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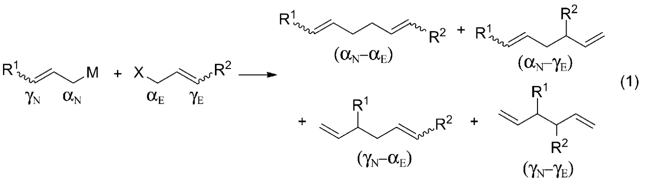
C–C Coupling

Copper-Catalyzed Borylative Allyl–Allyl Coupling Reaction**

*Kazuhiko Semba, Naoto Bessho, Tetsuaki Fujihara, Jun Terao, and Yasushi Tsuji**

Abstract: *Borylative allyl–allyl coupling using allenes, bis(pinacolato)diboron, and allyl phosphates has been developed in the presence of a copper catalyst bearing an N-heterocyclic carbene ligand. The reaction affords boryl-substituted 1,5-diene derivatives in good to high yields with high regioselectivity and Z selectivity.*

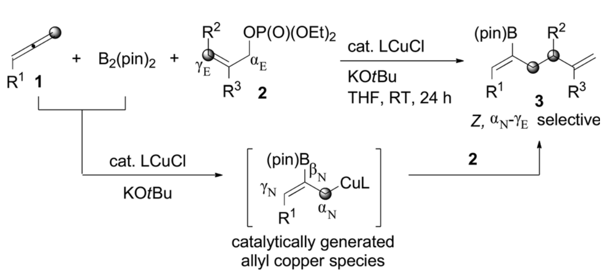
Allyl–allyl coupling[1] between allyl nucleophiles and allyl electrophiles is a powerful tool for providing direct access to 1,5-dienes, which are abundant in naturally occurring terpenes,[2] and are versatile building blocks in organic synthesis.[3] Stoichiometric amounts of allyl lithium,[1a,b] magnesium,[1c–h] tin,[1i,j] boron,[1k–n] silicon,[1o] and indium[1p] nucleophiles were reacted with allyl electrophiles. However, with unsymmetrical allyl reagents, the coupling would occur between either the α- or γ-position of the nucleophile (α_N or γ_N) and that of the electrophile (α_E or γ_E). Therefore, there are four possible regioisomers, and more isomers may appear if stereoisomers are also considered [Eq. (1)]. In fact, allyl–allyl couplings often suffer from low regio- and stereoselectivities, even if transition-metal catalysts such as copper,[1e–g] nickel,[1k] and palladium[1k,p] are employed. Thus, achieving both regio- and stereoselective allyl–allyl coupling is a challenging task. Recently, Morken and co-workers successfully developed a selective (γ_N–γ_E) allyl–allyl coupling reaction between allyl boronates and allyl electrophiles in the presence of a chiral palladium/bis(phosphane) catalyst.[1m]



(1)

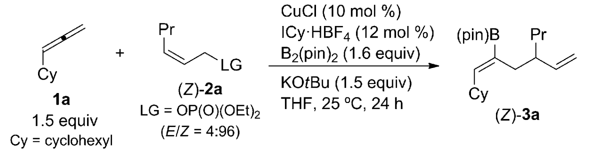
Herein, we report the first borylative allyl–allyl coupling reaction using allenes (**1**),[4] bis(pinacolato)diboron [$B_2(pin)_2$], and allyl phosphates (**2**)[1e,f] in the presence of a copper catalyst (Scheme 1). In the reaction, the allyl copper species bearing a boryl functionality at the β_N-position is generated catalytically,[4,5] and reacts with **2**. The reaction provides a variety of boryl-substituted 1,5-dienes (**3**) with excellent stereo- and regioselectivities (α_N–γ_E).[6] The boryl functionality is very useful for further derivatization.[7]

As shown in Table 1, the reaction conditions were optimized with **1a**, (*Z*)-**2a**, and $B_2(pin)_2$ as the substrates in



Scheme 1. Borylative allyl–allyl coupling.

Table 1: Reaction optimization.[a]



Entry	Changes from the standard conditions	(*Z*)-**3 a**	
		Yield [%][b]	Isomeric Purity [%][c]
1	none	84 (77)[d]	95 (98)[e]
2	SIMes·HBF_4 instead of ICy·HBF_4	90	94
3	IMes·HCl instead of ICy·HBF_4	88	91
4	^{Me}IMes·HCl instead of ICy·HBF_4	85	94
5	IPr·HCl instead of ICy·HBF_4	8	78
6	PCy_3 instead of ICy·HBF_4	84	91
7	dppb instead of ICy·HBF_4	71	90
8	(*E*)-**2 a** instead of (*Z*)-**2 a**	58	91
9	LG = Br: (*Z*)-**2 aα**	16	97
10	LG = OC(O)OMe: (*Z*)-**2 aβ**	1	–
11	LG = OAc: (*Z*)-**2 aγ**	0	–

[a] Standard conditions: **1 a** (0.38 mmol, 1.5 equiv), $B_2(pin)_2$ (0.40 mmol, 1.6 equiv), (*Z*)-**2 a** (LG = $OP(O)(OEt)_2$, 0.25 mmol), CuCl (0.025 mmol, 10 mol%), ICy·HBF_4 (0.030 mmol, 12 mol%), KO*t*Bu (0.38 mmol, 1.5 equiv), THF (2.0 mL), 25 °C, 24 h. [b] Yield of (*Z*)-**3 a** as determined by GC. [c] A ratio of (*Z*)-**3 a**/other isomers. [d] Yield of isolated (*Z*)-**3 a**. [e] Purity of the isolated product. THF = tetrahydrofuran.

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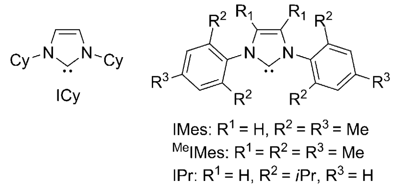
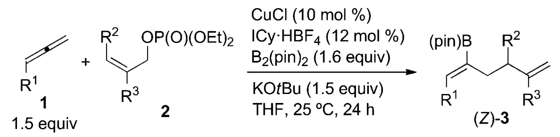
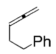
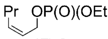
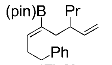
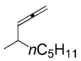
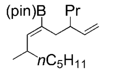
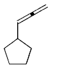
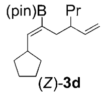
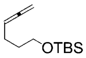
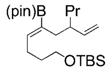
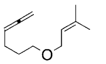
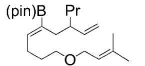
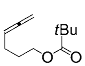
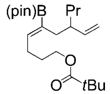
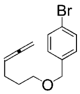
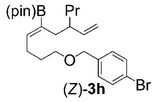
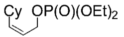
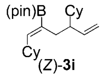
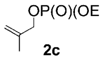
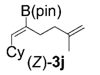
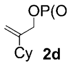
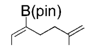


Figure 1. Structure of ligands.

Table 2: Borylative allyl–allyl coupling.[a]



1 1.5 equiv + **2** → (*Z*)-**3**

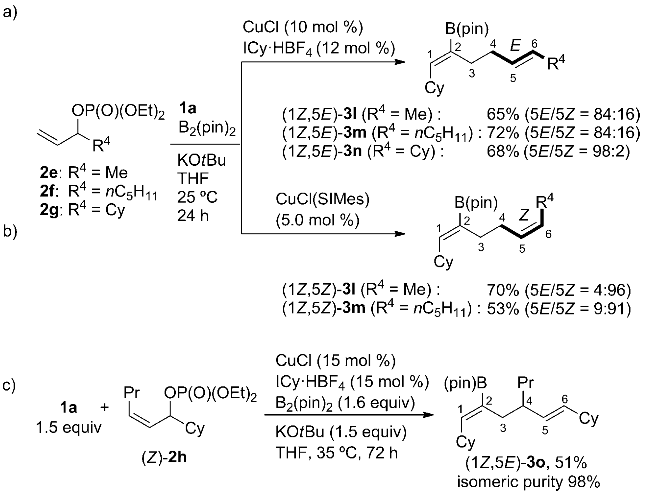
Entry	Allene	Allyl phosphate	(*Z*)-**3**	Yield [%][b]
1	 **1b**	 (*Z*)-**2a**	 (*Z*)-**3b**	76
2	 **1c**	(*Z*)-**2a**	 (*Z*)-**3c**	82
3	 **1d**	(*Z*)-**2a**	 (*Z*)-**3d**	75
4	 **1e**	(*Z*)-**2a**	 (*Z*)-**3e**	57
5	 **1f**	(*Z*)-**2a**	 (*Z*)-**3f**	84
6	 **1g**	(*Z*)-**2a**	 (*Z*)-**3g**	79
7	 **1h**	(*Z*)-**2a**	 (*Z*)-**3h**	72
8[c]	**1a**	 (*Z*)-**2b**	 (*Z*)-**3i**	62[d]
9	**1a**	 **2c**	 (*Z*)-**3j**	76
10	**1a**	 **2d**	 (*Z*)-**3k**	63

[a] Allene (0.75 mmol, 1.5 equiv), $B_2(pin)_2$ (0.80 mmol, 1.6 equiv), allyl phosphate (0.50 mmol), CuCl (0.050 mmol, 10 mol%), ICy·HBF_4 (0.060 mmol, 12 mol%), KO*t*Bu (0.75 mmol, 1.5 equiv), THF (4.0 mL), 25 °C, 24 h. [b] Yield of the isolated product: isomeric purity >95%. [c] CuCl (0.10 mmol, 20 mol%), ICy·HBF_4 (0.12 mmol, 24 mol%), KO*t*Bu (1.0 mmol, 2.0 equiv) and $B_2(pin)_2$ (1.1 mmol, 2.1 equiv). [d] Isomeric purity, 92%. TBS = *tert*-butyldimethylsilyl.

the presence of a catalytic amount of CuCl and a ligand in THF at 25 °C. The ligand ICy (Figure 1) was found to be the most effective, thus affording (*Z*)-**3a** in 84% yield with 95% isomeric purity (standard reaction conditions; Table 1, entry 1). Without the ligand, (*Z*)-**3a** was afforded in 2% yield. From the reaction mixture in entry 1, (*Z*)-**3a** was isolated in 77% yield with 98% isomeric purity. The *Z* configuration of the product was determined by X-ray crystal structure analysis.[8] Furthermore, the present procedure is easily amenable to a gram-scale reaction: by employing 1.0 gram of **1a** (8.2 mmol), 1.4 grams (75% yield with 98% isomeric purity) of (*Z*)-**3a** were obtained. Upon reducing the amount of KO*t*Bu to 0.30 equivalents, the yield of (*Z*)-**3a** decreased to 17%. Other carbene ligands such as SIMes, IMes, and ^{Me}IMes (Figure 1) also afforded the products in high yields, but the selectivity was somewhat decreased (Table 1, entries 2–4). With the bulky IPr as the ligand the yield was considerably reduced to 8% (entry 5). As for the phosphane ligands,[9] PCy_3 and dppb were efficient, thus affording (*Z*)-**3a** in good yields with greater than 90% selectivity (entries 6 and 7). In contrast, phosphanes such as dppp, dppe, dppbz, Xantphos, and PPh_3 provided the product in much lower yields and with lower selectivities (see Table S1 in the Supporting Information).[8] Even when employing (*E*)-**2a** instead of (*Z*)-**2a** as the allyl phosphate, the same (*Z*)-**3a** was obtained as the product in 58% yield with 91% isomeric purity (entry 8). With respect to the leaving group of the allyl electrophile, the corresponding allyl bromide (*Z*)-**2aα**, instead of the phosphate, afforded (*Z*)-**3a** in 16% yield (entry 9). Only a trace amount of (*Z*)-**3a**, if any, was provided from the corresponding allyl carbonate (*Z*)-**2aβ** and acetate (*Z*)-**2aγ** (entries 10 and 11).

Other allenes (**1b**–**h**) and allyl phosphates (**2a**–**d**) were reacted under the standard reaction conditions (Table 2). Various 1-monosubstituted allenes (**1b**–**h**) reacted with (*Z*)-**2a** to provide the corresponding products (*Z*)-**3b**–**h** in high yields upon isolation, regio- and stereoselectively (isomeric purities >95%; entries 1–7). Silyl ether[9] (entry 4), olefin (entry 5), ester (entry 6), and bromo (entry 7) functionalities were tolerated under these reaction conditions. In contrast, 1-phenylallene, and 1,1-di- and 1,3-disubstituted allenes did not give the desired products selectively. The γ-cyclohexyl-substituted allyl phosphate **2b** and **1a** afforded the corresponding adduct (*Z*)-**3i** in 62% yield, with a slightly lower isomeric purity of 92% (entry 8). In the case of β-methyl- (**2c**) and β-cyclohexyl-substituted (**2d**) allyl phosphates, the corresponding products, (*Z*)-**3j** and (*Z*)-**3k**, were obtained in good yields with high selectivities (entries 9 and 10). The *Z* configurations of (*Z*)-**3b**, (*Z*)-**3c**, and (*Z*)-**3h** were determined through NOESY measurements of these products. The *Z* geometries of all the other products were confirmed similarly after derivatization of (*Z*)-**3** through a Suzuki–Miyaura coupling reaction with 4-bromotoluene (see Scheme 3c and the Supporting Information).

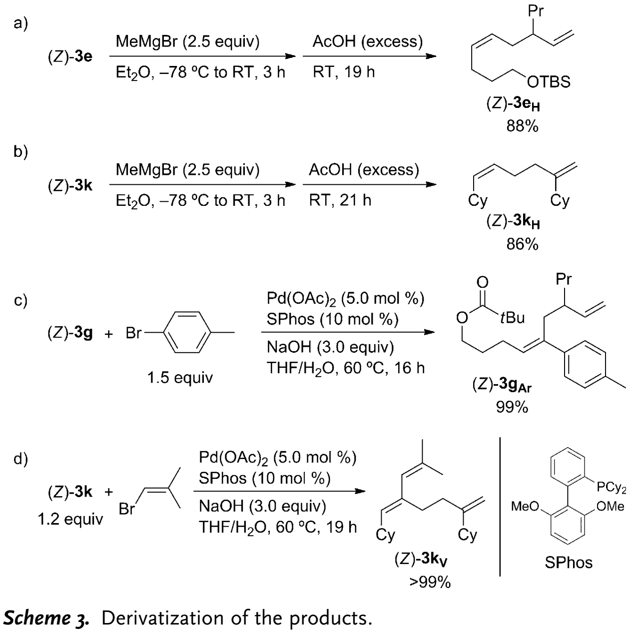
The reaction of α-substituted allyl phosphates (**2e**–**g**) may afford more stereoisomers (5*E* and 5*Z*). Gratifyingly, with ICy as the ligand under the standard reaction conditions (Table 1, entry 1), **2e**, **2f**, and **2g** gave the 5*E*-configured products (1*Z*,5*E*)-**3l**–**n** in good yields upon isolation with good (84%) to excellent (98%) 5*E* selectivities (Scheme 2a). Here, yields of the by-products other than (1*Z*,5*E*)-**3** and (1*Z*,5*Z*)-**3** were less than 5%. Remarkably, with SIMes as the ligand, the stereoselectivity was switched from 5*E* to 5*Z*. Thus, (1*Z*,5*Z*)-**3l** and (1*Z*,5*Z*)-**3m** were isolated in good yields with



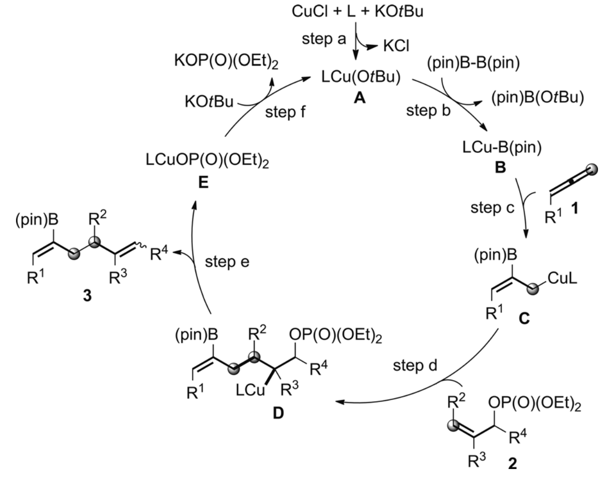
Scheme 2. Reactions with α-substituted allyl phosphates (**2e–h**).

high 5*Z* selectivity (96 % and 91 %, respectively; Scheme 2 b). Furthermore, the α,γ-di-substituted allyl phosphate (*Z*)-**2h** reacted with **1a** to afford (1*Z*,5*E*)-**3o** with 98 % isomeric purity (Scheme 2 c).

The boryl moieties of the adducts were removed easily through the protodeborylation reaction.[10] Thus, (*Z*)-**3e** and (*Z*)-**3k** provided high yields of the corresponding (*Z*)-1,5-dienes [(*Z*)-**3e**$_\mathrm{H}$ and (*Z*)-**3k**$_\mathrm{H}$] (Scheme 3 a,b), which are not easily prepared by the conventional allyl–allyl coupling reaction.[1f] Suzuki–Miyaura coupling[7] of (*Z*)-**3g** with 4-bromotoluene proceeded smoothly to afford (*Z*)-**3g**$_\mathrm{Ar}$ in 99 % yield (Scheme 3c). Similar coupling of (*Z*)-**3d–f**, (*Z*)-**3i–k**, (1*Z*,5*E*)-**3l–o**, and (1*Z*,5*Z*)-**3l–m** with 4-bromotoluene afforded the corresponding (*Z*)-**3d**$_\mathrm{Ar}$–**f**$_\mathrm{Ar}$, (*Z*)-**3i**$_\mathrm{Ar}$–**k**$_\mathrm{Ar}$, (1*Z*,5*E*)-**3l**$_\mathrm{Ar}$–**o**$_\mathrm{Ar}$, and (1*Z*,5*Z*)-**3l**$_\mathrm{Ar}$–**m**$_\mathrm{Ar}$ in good to quantitative yields (see Table S2).[8] The coupling reaction with vinyl bromide also provided the corresponding triene (*Z*)-**3k**$_\mathrm{V}$ quantitatively (Scheme 3 d).



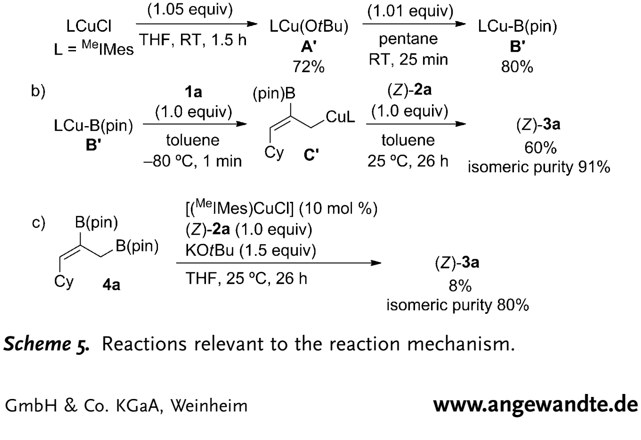
Scheme 3. Derivatization of the products.



Scheme 4. A possible catalytic cycle.

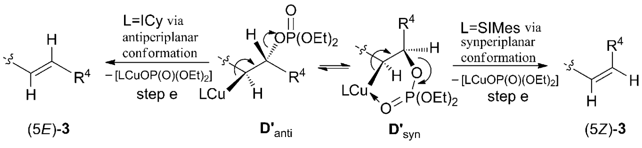
A possible catalytic cycle is shown in Scheme 4. The *tert*-butoxy copper species **A**[11] is generated from CuCl, the carbene ligand (L), and KO*t*Bu (step a). Then, **A** reacts with B$_2$(pin)$_2$ to afford the borylcopper species[5a,12] **B** (step b). The allene **1** reacts with **B** to generate the β-boryl (*Z*)-σ-allyl copper intermediate **C**[4,5] regio- and stereoselectively (step c). Addition of **C** to the C=C bond of **2** occurs,[13] thus giving **D** (step d). Subsequently, stereoselective β-elimination[13] releases the copper phosphate **E** and provides **3** as the product (step e). Finally, the reaction of **E** with KO*t*Bu regenerates **A** and the catalytic cycle is completed (step f).

These catalytic steps in Scheme 4 were confirmed by stoichiometric reactions[8] employing $^{\mathrm{Me}}$IMes as the ligand, which is an efficient ligand in the catalytic reaction (entry 4 in Table 1). As a model reaction for step a, the stoichiometric reaction of [($^{\mathrm{Me}}$IMes)CuCl] with NaO*t*Bu afforded [($^{\mathrm{Me}}$IMes)Cu(O*t*Bu)] (**A′**) in 72 % yield after recrystallization. As in step b, **A′** reacted with B$_2$(pin)$_2$ to give [($^{\mathrm{Me}}$IMes)Cu-B(pin)] (**B′**; Scheme 5 a).[5a,12] Moreover, reaction of **B′** with **1a** provided the β-boryl *Z*-σ-allyl copper **C′**[14] (Scheme 5 b; see step c). Finally, **C′** reacted with (*Z*)-**2a** to afford (*Z*)-**3a** in 60 % yield (Scheme 5 b; see steps d and e).[15] In contrast, there might be some possibility that allenes (**1**) and B$_2$(pin)$_2$ react first to give diboration adducts,[16] after which the adducts react with allyl phosphates (**2**) to afford **3**. Hence, the corresponding diboration adduct **4a** was prepared by a liter-



Scheme 5. Reactions relevant to the reaction mechanism.

ature method.[17] However, the reaction between **4a** and (Z)-**2a** was very sluggish[18] and the desired product (Z)-**3a** was afforded in only low yield (Scheme 5c). Therefore, these observations in Scheme 5 indicate that the catalytic reaction proceeds via the β-boryl (Z)-σ-allyl copper species **C** as shown in Scheme 4, rather than by the diboration of the allenes. As for the 5E/5Z switch with ICy and SIMes (Scheme 2), both the ligands might afford the same intermediate such as **D′**[19] (Scheme 6) in step d (Scheme 4). From **D′**, (5E)-**3** could be obtained with ICy by β-elimination (step e) through the antiperiplanar conformation[13] (**D′**$_{\mathbf{anti}}$; Scheme 6). In contrast, the less-electron-donating[20] SIMes might facilitate coordination of the phosphate moiety to the copper and the resulting synperiplanar conformation[13a] (**D′**$_{\mathbf{syn}}$) could afford (5Z)-**3**.



Scheme 6. Stereochemistry of step e in Scheme 4.

In conclusion, a highly stereo- and regioselective copper-catalyzed borylative allyl–allyl coupling has been developed. The reaction affords a wide variety of boryl-substituted 1,5-dienes in good to high yields. The reaction proceeds via the β-boryl (Z)-σ-allyl copper species as a key catalytic species. Further studies on the reaction, using optically active substrates and the reaction mechanism are now in progress.

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[9] Abbreviations: PCy_3, tricyclohexylphosphine; dppb, 1,4-bis(diphenylphosphino)butane; dppp, 1,3-bis(diphenylphosphino)propane; dppe, 1,2-bis(diphenylphosphino)ethane; dppbz, 1,2-diphenylphosphinobenzene; Xantphos, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; TBS, *tert*-butyldimethylsilyl.

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