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

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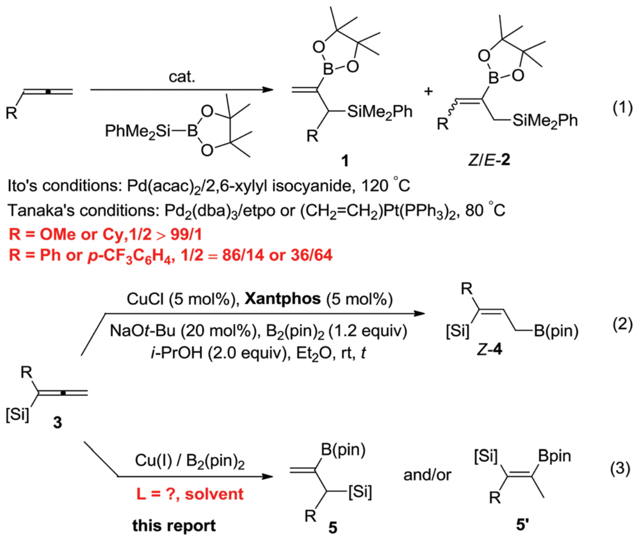
A highly chemo- and regioselective copper-catalyzed borylcupration of 1,2-allenylsilanes affords 2-borylallylsilanes by applying the ligand effect. Many synthetically attractive functional groups are well tolerated. As demonstrated, such 2-borylallylsilanes are very useful dimetallic reagents in organic 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.[1] Among them, 2-borylallylic silanes, which contain both vinylboronate and allylsilane units, would be very useful in various organic transformations since allylic silanes[2] are well-known for their wide applications in Hiyama couplings,[3] dihydroxylation,[4] aminohydroxylation,[5] epoxidation,[6] cyclopropanation,[7] and Lewis acid-mediated [2 + 2] and [3 + 2] annulation with electron-deficient olefins[8] or free radical additions.[9] While the vinylboronate moiety is very useful in Suzuki cross-coupling reactions.[10]

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 allenylsilanes affording 3-silylallylboronates *Z*-**4** exclusively (eqn (2)).[13] We envisioned whether such 1,2-allenylsilanes may be borylcuprated with $B_2(pin)_2$ 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 $B_2(pin)_2$ 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



Scheme 1 Previous reports and our concept.

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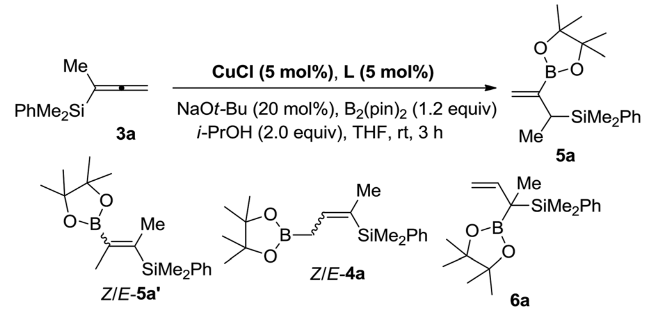
did not lead to better reaction media (entries 4 and 5). Compared with other copper catalysts such as CuBr and CuI, CuCl is the most efficient (entries 6 and 7). Control experiments showed that the ligand and base are both essential to the reaction (entries 8 and 9). Thus, we defined 5 mol% CuCl with 5 mol% BIPHEP as the catalyst, 20 mol% NaO*t*-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]

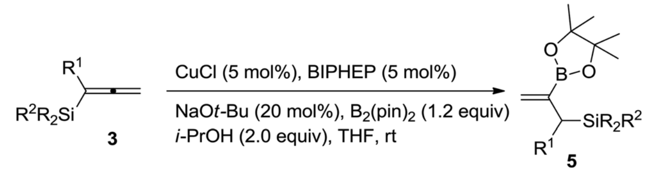


Entry	Ligand	NMR yield of **5a** (%)	Recovery of **3a** (%)
1	DPPE	30	59
2	*rac*-BINAP	96	—
3	BIPHEP	98	—
4[b]	BIPHEP	89	4
5[c]	BIPHEP	68	24
6[d]	BIPHEP	92	—
7[e]	BIPHEP	21	75
8	—	0	71
9[f]	BIPHEP	0	77

[a] Reaction conditions: 0.2 mmol of **3a**, 5 mol% CuCl, 5 mol% ligand, 20 mol% NaO*t*-Bu, 0.24 mmol of $B_2(pin)_2$, 0.4 mmol of i-PrOH in 3 mL of THF at rt for 3 h under an argon atmosphere. [b] $PhCH_3$ was used instead of THF. [c] Et_2O was used instead of THF. [d] CuBr was instead of CuCl. [e] CuI was instead of CuCl. [f] NaO*t*-Bu was not added.

With the optimized conditions in hand, we started to examine the substrate scope: with CH_3 and $SiMe_2Ph$ 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 $MePh_2$, Ph_3 or *t*-$BuMe_2$ (entries 3–5); the reaction of the allenylsilane with R^1 = H could also proceed smoothly in 76% yield (entry 6); R^1 may be an alkyl group beyond Me such as Et, *n*-C_3H_7 or *n*-C_8H_{17} (entries 7–9); other alkyl groups such as *i*-Bu, Bn or CH_2CH_2Ph may also work under the standard conditions (entries 10–12); R^1 may also be a phenyl group by conducting the reaction at 45 °C (entry 13). Furthermore, 1,2-allenylsilanes 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).

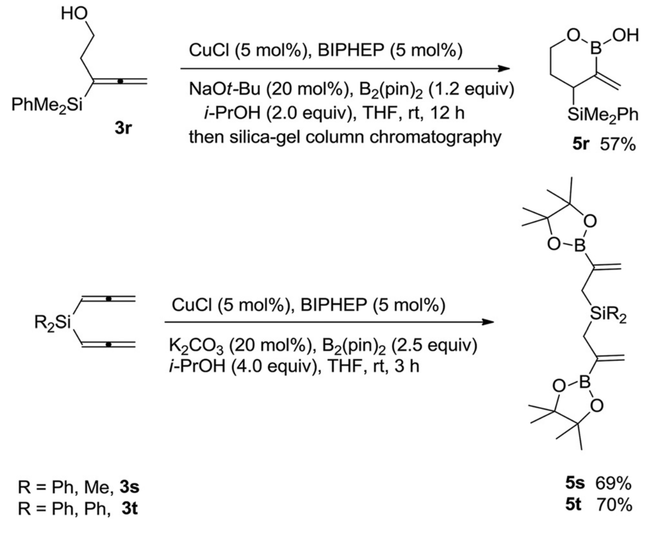
Table 2 Substrate scope[a]



Entry	R^1	R	R^2	Time (h)	Yield of **5** [b] (%)
1	Me	Me	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	*t*Bu (**3d**)	3	76 (**5d**)
6	H	Me	Ph (**3e**)	3	76 (**5e**)
7	Et	Me	Ph (**3f**)	2	89 (**5f**)
8	*n*-C_3H_7	Me	Ph (**3g**)	3	87 (**5g**)
9	*n*-C_8H_{17}	Me	Me (**3h**)	3	79 (**5h**)
10	*i*-Bu	Me	Me (**3i**)	3	87 (**5i**)
11	Bn	Me	Me (**3j**)	3	83 (**5j**)
12	CH_2CH_2Ph	Me	Me (**3k**)	3	85 (**5k**)
13[d]	Ph	Me	Ph (**3l**)	17	72 (**5l**)
14	CH_2COOMe	Me	Ph (**3m**)	4	85 (**5m**)
15[e]	CH_2CH_2CN	Me	Me (**3n**)	10	80 (**5n**)
16	CH_2COPh	Me	Me (**3o**)	13	62 (**5o**)
17	$(CH_2)_2OTBS$	Me	Me (**3p**)	3	72 (**5p**)
18	$(CH_2)_3OTBS$	Me	Me (**3q**)	3	71 (**5q**)

[a] Reaction conditions: 1.0 mmol of **3**, 0.05 mmol of CuCl, 0.05 mmol of BIPHEP, 0.2 mmol of NaO*t*-Bu, 1.2 mmol of $B_2(pin)_2$, 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 NaO*t*-Bu and 1.4 mmol of $B_2(pin)_2$ at 45 °C. [e] Conditions: 0.35 mmol of NaO*t*-Bu and 1.4 mmol of $B_2(pin)_2$ in 10 mL of THF.

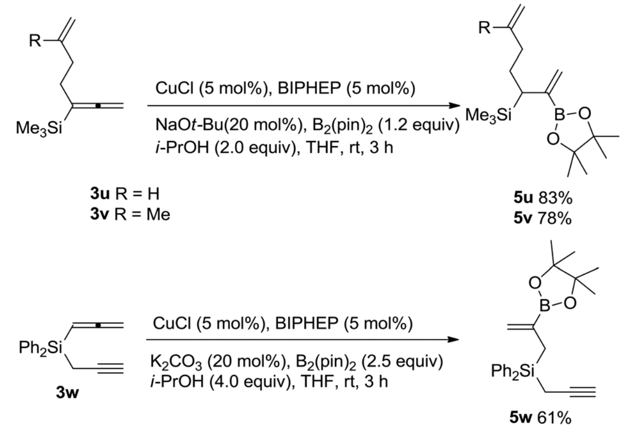
Interestingly, the substrate with an unprotected hydroxyl group **3r** afforded the cyclic boronic acid product **5r** in 57% yield after column chromatography (Scheme 2). Furthermore, the reaction of bis(propadienyl) silanes **3s** and **3t** afforded



Scheme 2 Borylation of diallenylsilanes.

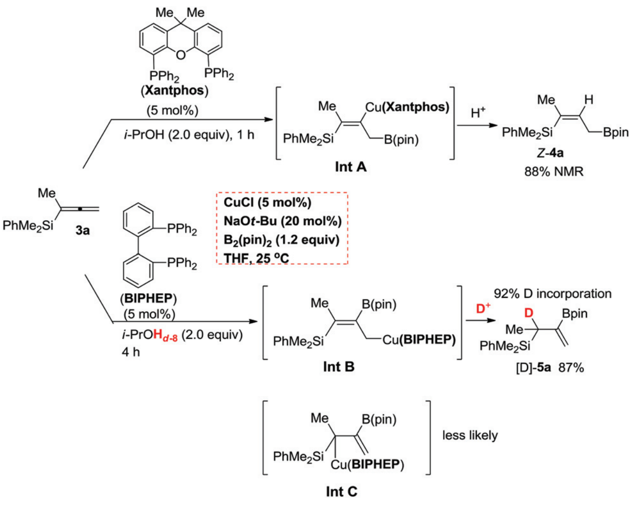
highly functionalized bis(2-borylallyl)silane products **5s** and **5t** in decent yields (Scheme 2).

It is also observed that the reactivity of such a silyl-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 Xantphos[17] 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 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).



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

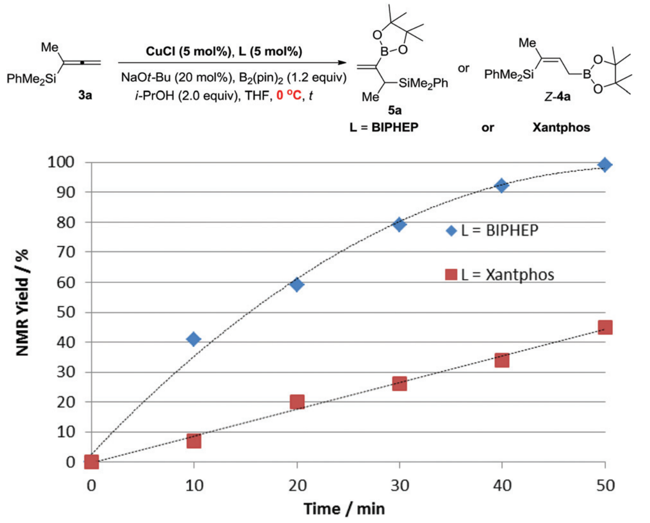
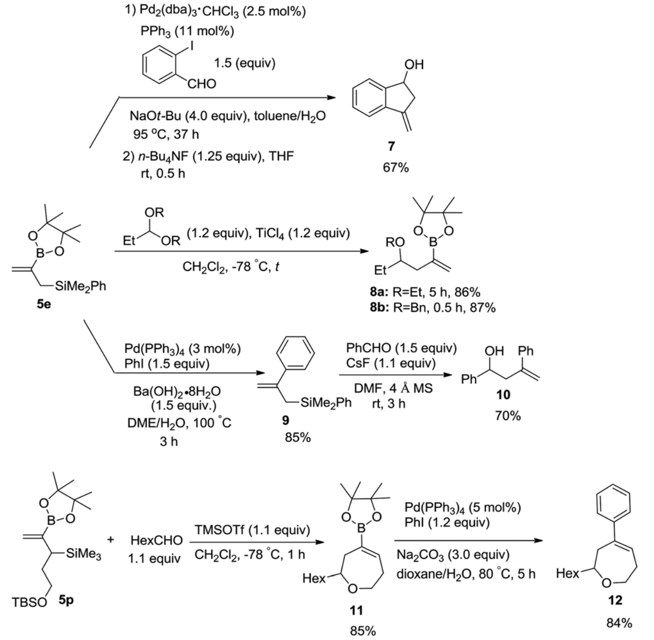


Fig. 1 Control reactions of **3a** with Xantphos or BIPHEP as the ligand.

Furthermore, the reaction of **3a** with BIPHEP in the presence of *i*-PrOH$_{d\text{-}8}$ (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 silyl 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*-Bu$_4$NF 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 TiCl$_4$ 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.[11*b*,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-allenylsilanes[21] 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

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