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Copper-catalyzed highly selective approach to 2-boroallylic silanes from allenylsilanes†

Liu Song,^a Weiming Yuan^b and Shengming Ma (1) *a,c

A highly chemo- and regioselective copper-catalyzed borylcupration of 1,2-allenylsilanes affords 2-boryl-allylsilanes by applying the ligand effect. Many synthetically attractive functional groups are well tolerated. As demonstrated, such 2-borylallylsilanes are very useful dimetallic reagents in organic synthesis. A rationale for the regioselectivity switch is provided.

The dimetallic reagents containing C–B bonds and C–Si bonds are very important synthetic intermediates in organic synthesis due to their relatively high stability, difference in reactivities, low toxicity and broad functional group compatibility. Among them, 2-borylallylic silanes, which contain both vinylboronate and allylsilane units, would be very useful in various organic transformations since allylic silanes are well-known for their wide applications in Hiyama couplings, dihydroxylation, aminohydroxylation, epoxidation, cyclopropanation, and Lewis acid-mediated [2 + 2] and [3 + 2] annulation with electron-deficient olefins or free radical additions. While the vinylboronate moiety is very useful in Suzuki cross-coupling reactions.

Due to the significance of such dimetallic reagents, highly selective approaches to such entities are of great importance. However, there are only a few examples reported and the related synthetic methods are rather limited:11 for example the palladium-catalyzed silaboration of allenes was developed independently by Ito and Tanaka in 1999, which affords a mixture of regioisomeric allylic silanes 1 with a terminal C=C bond and the regioisomer Z/E-2. In a very recent study, ¹² we also disclosed a copper-catalyzed borylcupration of allenylaffording 3-silylallylboronates Z-4 (eqn (2)).¹³ We envisioned whether such 1,2-allenylsilanes may be borylcuprated with B₂(pin)₂ for the highly selective preparation of 2-borylallylsilanes 5 by applying a different catalyst (eqn (3)). Herein, we report the realization of such a concept with an excellent regioselectivity by applying the ligand effect (Scheme 1).

Initially, when we conducted the reaction of 3a with 1.2 equiv. of $B_2(\text{pin})_2$ and 2.0 equiv. of i-PrOH in THF at room temperature with DPPE as the ligand, to our delight, a different product, 2-borylallylic silane 5a with a terminal C=C bond was indeed afforded, albeit only in 30% NMR yield with 59% recovery of 3a. The formation of alkenyl boronate Z/E-5a' and regioisomeric allylic boronates Z/E-4a 13 and 6a was NOT detected (Table 1, entry 1), indicating the excellent switch of regioselectivity compared to the reported results. 12 Inspired by this result, other bidentate ligands were further screened. The reaction with rac-BINAP as the ligand afforded 5a in a much higher yield of 96% (entry 2). Finally, we found that BIPHEP is the most efficient for this transformation yielding 5a in 98% yield (entry 3). Subsequently, a brief screening of the solvent

Ito's conditions: Pd(acac)₂/2,6-xylyl isocyanide, 120 $^{\circ}$ C Tanaka's conditions: Pd₂(dba)₃/etpo or (CH₂=CH₂)Pt(PPh₃)₂, 80 $^{\circ}$ C R = OMe or Cy.1/2 > 99/1

R = Ph or p-CF₃C₆H₄, 1/2 = 86/14 or 36/64

CuCl (5 mol%), Xantphos (5 mol%)

NaOt-Bu (20 mol%), B₂(pin)₂ (1.2 equiv)

i-PrOH (2.0 equiv), Et₂O, rt, t

$$\begin{array}{c}
R\\
Si]
\end{array}$$
Cu(l) / B₂(pin)₂
L = ?, solvent
this report
$$\begin{array}{c}
Cu(l) / B_2(pin)_2\\
R \\
Si]
\end{array}$$
and/or
$$\begin{array}{c}
R\\
Si]
\end{array}$$
and/or
$$\begin{array}{c}
R\\
Si]
\end{array}$$

$$\begin{array}{c}
R\\
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$$\begin{array}{c}
R\\
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$$\begin{array}{c}
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$$\begin{array}{c}
Sij\\
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$$Sij$$

$$Si$$

Scheme 1 Previous reports and our concept.

^aDepartment of Chemistry, Fudan University, 220 Handan Lu, Shanghai 200433, P. R. China. E-mail: masm@sioc.ac.cn

^bDepartment of Chemistry, East China Normal University, 3663 North Zhongshan Lu, Shanghai 200062, P. R. China

^cState Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, P. R. China

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did not lead to better reaction media (entries 4 and 5). Compared with other copper catalysts such as CuBr and CuI, CuCl is the most efficient (entries 6 and 7). Control experiments showed that the ligand and base are both essential to the reaction (entries 8 and 9). Thus, we defined 5 mol% CuCl with 5 mol% BIPHEP as the catalyst, 20 mol% NaOt-Bu as the base, and 2.0 equiv. of i-PrOH in THF at room temperature as the standard reaction conditions for the further study.

Table 1 Optimization of the reaction conditions for the copper-catalyzed regioselective borylcupration of allenylsilane 3a a

Entry	Ligand	NMR yield of 5a (%)	Recovery of 3a (%)	
1	DPPE	30	59	
2	rac-BINAP	96	_	
3	BIPHEP	98	_	
4^b	BIPHEP	89	4	
5 ^c 6 ^d	BIPHEP	68	24	
6^d	BIPHEP	92	_	
7^e	BIPHEP	21	75	
8	_	0	71	
9^f	BIPHEP	0	77	

^a Reaction conditions: 0.2 mmol of 3a, 5 mol% CuCl, 5 mol% ligand, 20 mol% NaOt-Bu, 0.24 mmol of B₂(pin)₂, 0.4 mmol of i-PrOH in 3 mL of THF at rt for 3 h under an argon atmosphere. ^bPhCH₃ was used instead of THF. ^c Et₂O was used instead of THF. ^d CuBr was instead of CuCl. ^e CuI was instead of CuCl. ^f NaOt-Bu was not added.

With the optimized conditions in hand, we started to examine the substrate scope: with CH3 and SiMe2Ph substituents, the reaction proceeded smoothly to afforded the desired product 5a in 90% yield (Table 2, entry 1); gratifyingly, the reaction could be conducted on a one-gram scale in an excellent yield with the same selectivity (entry 2); it is known that the substituents on silicon have serious influences on the properties of 1,2-allylsilanes, ^{2g} thus, we examine the substituents on silicon - the reaction could proceed smoothly in excellent yields irrespective of whether the Si-substituents are MePh₂, Ph₃ or t-BuMe₂ (entries 3-5); the reaction of the allenylsilane with R¹ = H could also proceed smoothly in 76% yield (entry 6); R¹ may be an alkyl group beyond Me such as Et, n-C₃H₇ or n-C₈H₁₇ (entries 7-9); other alkyl groups such as i-Bu, Bn or CH2CH2Ph may also work under the standard conditions (entries 10-12); R¹ may also be a phenyl group by conducting the reaction at 45 °C (entry 13). Furthermore, 1,2allenylsilanes with synthetically attractive functional groups such as ester, cyano, ketone, or TBS ether are also compatible to yield the corresponding products 5m-5q in decent yields (entries 14-18).

Table 2 Substrate scope

$$\begin{array}{c} R^1 \\ R^2 R_2 Si \end{array} \begin{array}{c} CuCl \ (5 \ mol\%), \ BIPHEP \ (5 \ mol\%) \\ \hline NaOt\text{-Bu} \ (20 \ mol\%), \ B_2 (pin)_2 \ (1.2 \ equiv) \\ \textit{i-PrOH} \ (2.0 \ equiv), \ THF, \ rt \end{array} \begin{array}{c} O \\ B = O \\ \hline \\ R^1 \ E \end{array}$$

Entry	R^1	R	\mathbb{R}^2	Time (h)	Yield of 5 b (
1	Me	Ме	Ph (3a)	3	90 (5a)
2^c	Me	Me	Ph (3a)	2.5	90 (5a)
3	Me	Ph	Me (3b)	3	88 (5b)
4	Me	Ph	Ph (3c)	3	90 (5c)
5	Me	Me	<i>t</i> Bu (3 d)	3	76 (5d)
6	H	Me	Ph (3e)	3	76 (5e)
7	Et	Me	Ph (3f)	2	89 (5f)
8	n-C ₃ H ₇	Me	Ph (3g)	3	87 (5g)
9	n-C ₈ H ₁₇	Me	Me (3h)	3	79 (5h)
10	<i>i</i> -Bu	Me	Me (3i)	3	87 (5i)
11	Bn	Me	Me (3j)	3	83 (5j)
12	CH ₂ CH ₂ Ph	Me	Me (3k)	3	85 (5k)
13^d	Ph	Me	Ph (31)	17	72 (51)
14	CH ₂ COOMe	Me	Ph (3m)	4	85 (5m)
15^e	CH ₂ CH ₂ CN	Me	Me (3n)	10	80 (5 n)
16	CH ₂ COPh	Me	Me (30)	13	62 (50)
17	(CH ₂) ₂ OTBS		Me (3p)	3	72 (5p)
18	(CH ₂) ₃ OTBS	Me	Me (3 q)	3	71 (5 q)

^a Reaction conditions: 1.0 mmol of 3, 0.05 mmol of CuCl, 0.05 mmol of BIPHEP, 0.2 mmol of NaOt-Bu, 1.2 mmol of B2(pin)2, 2.0 mmol of i-PrOH in 3 mL of THF at rt. ^b Isolated yield. ^c The reaction is carried out in a one-gram scale. ^d Conditions: 0.4 mmol of NaOt-Bu and 1.4 mmol of B₂(pin)₂ at 45 °C. ^e Conditions: 0.35 mmol of NaOt-Bu and 1.4 mmol of B₂(pin)₂ in 10 mL of THF.

Interestingly, the substrate with an unprotected hydroxyl group 3r afforded the cyclic boronic acid product 5r in 57% yield after column chromatography (Scheme 2). Furthermore, the reaction of bis(propadienyl) silanes 3s and 3t afforded

PhMe₂Si
$$\frac{\text{CuCl (5 mol\%), BIPHEP (5 mol\%)}}{\text{NaOt-Bu (20 mol\%), B}_2(\text{pin})_2 (1.2 \text{ equiv})}$$
 $\frac{\text{SiMe}_2\text{Ph}}{\text{Sir} \text{ 57}\%}$ $\frac{\text{CuCl (5 mol\%), BIPHEP (5 mol\%)}}{\text{SiMe}_2\text{Ph}}$ $\frac{\text{CuCl (5 mol\%), BIPHEP (5 mol\%)}}{\text{K}_2\text{CO}_3 (20 \text{ mol\%), B}_2(\text{pin})_2 (2.5 \text{ equiv})}$ $\frac{\text{SiR}_2}{\text{i-PrOH (4.0 equiv), THF, rt, 3 h}}$ $\frac{\text{CuCl (5 mol\%), BIPHEP (5 mol\%)}}{\text{K}_2\text{CO}_3 (20 \text{ mol\%), B}_2(\text{pin})_2 (2.5 \text{ equiv})}$ $\frac{\text{SiR}_2}{\text{i-PrOH (4.0 equiv), THF, rt, 3 h}}$ $\frac{\text{SiR}_2}{\text{SiR}_2}$ $\frac{\text{SiR}_2}{\text{S$

Scheme 2 Borylation of diallenylsilanes.

highly functionalized bis(2-borylallyl)silane products 5s and 5t in decent yields (Scheme 2).

It is also observed that the reactivity of such a silvl-substituted allene unit is much higher than those of C-C double bonds and C-C triple bonds: no reaction occurred in the C=C bond in 3u and 3v,14 the reaction of 1,2-allenyl propargyl silane 3w afforded allylic silane 5w with borylation occurring in the allene moiety exclusively (Scheme 3).¹⁵

Scheme 3 The selectivity of allene vs. alkene or alkyne.

According to the DFT study performed by Ito et al. for such a borylcupration with the C=C bond in alkenes by applying Xantphos as the ligand, the steric effect of the (pin)B unit dictates the regioselectivity.16 Thus, we reasoned that with Xantphos, the corresponding borylcupration reaction produces Int A with the B(pin) connected to the terminal carbon atom (Scheme 4).12 Due to the more sterically bulky bidentate nature of Xantphos¹⁷ we speculated that the reactivity of (pin) B-Cu(Xantphos) towards the allene unit should be much lower than that of (pin)B-Cu(BIPHEP). This was confirmed by the

Scheme 4 Deuterium-labelling experiment and a rationale for the regioselectivity.

collection of data from the control reactions of 3a in the same solvent, i.e., THF, at a lower temperature of 0 °C with Xantphos or BIPHEP, affording Z-4a and 5a, respectively (Fig. 1).

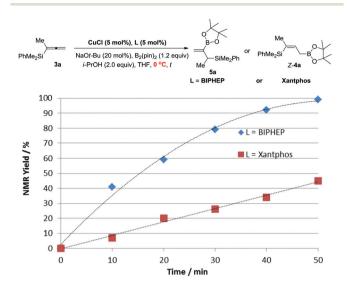


Fig. 1 Control reactions of 3a with Xantphos or BIPHEP as the ligand.

Furthermore, the reaction of 3a with BIPHEP in the presence of i-PrOH_{d-8} (99% D) formed the η^{1} -allylic Cu intermediate Int B, which was subsequently protonated regiospecifically at the γ-position to afford the observed product [D]-5a with 92% deuterium incorporation at the non-terminal allylic position exclusively in 87% yield (Scheme 4). Of course, the formation of Int C where the C-Cu bond is in the alpha position of the silvl group may NOT be completely excluded although it is NOT sterically favored. It should be noted that further study is required to unveil the interesting ligand effect.

To demonstrate the utility of these products, Suzuki-Miyaura coupling of 5e with 2-iodobenzaldehyde was conducted, which was followed by intramolecular allylation promoted with n-Bu₄NF to afford 3-methyleneindan-1-ol 7 in a combined yield of 67% (Scheme 5).18 Nucleophilic allylation of acetals with 5e in the presence of TiCl4 led to 2-boryl-substituted homoallyl ethers 8a and 8b in high yields. 19 The Suzuki coupling product of 5e with iodobenzene 9 was treated with benzaldehyde to produce homoallyl alcohol 10 in 70% yield. 11b,20 Under the catalysis of TMSOTf, the product 5p bearing a siloxyalkyl group may react with an aldehyde to undergo allylation and in situ etherification producing cyclic alkenyl boronate 11 in 85% yield, which may further be coupled with iodobenzene to afford 7-membered cyclic ether 12 in 84% yield. 19

In summary, we have developed the highly regioselective borylcupration of 1,2-allenylsilanes, which provides an efficient method for the preparation of 2-borylallylic silanes with a terminal C=C bond from readily available 1,2-allenylsilanes²¹ in good to excellent yields with an excellent regioselectivity under mild conditions by applying the ligand effect. The synthetic potential has been demonstrated. Further

Scheme 5 Synthetic applications of 5e and 5p.

studies including the interesting ligand effect are underway in this laboratory.

Acknowledgements

Research Article

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