TITLE:

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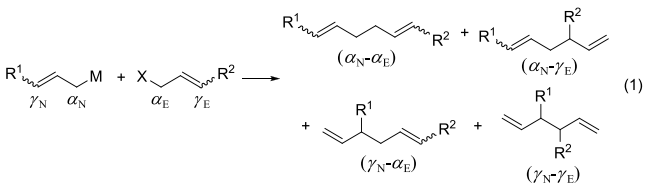
**Allyl-Allyl Coupling**

# Copper-Catalyzed Borylative Allyl–Allyl Coupling Reaction**

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

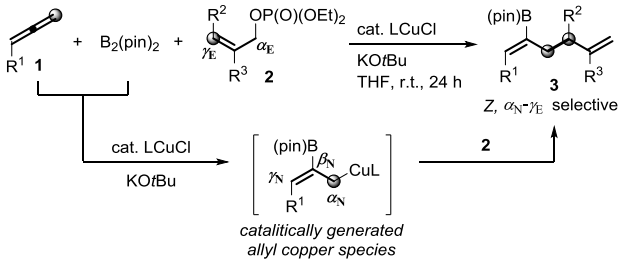
***Abstract:*** *Borylative allyl-allyl coupling using allenes, bis(pinacolato)diboron, and allyl phosphates has been developed in the presence of a copper catalyst bearing an N-heterocyclic carbene ligand. The reaction affords boryl-substituted 1,5-diene derivatives in good to high yields with high 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 $\alpha$- or $\gamma$-position of the nucleophile ($\alpha_N$ or $\gamma_N$) and that of the electrophile ($\alpha_E$ or $\gamma_E$). 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, Morken and co-workers successfully developed a selective ($\gamma_N$-$\gamma_E$) 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 ($B_2(pin)_2$), 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 $\beta_N$ 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- ($\alpha_N$-$\gamma_E$) 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 $B_2(pin)_2$ as the substrates in the presence of a catalytic amount of CuCl and a ligand in THF at 25 ºC. 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 KO*t*Bu to 0.30 equiv, 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 (entries 2–4). Bulky IPr as the ligand reduced the yield considerably to 8% (entry 5). As for the phosphane ligands,[9] $PCy_3$ 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 $PPh_3$ 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*)-**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).

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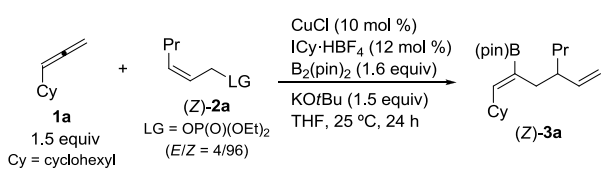
***Table 1:*** Reaction optimization.[a]




| Entry | Changes from the standard conditions | (Z)-3a Yield [%][b] | (Z)-3a 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*)-**2aα** | 16 | 97 |
| 10 | LG = OC(O)OMe: (*Z*)-**2aβ** | 1 | - |
| 11 | LG = OAc: (*Z*)-**2aγ** | 0 | - |

[a] Standard conditions: **1a** (0.38 mmol, 1.5 equiv), $B_2(pin)_2$ (0.40 mmol, 1.6 equiv), (*Z*)-**2a** (LG=OP(O)(OEt)$_2$, 0.25 mmol), CuCl (0.025 mmol, 10 mol %), ICy·$HBF_4$ (0.030 mmol, 12 mol %), KO*t*Bu (0.38 mmol, 1.5 equiv), THF (2.0 mL), 25 ºC, 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.

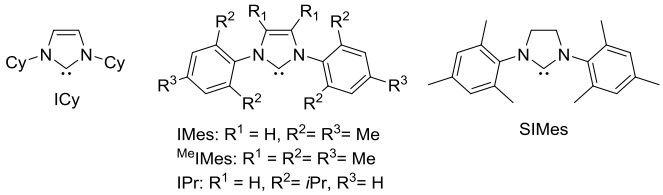
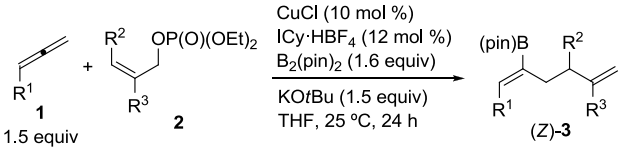
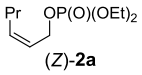
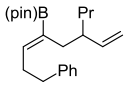
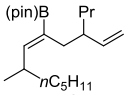
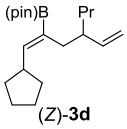
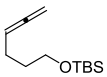
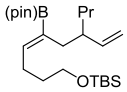
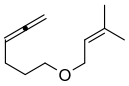
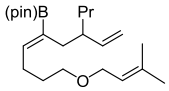
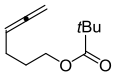
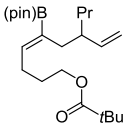
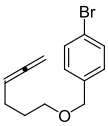
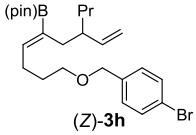
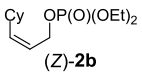
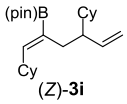
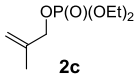
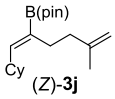
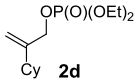
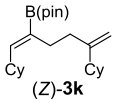



***Figure 1.*** Structure of Ligands.

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), $B_2(pin)_2$ (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 ºC, 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%.

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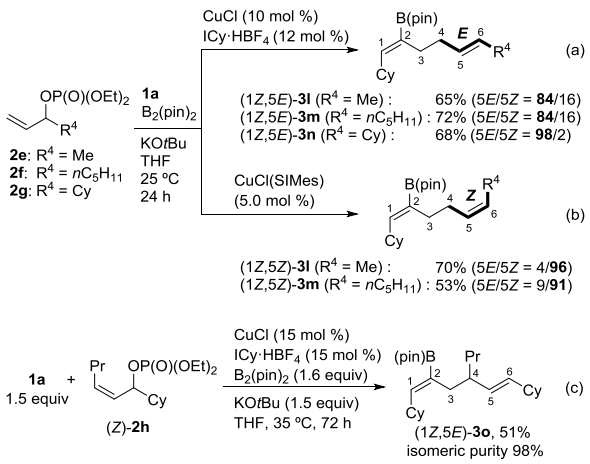
geometries of all the other products were confirmed similarly after derivatization of (*Z*)-**3** through a Suzuki–Miyaura coupling reaction with 4-bromotoluene (vide infra, Scheme 3c and Supporting Information).

The reaction of $\alpha$–substituted allyl phosphates (**2e–g**) may afford more stereo isomers (5*E* and 5*Z*). Gratifyingly, with ICy as the ligand under the standard conditions (entry 1, Table 1), **2e**, **2f**, and **2g** gave 5*E* products (1*Z*,5*E*)-**3l–n** in good isolated yields 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 <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 high (96% and 91%, respectively) 5*Z* selectivity (Scheme 2b). Furthermore, the $\alpha,\gamma$-di-substituted allyl phosphates ((*Z*)-**2h**) reacted with **1a** to afford (1*Z*,5*E*)-**3o** with 98% isomeric purity (Scheme 2c).

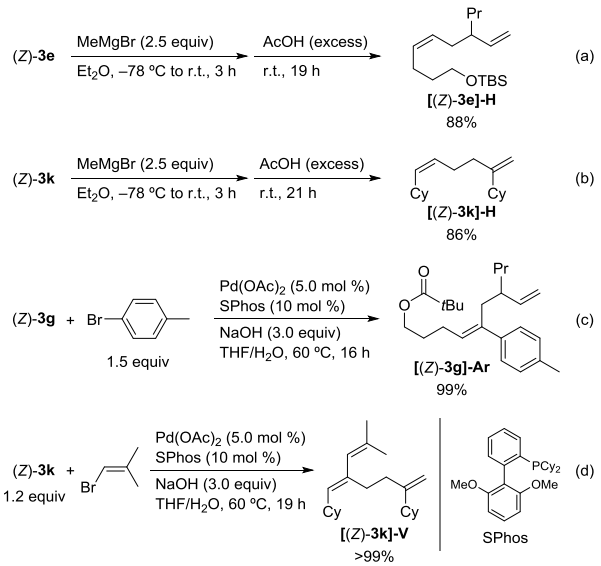



***Scheme 2.*** Reactions with. $\alpha$–substituted allyl phosphates (**2e–h**).

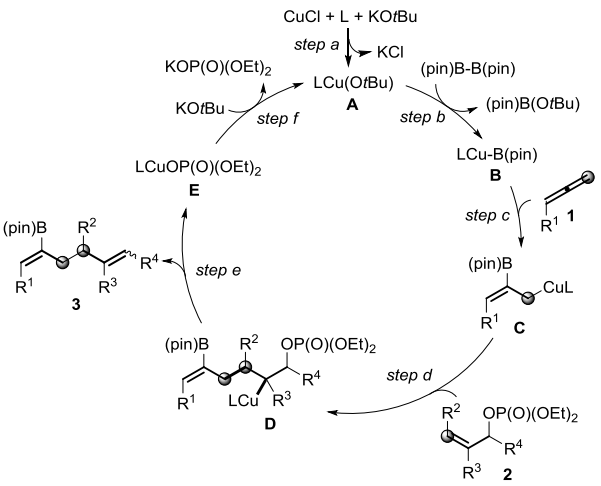
The boryl moieties of the adducts were removed easily through the proto-deborylation reaction.[10] Thus, (*Z*)-**3e** and (*Z*)-**3k** provided high yields of the corresponding (*Z*)-1,5-dienes (**[(*Z*)-3e]-H** and **[(*Z*)-3k]-H**) (Scheme 3a, b), which were not easily prepared by the conventional allyl–allyl coupling reaction.[1f] 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**, (1*Z*,5*E*)-**3l–o**, and (1*Z*,5*Z*)-**3l–m** with 4-bromotoluene afforded the corresponding **[(*Z*)-3d–f]-Ar**, **[(*Z*)-3i–k]-Ar**, **[(1*Z*,5*E*)-3l–o]-Ar** and **[(1*Z*,5*Z*)-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 $B_2(pin)_2$ to afford the borylcopper species[5a,12] (**B**) (step b). The allene (**1**) reacts with **B** to generate the $\beta$-boryl (*Z*)-$\sigma$-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 $\beta$-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 $B_2(pin)_2$ 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 $\beta$-boryl (*Z*)-$\sigma$-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 $B_2(pin)_2$ 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 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 $\beta$-boryl (*Z*)-$\sigma$-allyl copper species (**C**) as shown in Scheme 4, rather than via the diboration of the allenes. As for the 5*E*/5*Z* 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'**, (5*E*)-**3** could be obtained with ICy by the $\beta$-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 (5*Z*)-**3**.

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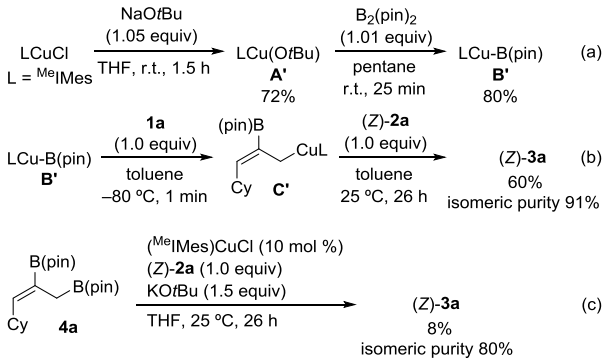
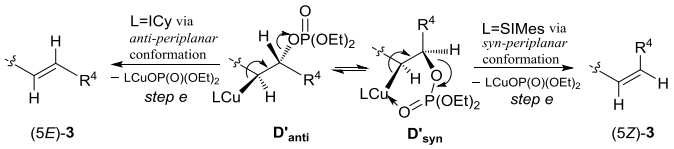



***Scheme 5.*** Reactions relevant to the reaction mechanism.




***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 $\beta$-boryl (*Z*)-$\sigma$-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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[8] See Supporting Information for detail.

[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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