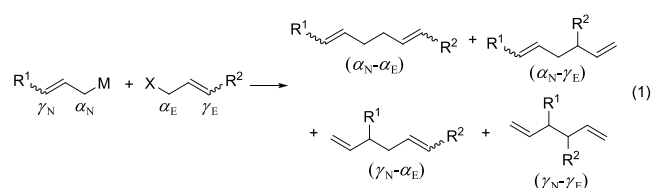


Copper-Catalyzed Borylative Allyl–Allyl Coupling Reaction**

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

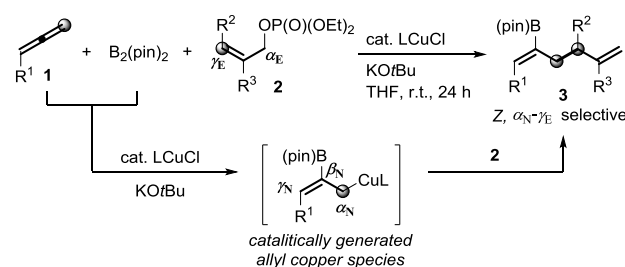
Abstract: Borylative allyl-allyl coupling using allenes, bis(pinacolato)diboron, and allyl phosphates has been developed in the presence of a copper catalyst bearing an *N*-heterocyclic carbene ligand. The reaction affords boryl-substituted 1,5-diene derivatives in good to high yields with high regio-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

Allyl–allyl coupling^[1] between allyl nucleophiles and allyl electrophiles is a powerful tool 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 Li,^[1a,b] Mg,^[1c–h] Sn,^[1i,j] B,^[1k–n] Si,^[1o] and In^[1p] nucleophiles were reacted with allyl electrophiles. However, with unsymmetrical allyl reagents, the coupling would occur between 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 Cu,^[1e–g] Ni,^[1k] and Pd^[1k,1p] are employed. Thus, achieving both regio- and stereoselective allyl–allyl coupling is a challenging task. Recently, Morcken 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 Pd-bisphosphane catalyst.^[1m]

Herein, we report the first borylative allyl-allyl coupling reaction using allenes (**1**),^[4] bis(pinacolato)diboron ($B_2(\text{pin})_2$), 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 regio- (α_N - γ_E) selectivities.^[6] The boryl functionality is very useful for further derivatization^[7] (vide infra).



Scheme 1. Borylative allyl-allyl coupling

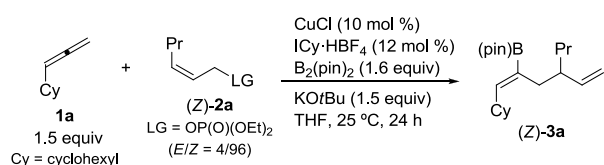
As shown in Table 1, the reaction conditions were optimized with **1a**, (*Z*)-**2a**, and $B_2(\text{pin})_2$ as the substrates in the presence of a catalytic amount of CuCl and a ligand in THF at 25 °C. As the ligand, ICy (see Figure 1 for structures of the carbene ligands) was found to be the most effective, affording (*Z*)-**3a** in 84% yield with 95% isomeric purity (standard reaction conditions, 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 g of **1a** (8.2 mmol), 1.4 g (75% yield with 98% isomeric purity) of (*Z*)-**3a** was obtained. Upon reducing the amount of KOtBu to 0.30 equiv, the yield of (*Z*)-**3a** decreased to 17%. Other carbene ligands such as SIMes, IMes, and MeIMes (Figure 1) also afforded the products in high yields, but the selectivity was somewhat decreased (entries 2–4). Bulky IPr as the ligand reduced the yield considerably to 8% (entry 5). As for the phosphane ligands,^[9] PCy₃ and dppb were efficient, affording (*Z*)-**3a** in good yields with >90% selectivities (entries 6 and 7). On the other hand, phosphanes such as dppp, dppe, dppbz, Xantphos, and PPh₃ provided the product in much lower yields and with lower selectivities (Table S1).^[8] Even 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*)-**2a** α) 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*)-**2a** β) and acetate ((*Z*)-**2a** γ) (entries 10 and 11).

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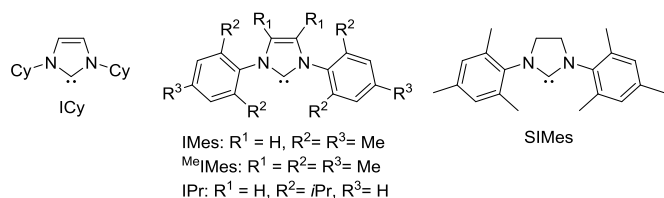


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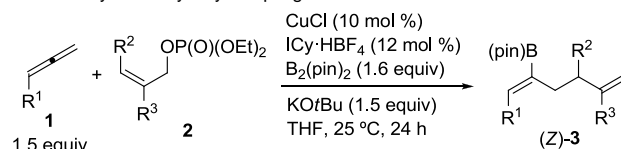
Table 1: Reaction optimization.^[a]

Entry	Changes from the standard conditions	(Z)-3a	
		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)-2a instead of (Z)-2a	58	91
9	LG = Br: (Z)-2a α	16	97
10	LG = OC(O)OMe: (Z)-2a β	1	-
11	LG = OAc: (Z)-2a γ	0	-

[a] Standard conditions: **1a** (0.38 mmol, 1.5 equiv), B₂(pin)₂ (0.40 mmol, 1.6 equiv), (Z)-**2a** (LG=OP(O)(OEt)₂, 0.25 mmol), CuCl (0.025 mmol, 10 mol %), ICy·HBF₄ (0.030 mmol, 12 mol %), KOtBu (0.38 mmol, 1.5 equiv), THF (2.0 mL), 25 °C, 24 h. [b] GC yield of (Z)-**3a**. [c] A ratio of (Z)-**3a**/other isomers. [d] Isolated yield of (Z)-**3a**. [e] Purity of the isolated product.

**Figure 1.** Structure of Ligands.

Other allenes (**1b–h**) and allyl phosphates (**2a–d**) were reacted under the standard reaction conditions (Table 2). Various 1-*mono*-substituted allenes (**1b–h**) reacted with (Z)-**2a** to provide the corresponding products ((Z)-**3b–h**) in high isolated yields 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, 1,1-*di*-, and 1,3-*di*-substituted 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 (**2d**) substituted allyl phosphates, the corresponding products, (Z)-**3j** and (Z)-**3k**, were obtained in good yields with high selectivity (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-

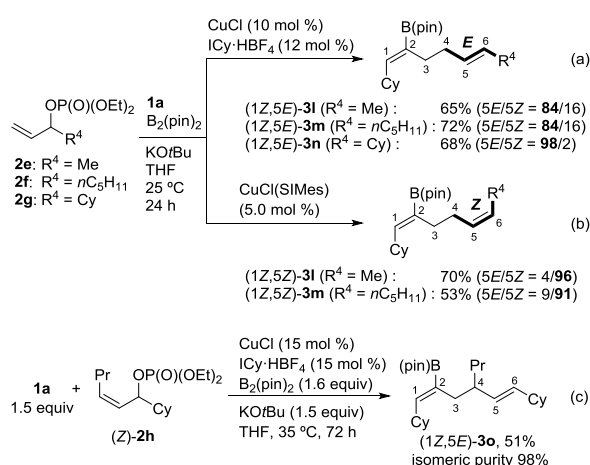
Table 2: Borylative allyl-allyl coupling.^[a]

Entry	Allene	Allyl Phosphate	(Z)-3	Yield of (Z)-3 [%] ^[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), B₂(pin)₂ (0.80 mmol, 1.6 equiv), allyl phosphate (0.50 mmol), CuCl (0.050 mmol, 10 mol %), ICy·HBF₄ (0.060 mmol, 12 mol %), KOtBu (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·HBF₄ (0.12 mmol, 24 mol %), KOtBu (1.0 mmol, 2.0 equiv) and B₂(pin)₂ (1.1 mmol, 2.1 equiv). [d] Isomeric purity, 92%.

geometries of all the other products were confirmed similarly after derivatization of (*Z*)-**3** through a Suzuki–Miyaura coupling reaction with 4-bromotoluene (vide infra, Scheme 3c and Supporting Information).

The reaction of α -substituted allyl phosphates (**2e–g**) may afford more stereo isomers (*5E* and *5Z*). Gratifyingly, with ICy as the ligand under the standard conditions (entry 1, Table 1), **2e**, **2f**, and **2g** gave *5E* products (*1Z,5E*)-**3l–n** in good isolated yields with good (84%) to excellent (98%) *5E* selectivities (Scheme 2a). Here, yields of the by-products other than (*1Z,5E*)-**3** and (*1Z,5Z*)-**3** were <5%. Remarkably, with SIMes as the ligand, the stereoselectivity was switched from *5E* to *5Z*. Thus, (*1Z,5Z*)-**3l** and (*1Z,5Z*)-**3m** were isolated in good yields with high (96% and 91%, respectively) *5Z* selectivity (Scheme 2b). Furthermore, the α,γ -di-substituted allyl phosphates ((*Z*)-**2h**) reacted with **1a** to afford (*1Z,5E*)-**3o** with 98% isomeric purity (Scheme 2c).

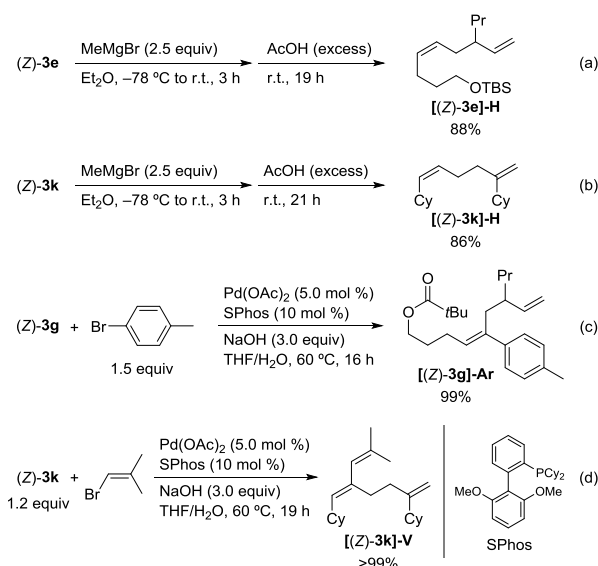


Scheme 2. Reactions with α -substituted allyl phosphates (**2e–h**).

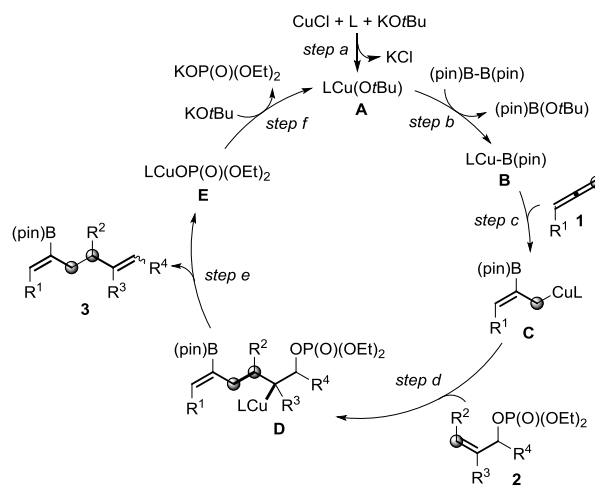
The boryl moieties of the adducts were removed easily through the proto-deborylation reaction.^[10] Thus, (*Z*)-**3e** and (*Z*)-**3k** provided high yields of the corresponding (*Z*)-1,5-dienes ([(*Z*)-**3e**]-**H** and [(*Z*)-**3k**]-**H**) (Scheme 3a, b), which were not easily prepared by the conventional allyl–allyl coupling reaction.^[14] Suzuki–Miyaura coupling^[7] of (*Z*)-**3g** with 4-bromotoluene proceeded smoothly to afford [(*Z*)-**3g**]-**Ar** in 99% yield (Scheme 3c). Similar coupling of (*Z*)-**3d–f**, (*Z*)-**3i–k**, (*1Z,5E*)-**3l–o**, and (*1Z,5Z*)-**3l–m** with 4-bromotoluene afforded the corresponding [(*Z*)-**3d–f**]-**Ar**, [(*Z*)-**3i–k**]-**Ar**, [(*1Z,5E*)-**3l–o**]-**Ar** and [(*1Z,5Z*)-**3l–m**]-**Ar** in good to quantitative yields (Table S2).^[8] The coupling reaction with vinyl bromide also provided the corresponding triene, [(*Z*)-**3k**]-**V**, quantitatively (Scheme 3d).

A possible catalytic cycle is shown in Scheme 4. *t*-Butoxy copper species (**A**)^[11] is generated from CuCl, the carbene ligand (L), and KO*t*Bu (step a). Then, **A** reacts with B₂(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] giving **D** (step d). Subsequently, stereoselective β -elimination^[13] releasing the copper phosphate (**E**) provides **3** as the product (step e). Finally, the reaction of **E** with KO*t*Bu regenerates **A** and the catalytic cycle is closed (step f).

These catalytic steps in Scheme 4 were confirmed by stoichiometric reactions^[8] employing ^{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 (^{Me}IMes)CuCl with NaO*t*Bu afforded (^{Me}IMes)Cu(O*t*Bu) (**A'**) in 72% yield after recrystallization. As in step b, **A'** reacted with B₂(pin)₂ to give (^{Me}IMes)Cu-B(pin) (**B'**) (Scheme 5a).^[5a,12] Moreover,

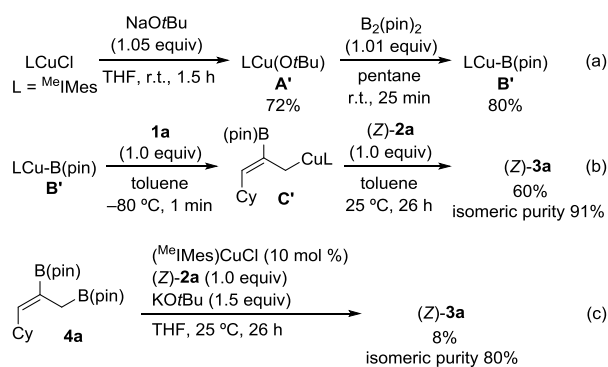


Scheme 3. Derivatization of the products.

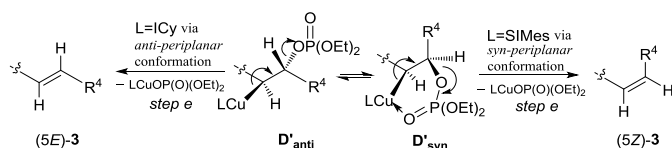


Scheme 4. A possible catalytic cycle.

reaction of **B'** with **1a** provided the β -boryl (*Z*)- σ -allyl copper (**C'**)^[14] (Scheme 5b, cf. step c). Finally, **C'** reacted with (*Z*)-**2a** to afford (*Z*)-**3a** in 60% yield (Scheme 5b, cf. steps d and e).^[15] On the other hand, there might be some possibility that allenes (**1**) and B₂(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 literature 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 via 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 the β -elimination (step e) via *anti*-periplanar conformation^[13] (**D'**_{anti}, Scheme 6). On the other hand, less electron-donating^[20] SIMes might facilitate coordination of the phosphate moiety to the copper and the resulting *syn*-periplanar conformation^[13a] (**D'**_{syn}) could afford (*5Z*)-**3**.



Scheme 5. Reactions relevant to the reaction mechanism.



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.

Keywords: Allenes • Allylic compounds • C-C Coupling • Boron • Copper

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- [9] Abbreviations: PCy₃, 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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