MS and ^{1}H NMR in ca. 4% yield from the reaction of 1,1-dimethylallene (**1n**), borylsilane **5**, and *p*-iodoacetophenone (**3b**). The role of silyl iodide **9** in the catalytic cycle is also supported by the fact that Me$_3$SiI is an effective initiator for the present catalytic reaction. The observation that phosphine retards the catalytic reaction may be explained in terms of the competition of phosphine and the allene substrate for coordination to palladium intermediate **10**.

Scheme 5



Similar behavior was found in the carbosilylation of allenes catalyzed by palladium complexes.[11a,c]

The nature of the present catalytic silaboration reaction is further unraveled from the results of silaboration of phenylallene (**1a**) with borylsilane **5** in the presence of various amount of 3-iodo-2-methyl-2-cyclohexen-1-one (**3a**) catalyzed by Pd(dba)$_2$ (5%). In the absence of **3a**, the reaction gave products **6a** and **6b** (see Scheme 2), while in the presence of 2−4% **3a** relative to borylsilane **5**, the silaboration gave a mixture of **6a**, **6b**, and **7a**. Products **6a** and **6b** were totally inhibited as **3a** employed in the reaction solution was increased to 8%. Further increase of **3a** did not significantly change the yield of **7a**, and a substantial amount of organic iodide **3a** was left unreacted in the solution. These experiments appear to show that silaboration of allenes via direct oxidative addition of **5** to Pd(0) (Scheme 2) is completely inhibited if the organic iodide **3a** present is greater than the Pd catalyst used. Similar results were also observed for the silaboration of allene **1n** with borylsilane **5** in the presence of various amount of *p*-iodoacetophenone (**3b**) catalyzed by Pd(dba)$_2$. The above results indicate that silyl iodide **9** is much more reactive toward Pd(0) than most organic iodides **3**. In summary, during the present catalytic reaction, organic iodide **3**, borylsilane **5**, and silyl iodide **9** are competing for the palladium(0), and it appears that **5** $\ll$ **3** $\ll$ **9** in the reactivity for the oxidative addition to the palladium(0). The initial amount of silyl iodide **9** produced was controlled by the reaction shown in Scheme 4. The high reactivity of **9** compared to that of **3** toward Pd(0) leads to the result that the three-component assembling reaction in Scheme 4, mediated by the Pd complex, is limited to about one turnover. The amount of three-component assembling product **8** (4% for **8b** ($R^1 = R^2 =$ Me; R = *p*-$MeCOC_6H_4$) is approximately equal to that of the Pd catalyst used (5%).

The observed regioselectivity is determined at the step of transmetalation of **12** with **5**. A completely different regioselectivity for the product would result if a boryl iodide was generated instead of silyl iodide **9**. The observed stereoselectivity may be explained on the basis of a face-selective coordination of allenes to the Pd center (Scheme 6). For a monosubstituted allene, selective coordination of the terminal double bond to the Pd moiety at the face opposite to the substituents R^1 (structure **11a**) is favorable to avoid steric congestion. This face selection leads to the formation of Pd−π-allyl species **12**, having an anti stereochemistry, and eventually to the formation of *E*-form products.

Scheme 6

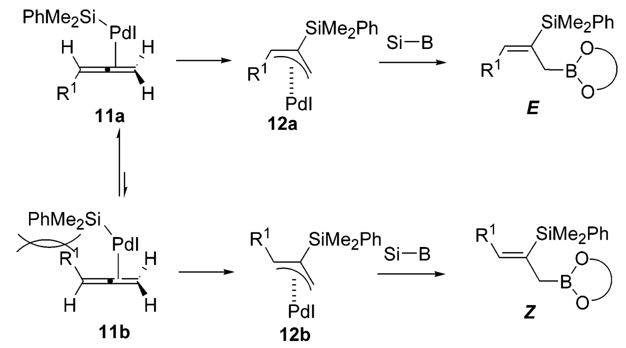
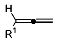
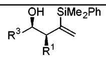


Table 2. Results of Allylation of Aldhydes[a]

entry	allene		aldehyde		product	*syn/anti*	yield
		R^1	R^3CHO	R^3			(%)[b]
1	**1a**	Ph	**14a**	Ph	**15a**	>99/1	96
2	**1a**	Ph	**14b**	*p*-$MeOC_6H_4$	**15b**	>99/1	55
3	**1a**	Ph	**14c**	*p*-$MeOCOC_6H_4$	**15c**	>99/1	93
4	**1a**	Ph	**14d**	*p*-ClC_6H_4	**15d**	>99/1	92
5	**1a**	Ph	**14e**	*p*-MeC_6H_4	**15e**	>99/1	70
6	**1a**	Ph	**14f**	*p*-$MeOCC_6H_4$	**15f**	>99/1	60
7	**1a**	Ph	**14g**	*p*-CNC_6H_4	**15g**	>99/1	85
8	**1a**	Ph	**14h**	2-thienyl	**15h**	>99/1	74
9	**1a**	Ph	**14i**	*n*-pentyl	**15i**	>99/1	67
10	**1a**	Ph	**14j**	*n*-propyl	**15j**	>99/1	70
11	**1i**	*p*-$MeOCC_6H_4$	**14a**	Ph	**15k**	>99/1	86
12	**1j**	*p*-$EtO_2CC_6H_4$	**14a**	Ph	**15l**	>99/1	87
13	**1c**	*p*-$MeOC_6H_4$	**14a**	Ph	**15m**	>99/1	70
14[c]	**1k**	*n*-Bu	**14a**	Ph	**15n**	95/5	92
15	**1o**	cyclohexyl	**14a**	Ph	**15o**	93/7	75
16	**1l**	cyclopentyl	**14a**	Ph	**15p**	93/7	85

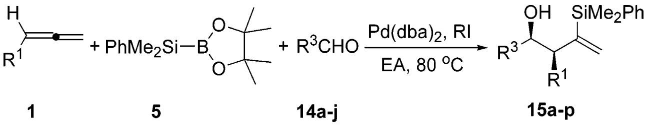
[a] Unless stated otherwise, all reactions were carried out using **3a** (0.0500 mmol, 10 mol %), Pd(dba)$_2$ (0.0250 mmol, 5 mol %), borylsilane **5** (0.500 mmol), allene **1** (1.00 mmol), and aldehyde **14** (1.00 mmol) in ethyl acetate (0.50 mL) at 80 °C for 5 h. [b] Isolated yields based on the borylsilane used. [c] The reaction experiment was run for 48 h at room temperature instead of 80 °C for 5 h.

4. Application of Silaboration of Allenes

4.1. Stereoselective One-Pot Allylation of Aldehydes. The allylation of aldehydes to give homoallylic alcohols is one of the most powerful synthetic methods in modern organic chemistry.[17] Functionalized homoallylic alcohols are a class of valuable synthetic intermediates used in the construction of a wide variety of complex natural products.[18] Despite numerous methods that are available, only a few of them offer highly stereocontrolled routes for the allylation of aldehydes.[19] Herein, we wish to describe a new and convenient way for the preparation of homoallylic alcohols via the application of the present silaboration chemistry.

Treatment of phenylallene (**1a**) (2 equiv) with borylsilane **5** and benzaldehyde (**14a**) (2 equiv) in the presence of Pd(dba)$_2$ (5 mol %) and alkenyl iodide **3a** (10 mol % relative to **5**) at 80 °C in ethyl acetate for 5 h afforded homoallylic alcohol **15a** in 96% yield (Scheme 7 and Table 2) with excellent syn selectivity (>99%). Product **15a** with the silyl group of **5** adding to the central carbon and the benzaldehyde moiety adding to the phenyl-substituted carbon of allene **1a** was fully characterized by its ^{1}H and ^{13}C NMR and mass spectral data. The ^{1}H NMR spectrum of **15a** showed characteristic resonances at δ 6.13 and

Scheme 7



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(16) For the synthesis of 2-(dimethylphenylsilanyl)-4,4,5,5-tetramethyl[1,3,2]-dioxaborolane (**5**), see: Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647.

(17) For a recent review on allylmetal addition, see: (a) Denmark, S. E.; Almstead, N. G. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH: Weinheim, Germany, 2000; Chapter 10, pp 299−402. (b) *Stereoselective Synthesis, Methods of Organic Chemistry* (Houben-Weyl), Edition E21; Helmchen, G., Hoffmann, R., Mulzer, J., Schaumann, E., Eds.; Thieme: Stuttgart, Germany, 1996; Vol. 3, p 1357.

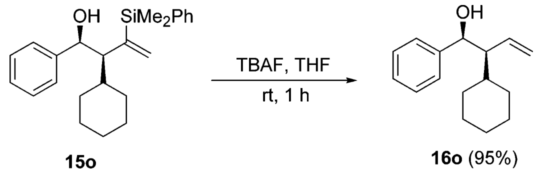
(18) Chemler, S. R.; Roush, W. R. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH: Weinheim, Germany, 2000; Chapter 10, pp 403−490.

(19) For a mini review on allylation reaction by addition of boron and silicon reagents, see: Kennedy, J. W. J.; Hall, D. G. *Angew. Chem., Int. Ed.* **2003**, *42*, 4732.

5.67 ppm for the geminal methylene protons and at δ 5.14 and 3.79 ppm, both as doublets for the protons on the methine carbons to which the OH and R^1 (Ph) groups are attached, respectively. This multiple component assembling reaction provides a unique route for the synthesis of homoallylic alcohols in one pot in high yields with excellent regio- and stereoselectivity. The present allylation of benzaldehyde (**14a**) also proceeded if **14a** was added after the silaboration of phenylallene by borylsilane **5** was complete, but the yield of product **15a** is only 72%.

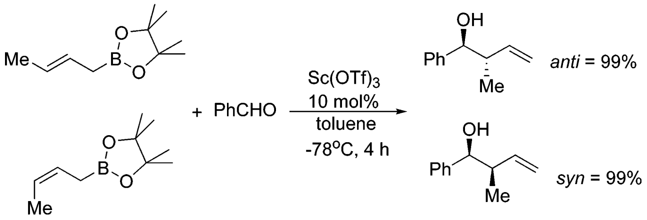
To examine the scope and limitation of this Pd-catalyzed and organic iodide-initiated reaction, different allenes and aldehydes were tested, and the results are summarized in Table 2. Under reaction conditions similar to those for the formation of **15a**, various aromatic and aliphatic aldehydes **14b**−**j** react effectively with phenylallene (**1a**) and borylsilane **5** to afford the corresponding homoallylic products **15b**−**j**, respectively, in good to excellent yields with very high syn selectivity (entries 2−10). Even thiophene-2-carbaldehyde reacts with phenylallene and borylsilane to give the expected homoallylic alcohol **15h** in 74% yield (entry 8). In addition to phenylallene (**1a**), substituted phenylallenes also reacted smoothly with benzaldehyde **14a** and **5** to furnish the corresponding allylation products **15k**−**m** in 70−87% yields, with extremely high syn selectivity. Similarly, the assembling reaction of aliphatic allenes, such as *n*-butylallene **1k**, cyclopentylallene **1l**, and cyclohexylallene **1o**, with **5** and **14a** furnishes the corresponding homoallylic alcohols **15n**−**p** in 75−92% yields. The reaction tolerates a variety of functionalities, such as alkyl, cyano, chloro, acetyl, methoxy, and ester groups, on the aromatic ring of aldehydes and of allenes. In all cases, syn homoallylic alcohols are formed predominately. The syn/anti ratios are greater than 99/1 for aromatic allenes (entries 1−13), but the ratios drop slightly to ~93/7 for aliphatic allenes (entries 14−16). The syn stereochemistry of product **15o** was further confirmed by the desilylation of this compound by TBAF ($(n\text{-Bu})_4N^+F^-$) in THF at room temperature (Scheme 8). The ^{1}H NMR data of desilylated product **16o** are identical to those of a compound reported previously that has the same structure and stereochemistry as shown in **16o**.[20] The scope of the present palladium-catalyzed multiple component reaction is limited to aldehydes and monosubstituted allenes. Attempts to use ketones and disubstituted allenes, such as **1n**, as substrates for the reaction failed to give any expected products.

Scheme 8



The excellent *E* selectivity of the silaboration product formed in situ is responsible for the formation of homoallylic alcohols with excellent syn selectivity. The product is formed with the *preservation of diastereospecificity*, and the results are in agreement with the literature methods for the addition of allylboranes to aldehydes.[19] For example, it is known that the (*E*)- or (*Z*)-crotylboron pinacolates react with benzaldehyde in the presence of $Sc(OTf)_3$ to give homoallylic products with exclusive anti and syn selectivity, respectively (Scheme 9).[21]

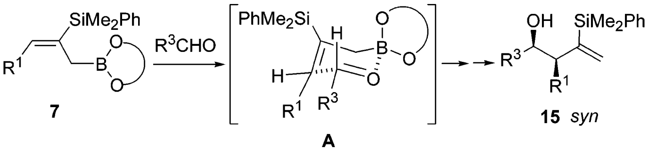
Scheme 9



There are several appealing features of the present reaction. First, the reaction proceeds via multiple bond formation and breaking steps, and yet the final homoallylic alcohols are obtained in excellent yields and stereoselectivity, indicating that each step in the reaction is highly efficient and selective. Second, in contrast to most allylation reactions of aldehydes using allylboronates, the formation of allylic alcohol **15** does not require an external Lewis acid, such as $AlCl_3$, $BF_3{\cdot}OEt_2$, or $Sc(OTf)_3$.[21,22] Third, unlike other reactions known for the synthesis of allylic alcohols, the present allylation of aldehydes proceeds via a one-pot multicomponent assembling reaction of allenes, borylsilanes, and aldehydes. Finally, these homoallylic alcohols consist of a vinylsilyl group,[23] providing the possibility for further transformation.

4.2. Mechanism for Allylation of Aldehydes. The formation of homoallylic alcohols from this palladium-catalyzed reaction of allenes, silaborane, and aldehydes is intriguing in view of the extensive bond formation and breaking processes required. The catalytic reaction probably occurs via two separated parts. A mechanistic pathway similar to that for the silaboration of allenes, as shown in Schemes 4 and 5, to give the corresponding 2-silylallylboronates **7** likely occurs first. The 2-silylallylboronate product then undergoes allylation with aldehydes **14** in a highly selective fashion to give the final homoallylic alcohols **15**. A key evidence for this two-part mechanism comes from the observation that silaboration product **7a** reacts with benzaldehyde (**14a**) directly at room temperature for 24 h to afford the expected homoallylic product **15a** in 60% yield. To account for the exceedingly high syn selectivity of the reaction, we proposed that the allylation of aldehydes by 2-silylallylboronates **7** proceeds via a six-membered chairform cyclic transition state **A**, with the silyl and R^3 group from the aldehyde occupying the equatorial positions and the R^1 from allene occupying the axial position of **A**, as depicted in Scheme 10. Similar cyclic transition states have been employed for the allylation of aldehydes by various allylmetal reagents.[19]

Scheme 10



Six-membered cyclic transition state

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[20] Chang, H.-M.; Cheng, C.-H. *Org. Lett.* **2000**, *2*, 3439. (b) Brown, H. C.; Narla, G. *Tetrahedron Lett.* **1997**, *38*, 219. (c) Knochel, P.; Sidduri, A.; Rozema, M. *J. Org. Chem.* **1993**, *58*, 2694.

[21] Ishiyama, T.; Ahiko, T. A.; Miyaura, N. *J. Am. Chem. Soc*, **2002**, *124*, 12414.

[22] Lachance, H.; Lu, X.; Gravel, M.; Hall, D. *J. Am. Chem. Soc.* **2003**, *125*, 10160 and references therein.

[23] Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981; pp 97−124. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer: Berlin, 1983; pp 173−205. (c) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988; pp 25−37. (d) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1988; Part 2. (e) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063.

5. Conclusions

We have demonstrated a new and efficient method for silaboration of allenes catalyzed by palladium complexes and initiated by organic iodides. The present methodology provides a convenient and general route to various 2-silylallylboronates **7** in good yields with excellent regio- and stereoselectivity. The mechanism for the silaboration of allenes is extraordinary and proceeds via an unusual three-component assembling pathway. The products formed are totally different in regio- and stereochemistry from those reported previously using palladium complexes as the catalysts. In addition, a new method for the stereoselective synthesis of homoallylic alcohols from the reaction of borylsilane, allenes, and aldehydes catalyzed by palladium complexes and initiated by organic iodide is described. Extensive bond formation and breaking processes are required for the formation of homoallylic alcohols, and yet the yield and selectivity are excellent. The methodology is compatible with a wide variety of functional groups on both allenes and aldehydes.

6. Experimental Section

Procedure for 2-(Dimethylphenylsilanyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (5). To a stirred solution of 4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (pinacolborane) (128.0 mmol) in hexane (60 mL) was added dimethylphenylsilyllithium (ca. 1.0 mol/L in THF, 62 mL, 62 mmol) dropwise at 0 °C over 30 min. Dimethylphenylsilyllithium (ca. 1.0 mol/L in THF) was freshly prepared by treating chlorodimethylphenylsilane with 4.0 equiv of lithium in THF. After the addition, the cooling bath was removed. The mixture was stirred overnight at room temperature. Evaporation of the volatile materials gave a white residual solid, which was taken up to remove material insoluble in hexane. After suction filtration under nitrogen, the filtrate was concentrated in vacuo. Distillation of the residue gave silylborane **5** as colorless liquid.[16]

Procedure for the Silaboration of Allenes. To a 10 mL sidearm flask were added 3-iodo-2-methyl-2-cyclohexen-1-one (**3a**) (0.0500 mmol, 10 mol %), Pd(dba)$_2$ (0.0250 mmol, 5 mol %), and 2-(dimethylphenylsilanyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**5)** (0.500 mmol). The system was evacuated and purged with nitrogen three times. Ethyl acetate (0.50 mL) and allene (**1**) (1.00 mmol) were added to the system, and the reaction mixture was stirred at 80 °C for 5 h. After the reaction was complete, the reaction mixture was concentrated. The residue was distilled over a Kugelrohr oven to give the desired product. Compounds **7a−n** were prepared according to this method. The product yield of each reaction is listed in Table 1, while the spectroscopic data of these compounds are shown in the Supporting Information.

Procedure for the Allylation of Aldehydes. To a 10 mL sidearm flask were added 3-iodo-2-methyl-2-cyclohexen-1-one (**3a**) (0.0500 mmol, 10 mol %), Pd(dba)$_2$ (0.0250 mmol, 5 mol %), and 2-(dimethylphenylsilanyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**5**) (0.500 mmol). The system was evacuated and purged with nitrogen three times. Ethyl acetate (0.5 mL), allene (**1**) (1.00 mmol), and aldehyde (**14**) (1.00 mmol) were added to the system, and the reaction mixture was stirred at 80 °C for 5 h. After the reaction was complete, ethyl acetate (50 mL) was added to the reaction mixture, and the mixture was washed with brine (25 mL) three times. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was chromatographed on a silica gel column using ethyl acetate and hexanes as eluent to give the desired three-component assembly product **15**. Compounds **15a−p** were prepared according to this method. The product yield of each reaction is listed in Table 2, while the spectroscopic data of these products are shown in the Supporting Information.

Acknowledgment. We thank the National Science Council of the Republic of China (NSC 92-2113-M-007-044) for the support of this research.

Supporting Information Available: Spectroscopic data and ^{1}H NMR spectra for compounds **7a−n**, **8b**, and **15a−p**. NOE experimental data of compounds **7a**, **7k**, and **7l**. This material is available free of charge via the Internet at http://pubs.acs.org

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