Allylic Compounds

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Copper-Catalyzed Borylcupration of Allenylsilanes

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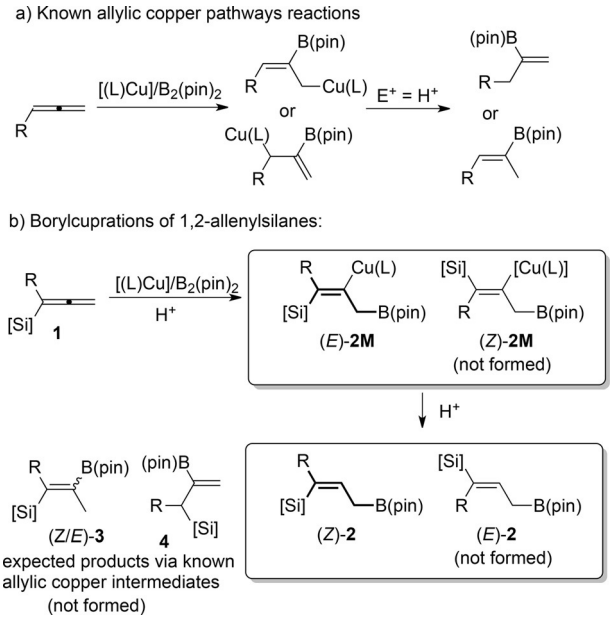
Abstract: *A highly regio- and stereoselective copper-catalyzed borylcupration of 1,2-allenylsilanes affords an unexpected regioreversed allylic boronate bearing an extra C–Si bond at the 3-position, with a thermodynamically disfavored Z geometry. Such stereodefined allylic boronates containing an extra alkenyl silane moiety are very useful organodimetallic reagents for organic synthesis.*

Recently, the highly regio- and stereoselective copper-catalyzed borylcupration of allenes with bis(pinacolato)diboron [$B_2(pin)_2$], thus providing 1-alkenyl boronates, was established to proceed via favored allylic copper intermediates (Scheme 1 a).[1–4] On the other hand, allylic metallic compounds with an extra carbon–metallic bond, such as allylic boronates with a C–Si bond (**2;** Scheme 1 b), are important synthetic reagents because of the stability, low toxicity, versatile reactivity as a result of the allylic nature,[5,6] and broad functionality compatibility, thus leading to polyfunctional compounds efficiently by the reactions of both C–M bonds.[7] The preparation of compounds of type **2**, which are thermodynamically stable *E* isomers, has been established.[8] However, the thermodynamically disfavored stereoisomers (*Z*)-**2** are still difficult to access.[9] Thus, the development of an efficient approach towards the stereodefined 3-silylalk-2(*Z*)-enyl boronates is of high interest. Herein, we report an unexpected observation that the borylcupration of the allenylsilanes **1** exclusively afforded the 3-silylalk-2(*Z*)-enyl boronates (*Z*)-**2**, via the 1-alkenyl copper intermediate (*E*)-**2M**, with the opposite regioselectivity and thermodynamically disfavored stereoselectivity as compared to the reaction shown in Scheme 1 a. In addition, the usually expected products, the 1-alkenyl boronates (*Z*)-**3**, (*E*)-**3**, and **4**, via the most favored allylic copper intermediates, were not formed.

We initially studied the borylcupration of the allenylsilane **1m**[10] with $B_2(pin)_2$ (Table 1). Firstly, a series of monodentate phosphine ligands was screened: the expected 1-alkenyl boronate **4m**, via an allylic copper intermediate, was formed as the only product with a very low yield; most of the starting material was recovered (entries 1–6). No allylboronate product was detected. Subsequently, bidentate ligands were investigated and when DPEphos was used we observed the formation of the 3-silylallylboronate **2m**, having exclusively a *Z* geometry, albeit together with the regioisomer **4m** (entry 7). Xantphos[11] demonstrated the best result with the exclusive formation of (*Z*)-**2m** in 88% yield within 1 hour (entry 8). Screening of other solvents led to the observation that the reaction in Et_2O yielded (*Z*)-**2m** in a higher yield of 95% with the same excellent selectivity (entry 9). Thus, we successfully established the standard reaction conditions: CuCl (5 mol%), Xantphos (5 mol%), NaO*t*Bu (20 mol%), $B_2(pin)_2$ (1.2 equiv), *i*PrOH (2.0 equiv), Et_2O at RT, for the exclusive formation of the (*Z*)-**2**. The formation of the thermodynamically more stable (*E*)-**2m**, the related **3**-type of product (see Scheme 1), and **4m** was not observed.



Scheme 1. Background information and new observation for allene borylcuprations.

With the optimized reaction conditions in hand, we next explored the scope of the reaction (Table 2). Firstly, when [Si] = TMS, substrates with various primary alkyl groups led to good results (entries 1–3). With secondary alkyl substituents, such as *i*Pr or Cy, the reaction afforded a mixture of (*Z*)-**2d** and **4d** and (*Z*)-**2e** and **4e**, respectively, with a slightly lower regioselectivity. These regioisomers could be easily separated by chromatography on silica gel (entries 4 and 5). Moreover, when R = *i*Bu, Bn, or CH_2CH_2Ph, the reactions proceeded with excellent regio- and stereoselectivities (entries 6–8). To our delight, unsaturated functional groups

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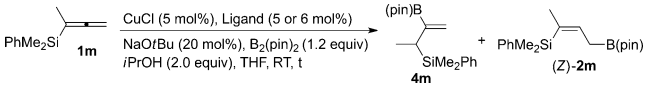
Table 1: Optimization of the reaction conditions for copper-catalyzed selective borylcupration of the allenylsilane **1m** to produce the 3-silyl-2(*Z*)-allylic boronate (*Z*)-**2m**.[a]



Entry	Ligand	*t* [h]	Yield [%][b] **4m**[c]	(*Z*)-**2m**	(*Z*)-**2m**/**4m**[d]
1[e]	PPh_3	4	10 (67)	n.d.	–
2[e]	TFP	4	7 (71)	n.d.	–
3[e]	PCy_3	4	13 (65)	n.d.	–
4[e]	$P(tBu)_3$	4	12 (66)	n.d.	–
5[e]	$P(p\text{-}MeOC_6H_4)_3$	4	12 (74)	n.d.	–
6[e]	LBphos	4	14 (74)	n.d.	–
7[f]	DPEphos	1	49	39	44:56
8[f]	Xantphos	1	n.d.	88	>99:1
9[f,g]	Xantphos	1	n.d.	95	>99:1

[a] Reaction conditions: 0.2 mmol of **1m**, 5 mol% CuCl, 20 mol% NaO*t*Bu, 0.24 mmol of $B_2(pin)_2$, 0.4 mmol of *i*PrOH in 2 mL of THF at RT. [b] Determined by NMR spectroscopy using 1,3,5-trimethylbenzene as an internal standard. [c] The value within the parentheses is that of the recovered of starting material. [d] The selectivity was determined by ^{1}H NMR analysis of the crude reaction mixture. [e] 6 mol% ligand was used. [f] 5 mol% ligand was used. [g] The solvent was Et_2O. TFP = tri(2-furyl)phosphine.

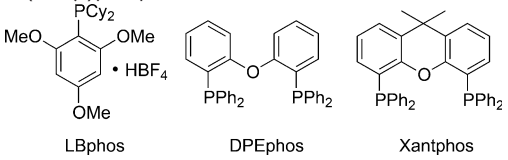
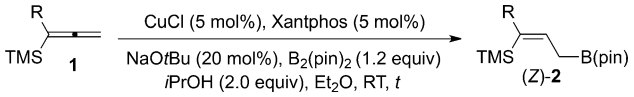


Table 2: Highly selective ligand-controlled borylcupration of allenylsilanes yielding 3-silyl-2(*Z*)-allylboronates [(*Z*)-**2**].[a]



Entry	R	*t* [min]	Yield [%][b]
1	nC_4H_9 (**1a**)	40	84 [(*Z*)-**2a**]
2	nC_5H_{11} (**1b**)	40	86 [(*Z*)-**2b**]
3	nC_8H_{17} (**1c**)	60	85 [(*Z*)-**2c**]
4	*i*Pr (**1d**)	60	81 [(*Z*)-**2d**][c]
5	Cy (**1e**)	60	81 [(*Z*)-**2e**][d]
6	*i*Bu (**1f**)	60	84 [(*Z*)-**2f**]
7	Bn (**1g**)	60	80 [(*Z*)-**2g**]
8	CH_2CH_2Ph (**1h**)	60	85 [(*Z*)-**2h**]
9	$(CH_2)_2CH{=}CH_2$ (**1i**)	40	81 [(*Z*)-**2i**]
10	$(CH_2)_2C(Me){=}CH_2$ (**1j**)	40	80 [(*Z*)-**2j**]
11	$(CH_2)_2OTBS$ (**1k**)	60	75 [(*Z*)-**2k**]
12	$(CH_2)_3OTBS$ (**1l**)	90	74 [(*Z*)-**2l**]

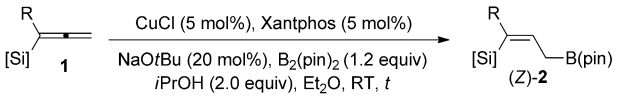
[a] Reaction conditions: 1.0 mmol of **1**, 5 mol% CuCl, 5 mol% Xantphos, 20 mol% NaO*t*Bu, 1.2 mmol of $B_2(pin)_2$, 2.0 mmol of *i*PrOH in 3 mL of Et_2O at RT. [b] Yield of isolated product. [c] The ratio of (*Z*)-**2d**/**4d** = 96:4. [d] The ratio of (*Z*)-**2e**/**4e** = 92:8.

such as homoallylic substituents were also tolerated under the standard reaction conditions to afford the corresponding products with exciting results (entries 9 and 10), thus indicating that the reactivity of the C=C bond in the allene unit is much higher than that of an alkene. Furthermore, a substrate having a TBS-protected hydroxy group also worked well (entries 11 and 12).

Furthermore, with R = CH_3, the reactions proceeded smoothly to afford the corresponding allylic boronates (*Z*)-**2** products in decent yields with excellent selectivities irrespective of whether the silyl group is $SiMe_2Ph$, $SiMePh_2$, $SiPh_3$, or $SitBuMe_2$ (Table 3, entries 1–5). In addition, R may also be Et or *n*Pr (entries 6 and 7). For R = aryl, the amount of base and $B_2(pin)_2$ had to be increased and the reaction time prolonged to 15–17 hours to ensure full conversion (entries 8–11). Gratifyingly, the reaction could be run on a one-gram scale to give excellent yield and the same selectivity (entry 2). Moreover, the stereochemistry of the products was established by single-crystal X-ray diffraction of (*Z*)-**2o** (Figure 1).[12]

To demonstrate the factors controlling the stereoselectivity, the silyl group was replaced with *t*Bu, and the reaction still afforded (*Z*)-**2w** with high stereoselectivity (Scheme 2). However, when the silyl group was replaced with *n*Bu, the reaction afforded **2x** in a 73:27 *E*/*Z* mixture, thus indicating the importance of the steric bulkiness of the silyl group on the

Table 3: Highly selective ligand-controlled borylcupration of allenylsilanes using various silyl substituents.[a]



Entry	R/[Si]	*t*	Yield [%][b]
1	$Me/SiMe_2Ph$ (**1m**)	40 min	90 [(*Z*)-**2m**]
2[c]	$Me/SiMe_2Ph$ (**1m**)	30 min	90 [(*Z*)-**2m**]
3	$Me/SiMePh_2$ (**1n**)	35 min	88 [(*Z*)-**2n**]
4	$Me/SiPh_3$ (**1o**)	40 min	86 [(*Z*)-**2o**]
5	$Me/SitBuMe_2$ (**1p**)	60 min	85 [(*Z*)-**2p**]
6	$Et/SiMe_2Ph$ (**1q**)	40 min	80 [(*Z*)-**2q**]
7	$nC_3H_7/SiMe_2Ph$ (**1r**)	60 min	88 [(*Z*)-**2r**]
8[d]	$Ph/SiMe_2Ph$ (**1s**)	15 h	82 [(*Z*)-**2s**]
9[d]	$4\text{-}MeC_6H_4/SiMe_2Ph$ (**1t**)	17 h	73 [(*Z*)-**2t**]
10[d]	$3\text{-}MeOC_6H_4/SiMe_2Ph$ (**1u**)	17 h	85 [(*Z*)-**2u**]
11[d]	2-Naphthyl/$SiMe_2Ph$ (**1v**)	17 h	65 [(*Z*)-**2v**]

[a] Reaction conditions: 1.0 mmol of **1**, 5 mol% CuCl, 5 mol% Xantphos, 20 mol% NaO*t*Bu, 1.2 mmol of $B_2(pin)_2$, 2.0 mmol of *i*-PrOH in 3 mL of Et_2O at RT. [b] Yield of isolated product. [c] The reaction was conducted on one gram scale. [d] 40 mol% NaO*t*Bu and 1.4 mmol of $B_2(pin)_2$ were used.

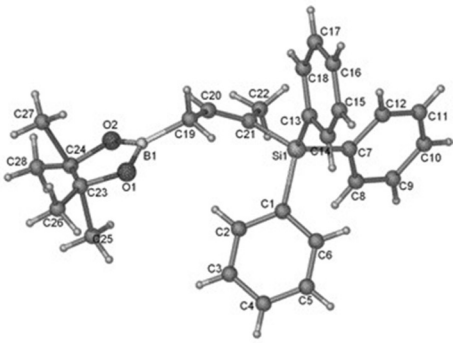
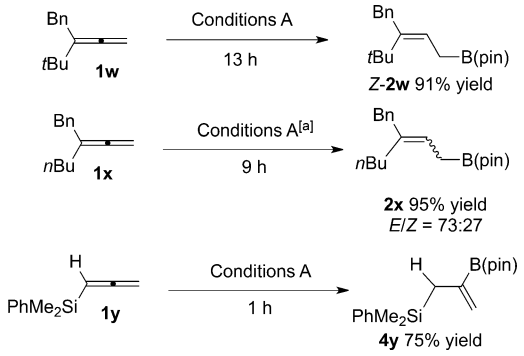


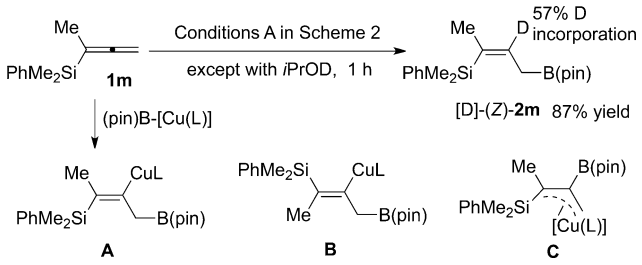
Figure 1. ORTEP representation of (*Z*)-**2o**.



Scheme 2. Factors controlling the regio- and stereoselectivities. Conditions A: CuCl (5 mol%), Xantphos (5 mol%), NaO*t*Bu (20 mol%), $B_2(pin)_2$ (1.2 equiv), *i*PrOH (2.0 equiv), Et_2O, RT. [a] Used 1.5 equiv $B_2(pin)_2$.

stereoselectivity. In addition, the reaction of **1y** afforded the vinylboronate **4y**, thus indicating the effect of the R group, as shown in the equations for Tables 2 and 3, on the regioselectivity.

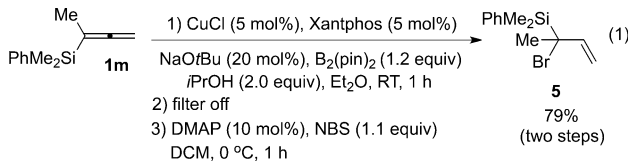
To capture the organocopper intermediate, the reaction of **1m** was conducted with *i*PrOD, with 80% D-labelling, instead of *i*PrOH, and it afforded an 87% yield of [D]-(*Z*)-**2m** with 57% deuterium incorporation at the vinylic position (Scheme 3). This result indicates that the vinylic copper



Scheme 3. Deuterium-labelling experiment and mechanism for the regio- and stereoselectivity.

intermediate **A** was formed in the reaction. Based on these factors, a mechanism for this reaction is proposed, as shown in Scheme 3. The preferable formation of **A** over **B** is due to the favorable *trans* orientation of the C–CuL bond and C–Si bond in **A**, and is caused by steric effects. The regioselectivity was most probably determined by the crowded nature of delocalized allylic copper intermediate **C** since the reaction of **1y** afforded the allylic copper-based product **4y** (Scheme 3).

As a synthetic application, a two-step synthesis of the allylic silane **5** with a terminal C=C bond was prepared in a 79% combined yield [Eq. (1); DCM = dichloromethane, DMAP = 4-(*N*,*N*-dimethylamino)pyridine].



In conclusion, we have developed highly selective copper-catalyzed borylcuprations of the simple 1,2-allenylsilanes, thereby providing an efficient method for the synthesis of the thermodynamically disfavored 3-silylalk-2(*Z*)-enylboronates in high yields and excellent selectivities starting from allenylsilanes. Notably, it is the first observation of a boryl group, B(pin), connected to the terminal carbon atom of an allene to produce the regioreversed allylboronates in copper-catalyzed borylcupration of allenes with $B_2(pin)_2$. Control experiments show that both the steric effects of the ligand and substrates determine the regio- and stereoselectivities. Further studies, including a look at the mechanism and synthetic applications, are underway in this laboratory.

Experimental Section

CuCl (5.0 mg, 0.05 mmol), Xantphos (29.1 mg, 0.05 mmol), NaO*t*Bu (19.3 mg, 0.2 mmol), bis(pinacolato)diboron (304.6 mg, 1.2 mmol)/Et_2O (2 mL), **1a** (169.6 mg, 1.0 mmol)/Et_2O (1 mL), *i*PrOH (153 μL, $d = 0.784\ g\,mL^{-1}$, 120.2 mg, 2.0 mmol) were added sequentially to an oven-dried Schlenk tube under argon. The mixture was stirred at RT for 40 min and monitored by TLC. The resulting mixture was filtered through a short column of silica gel, eluting with Et_2O (3x20 mL) and concentrated. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl ether = 50:1) to afford (*Z*)-**2a** (249.3 mg, 84%) as a liquid: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.06$ (t, $J = 8.6$ Hz, 1H, = CH), 2.04 (t, $J = 8.6$ Hz, 2H, CH_2), 1.78 (d, $J = 8.1$ Hz, 2H, = CCH_2), 1.32–1.19 (m, 16H, 2 × CH_2 and B(pin)), 0.87 (t, $J = 6.8$ Hz, 3H, CH_3), 0.13 ppm (s, 9H, $SiMe_3$); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 138.6$, 137.1, 83.0, 38.2, 33.2, 24.7, 22.3, 14.0, 0.2 ppm; IR (neat): $\tilde{\nu} = 2957$, 2926, 2857, 1607, 1465, 1323, 1248, 1144 cm^{-1}; MS (ESI) *m*/*z* (%) 319 $[M+Na]^+$; HRMS Calcd. for $C_{16}H_{33}{}^{11}BO_2Si$ $[M]^+$: 296.2343, Found: 296.2345.

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Keywords: allylic compounds · boron · copper · regioselectivity · stereoselectivity

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[12] X-ray crystal data for compound (*Z*)-**2o**: $C_{28}H_{33}BO_2Si$; MW = 440.44, monoclinic space group $P2(1)/c$; final R indices [$I > 2\sigma(I)$], $R1 = 0.0658$, $wR2 = 0.1705$, *R indices* (all data) $R1 = 0.0893$, $wR2 = 0.1907$; $a = 11.1944(3)$ Å, $b = 19.1263(5)$ Å, $c = 12.3819(3)$ Å, $\alpha = 90°$, $\beta = 93°$, $\gamma = 90°$; $V = 2646.62(12)$ Å^3; $T = 296(2)$ K; $Z = 4$; reflections collected/ unique 30458/4664 [$R_{int} = 0.0551$], number of observations [$I > 2\sigma(I)$] 3395, parameters: 290. CCDC 1010390 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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