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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 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, 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 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 ^{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] 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*)-**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]

		$\text{CuCl (10 mol \%)}$ $\text{ICy}\cdot\text{HBF}_4 \text{ (12 mol \%)}$ $\text{B}_2(\text{pin})_2 \text{ (1.6 equiv)}$ KOtBu (1.5 equiv) $\text{THF, 25 }^\circ\text{C, 24 h}$

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]

		$\text{CuCl (10 mol \%)}$ $\text{ICy}\cdot\text{HBF}_4 \text{ (12 mol \%)}$ $\text{B}_2(\text{pin})_2 \text{ (1.6 equiv)}$ KOtBu (1.5 equiv) $\text{THF, 25 }^\circ\text{C, 24 h}$

Entry	Allene	Allyl Phosphate	(Z)-3 Yield of (Z)-3 [%] ^[b]
1			76
2		(Z)- 2a	82
3		(Z)- 2a	75
4		(Z)- 2a	57
5		(Z)- 2a	84
6		(Z)- 2a	79
7		(Z)- 2a	72
8 ^[c]	1a		62 ^[d]
9	1a		76
10	1a		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 (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 α,γ -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 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.^[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 KOtBu (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 KOtBu 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 NaOtBu afforded (^{Me}IMes)Cu(OrBu) (**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 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 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 (5*Z*)-**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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- 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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