## Highly Selective Copper-Catalyzed Hydroboration of Allenes and 1,3-Dienes

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**Abstract:** The highly selective coppercatalyzed hydroboration of allenes has been developed. Allylboranes and alkenylboranes were selectively prepared by the judicious choice of catalytic species (copper hydride and boryl copper). Furthermore, two types of alkenylboranes could be selectively synthesized by the choice of an appropriate ligand. Mechanistic studies confirmed that the protonation of a (Z)- $\sigma$ -allyl copper species, which was isolated and structural-

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diffraction, was a key step in these reactions. Besides allenes, this method is also applicable to the selective hydroboration of 1,3-diene derivatives to afford allylboranes and homoallylboranes.

ly characterized by single-crystal X-ray

### Introduction

Pinacolborane  $(HB(pin))^{[1]}$  and bis(pinacolato)diboron  $(B_2(pin)_2)^{[2]}$  are stable and easy-to-handle representative borylation reagents. Various transition-metal catalysts show good catalytic activity in borylation reactions with HB(pin) or B<sub>2</sub>(pin)<sub>2</sub>.<sup>[1,2]</sup> In particular, in the presence of a copper catalyst, HB(pin) generates copper hydride  $(Cu-H)^{[3]}$  and B<sub>2</sub>-(pin)<sub>2</sub> affords boryl copper  $(Cu-B)^{[4]}$  catalytic species. Recently, we reported the regioselective copper-catalyzed hydroboration of unsymmetrical internal alkynes through a clean generation of one of the two catalytic species (Cu–H or Cu–B, Scheme 1).<sup>[5]</sup>

As for the hydroboration of allenes,<sup>[6]</sup> even mono-substituted substrates may provide up to six regio- and stereo-



Scheme 1. Copper-catalyzed regioselective hydroboration of unsymmetrical internal alkynes.

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isomers (Scheme 2).<sup>[7]</sup> In the uncatalyzed hydroboration of allenes with reactive di(alkyl)boranes, such as 9-BBN (9-borabicyclo[3.3.1]nonane),<sup>[8a]</sup> HBCy<sub>2</sub> (Cy=cyclohexyl),<sup>[8a]</sup> HB(sia)<sub>2</sub> (sia=1,2-dimethylpropyl),<sup>[8b]</sup> and 10-TMS-9-BBD-H (10-TMS-9-borabicyclo[3.3.2]decane),<sup>[8c]</sup> allylboranes (2) were afforded as the major products. However, the drawback of the methods involving these reactive di-(alkyl)boranes is substantial instability of both the borane reagents and the resulting hydroboration products. Furthermore, these reactions often suffered from low regioselectivity and/or the formation of di-hydroborated byproducts.<sup>[8a,b]</sup> In contrast, di(alkoxy)boranes are much more stable and easy-to-handle reagents and the resulting allylborane<sup>[9]</sup> or alkenylborane products<sup>[10]</sup> can be isolated and stored for further reactions. However, the uncatalyzed hydroboration reaction with these less-reactive di(alkoxy)boranes required harsh reaction conditions (130°C), as indicated by the reaction of 4,4,6-trimethyl-1,3,2-dioxaborinane (HBR<sub>2</sub>, R<sub>2</sub>=OC-Me<sub>2</sub>CH<sub>2</sub>CHMeO) with allenes,<sup>[8d]</sup> and the selectivity between allylboranes and alkenylboranes was insufficient.

To utilize these stable di(alkoxy)boranes, transition-metalcatalyzed reaction are beneficial because of the mild reaction conditions. However, surprisingly, there are only two precedents for the transition-metal-catalyzed hydroboration of allenes.<sup>[11a,b]</sup> Firstly, Miyaura and co-workers reported the transition-metal-catalyzed hydroboration of terminal allenes by employing HB(pin) in the presence of a platinum catalyst.<sup>[11a]</sup> The selectivities of the products (**2**, **4**, and **5**) varied considerably depending on the allene substituents and the nature of the added phosphane ligands. Secondly, during the preparation of this manuscript,<sup>[12]</sup> Yuan and Ma reported the copper-catalyzed hydroboration of mono-substituted allenes by using B<sub>2</sub>(pin)<sub>2</sub>, thereby providing compounds (*Z*)-**4** and **5**.<sup>[11b]</sup>

Herein, we report the copper-catalyzed hydroboration of allenes by employing HB(pin) or  $B_2(pin)_2$  as a borylating reagent (Scheme 3). The selectivity for allylboranes ((*E*)-2)

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Scheme 2. Plausible products from the hydroboration of 1-substituted allenes.



Scheme 3. Copper-catalyzed hydroboration of allenes.

and alkenylboranes ((Z)-4 and 5) was successfully controlled by a judicious choice of the catalytic species (Cu–H or Cu– B). Notably, two types of alkenylboranes ((Z)-4 and 5) were selectively obtained by choosing suitable ligands. Thus, this method can selectively afford three different hydroboration products from a single substrate. Furthermore, this catalytic procedure can also be applicable to the selective hydroboration of 1,3-dienes.

### **Results and Discussion**

Hydroboration of allenes with HB(pin) to afford allylboranes (2): First, the copper-catalyzed hydroboration of cyclohexylallene ( $\mathbf{R}^1 = \mathbf{Cy}$ : **1a**) was performed by employing HB-(pin) as a hydroborating agent in the presence of various ligands (Table 1). Monodentate phosphane ligands, such as PPh<sub>3</sub> and PCy<sub>3</sub>, were not effective and almost no allylborane (2a) was obtained (Table 1, entries 1 and 2). With bidentate phosphane ligands, such as 1,2-diphenylphosphinobenzene (dppbz), Xantphos (Xan, 4,5-bis(diphenylphosphanyl)-9,9dimethylxanthene), Me-ArXan, and CF<sub>3</sub>-ArXan (for the structures of these ligands, see Figure 1), the yields were dramatically improved and compound 2a was obtained in good-to-high yields with high E selectivities (Table 1, entries 3-6). Among these ligands, CF<sub>3</sub>Ar-Xan<sup>[5]</sup> was the most effective, thus giving compound 2a in 99% yield with high selectivity (E/Z, 95:5; Table 1, entry 6). Notably, compound (E)-2a could be isolated in its pure form by column chromatography on silica gel in air in 78% yield. When N-heterocyclic carbene (NHC) ligands, such as IPr and IMes (Figure 1), were used, both the yields and regioselectivities decreased considerably (Table 1, entries 7 and 8). In all of these cases, other isomers, such as allylborane **3a** and alkenylboranes **4a** and **5a**, were not produced.

The hydroboration of various allenes to afford allylboranes (2) was achieved by employing HB(pin) in the presence of a catalytic amount of CuCl with  $CF_3Ar$ -Xan as a ligand (Table 2). Allenes that con-

tained a primary alkyl group (**1b** and **1c**) afforded their corresponding allylboranes (**2b** and **2c**) in good yields, albeit with slightly low E/Z ratios (Table 2, entries 1 and 2). In contrast, allenes that contained secondary or tertiary alkyl substituents (**1d** and **1e**) afforded their corresponding allylboranes (**2d** and **2e**) in good yields with high E/Z ratios (Table 2, entries 3 and 4). In the case of allenes that were conjugated with an aromatic ring, the products (**2f–2h**) were obtained with perfect stereoselectivity (Table 2, entries 5–7). The reaction of a 1,1-disubstituted allene (**1i**) also provided its corresponding allylborane (**2i**; Table 2, entry 8).

Table 1. Hydroboration of cyclohexylallene (1a) with HB(pin) by using various copper catalysts.<sup>[a]</sup>

	Cu cat NaOtE	(2.0 mol %) 3u (12 mol %) ► Cv₂ ∽∽₂ .B(pin	)
	1a HB(pin dioxar	n) (1.2 equiv) ne, 28 °C, 2 h ( <i>E</i> )- <b>2a</b> or ( <i>Z</i> )- <b>2a</b>	,
Entry	Cu catalyst	Yield [%] <sup>[b]</sup>	$E/Z^{[c]}$
1	CuCl/PPh <sub>3</sub>	<1	_
2	CuCl/PCy <sub>3</sub>	<1	-
3	CuCl/dppbz	78	88:12
4	CuCl/Xan	85	>99:1
5	CuCl/MeAr-2	Kan 99	93:7
6	CuCl/CF3Ar-	Xan 99 (78) <sup>[d]</sup>	95:5
7	[(IPr)CuCl]	68	65:35
8	[(IMes)CuCl]	12	49:51

[a] Reaction conditions: Cyclohexylallene (0.50 mmol), HB(pin) (0.60 mmol), CuCl (0.010 mmol, 2.0 mol%)/ligand (0.010 mmol, 2.0 mol%) or [(NHC)CuCl] (0.010 mmol, 2.0 mol%), NaOtBu (0.060 mmol, 12 mol%), 1,4-dioxane (4.0 mL), 28°C, 2 h. [b] Yield of compound **2a**, as determined by GC with an internal standard. [c] Ratio of the E/Z isomers, as determined by GC. [d] Yield of isolated product, after column chromatography on silica gel.



Xan:  $R^1 = R^2 = H$ MeAr-Xan:  $R^1 = Me$ ,  $R^2 = H$ CF<sub>3</sub>Ar-Xan:  $R^1 = CF_3$ ,  $R^2 = H$ CIAr-Xan:  $R^1 = CI$ ,  $R^2 = H$ DTBMAr-Xan:  $R^1 = tBu$ ,  $R^2 = OMe$ 



Figure 1. Ligands used in this study.

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Table 2. Copper-catalyzed hydroboration of various allenes to afford allylboranes.<sup>[a]</sup>

	$R^1$ $R^3$	CF <sub>3</sub> Ar-Xan (2.0 mol %) NaOtBu (12 mol %)	<sup>1</sup>	
	۲ R <sup>2</sup> 1b-j	HB(pin) (1.2 equiv) dioxane, 28 °C, 2 h	R <sup>2</sup> R <sup>3</sup> ( <i>E</i> ) or ( <i>Z</i> )- <b>2b-j</b>	
Entry	Substrate	Product	Yield [%] <sup>[b]</sup>	$E/Z^{[c]}$
1	Ph	PhB(pin) ( <i>E</i> )- <b>2b</b>	74	91:9
2	TBSO	$TBSO^{\{\prime\}} \mathcal{B}(pin)$ $(E)-\mathbf{2c}$	71	89:11
3	1d	( <i>E</i> )-2d	70	98:2
4	Ph1e	Ph ( <i>E</i> )- <b>2e</b>	78	100:0
5	Ph 1f	PhB(pin) ( <i>E</i> )- <b>2</b> f	60	100:0
6	MeO 1g	MeO ( <i>E</i> )- <b>2g</b>	68	100:0
7	Cl 1h	Cl ( <i>E</i> )- <b>2h</b>	58	100:0
8	1i	B(pin) 2i	66	
9	Ph Tj	Ph B(pin) C <sub>3</sub> H <sub>7</sub> ( <i>E</i> )- <b>2j</b>	52	100:0

[a] Reaction conditions: Allene (0.50 mmol), HB(pin) (0.60 mmol), CuCl (0.010 mmol, 2.0 mol%), CF<sub>3</sub>Ar-Xan (0.010 mmol, 2.0 mol%), NaOtBu (0.060 mmol, 12 mol%), 1,4-dioxane (4.0 mL), 28°C, 2 h. [b] Yield of the isolated product. [c] Ratio of the E/Z isomers, as determined by GC.

It should be noted that an unsymmetrical 1,3-disubstituted allene (1j) successfully smoothly underwent the hydroboration reaction to afford the product as a single isomer (2j). Table 2, entry 9). This is the first example of the transition-metal-catalyzed hydroboration of 1,3-disubstituted allenes.

Hydroboration of allenes with  $B_2(pin)_2$  to afford alkenylboranes (4 or 5): The hydroboration of compound 1a was carried out by employing  $B_2(pin)_2$  in place of HB(pin) in the presence of a catalytic amount of CuCl with various ligands (Table 3). Remarkably, compared with the hydroboration reactions with HB(pin), the regioselectivity was completely switched to afford alkenylboranes ((Z)-4a and 5a) and no other isomers, such as compounds 2a, 3a, or (E)-4a, were produced (Table 3). The use of monodentate phosphanes, such as PPh<sub>3</sub> and PCy<sub>3</sub>, led to a mixture of compounds (Z)-4a and 5a with low selectivities (Table 3, entries 1 and 2). The NHC ligand, IMes, tended to preferentially produce compound (Z)-4a (84% yield; (Z)-4a/5a, 77:23; Table 3, entry 3). The <sup>Me</sup>IMes ligand, which contained methyl subTable 3. Hydroboration of compound  ${\bf 1a}$  with  $B_2(\text{pin})_2$  by using various copper catalysts.^ $^{[a]}$ 

	Cu cat. (2.0 mol %) NaOtBu (12 mol %)	Cy Cy	B(pin)	
Cy1a	B <sub>2</sub> (pin) <sub>2</sub> (1.1 equiv) MeOH (2.0 equiv) toluene, 28 °C, 2 h	(Z)- <b>4a</b>	5a	
Entry	Cu catalyst	Yield [%] <sup>[b]</sup>	$(Z)-4a/5a^{[c]}$	
1	CuCl/PPh3	40	84:16	
2	CuCl/PCy <sub>3</sub>	56	47:53	
3	[(IMes)CuCl]	84	77:23	
4	[(MeIMes)CuCl]	92	86:14	
5 <sup>[d]</sup>	[( <sup>Me</sup> IMes)CuCl]	99 (90) <sup>[e]</sup>	99:1	
6	CuCl/Xan	66	28:72	
7	CuCl/CF3Ar-Xan	73	2:98	
8	[(IPr)CuCl]	92	35:65	
9	[( <sup>CI</sup> IPr)CuCl]	99	9:91	
10	[( <sup>Cl</sup> IPr <sup>CPh<sub>3</sub></sup> )CuCl]	99	2:98	
11 <sup>[f]</sup>	[( <sup>Cl</sup> IPr <sup>CPh<sub>3</sub></sup> )CuCl]	99 (94) <sup>[e]</sup>	1:99	

[a] Reaction conditions: Compound **1a** (0.50 mmol),  $B_2(pin)_2$  (0.53 mmol), MeOH (1.0 mmol), CuCl (0.010 mmol, 2.0 mol%)/ligand (0.010 mmol, 2.0 mol%) or [(NHC)CuCl] (0.010 mmol, 2.0 mol%), NaOtBu (0.060 mmol, 12 mol%), toluene (1.0 mL), 28 °C, 2 h. [b] Yield of the product, as determined by GC with an internal standard. [c] Ratio of compounds (*Z*)-4a/5a, as determined by GC. [d] MeOH (4.0 mmol), -20 °C. [e] Yield of the isolated product, after column chromatography on silica gel. [f]  $B_2(pin)_2$  (0.60 mmol), THF (2.0 mL).

stituents on the N-heterocyclic ring, was the most efficient, giving compound (Z)-4a in high yield and selectivity (92%) yield; (Z)-4a/5a, 86:14; Table 3, entry 4). Gratifyingly, by lowering the reaction temperature to -20 °C, compound (Z)-4a was obtained almost exclusively and in quantitative yield (99% yield; (Z)-4a/5a, 99:1; Table 3, entry 5). From the reaction mixture, compound (Z)-4a was isolated in 90% yield in its pure form. Thus, the catalytic system shown in Table 3, entry 5 (with MeIMes as the ligand) was best for the preparation of compounds (Z)-4. Compound 5a was afforded as the major product with the use of Xan as a ligand ((Z)-4a/5a, 28:72), although the yield and selectivity were unsatisfactory (Table 3, entry 6). By employing CF<sub>3</sub>Ar-Xan as a ligand, compound **5a** was selectively obtained ((Z)-4a/5a, 2:98) in 73% yield (Table 3, entry 7). When IPr was used as the ligand, the yield of the products increased to 92% yield, but with low selectivity ((Z)-4a/5a, 35:65;Table 3, entry 8). In the case of <sup>CI</sup>IPr, which contained Cl substituents on the N-heterocyclic ring, both the yield and selectivity dramatically improved (99% yield; (Z)-4a/5a, 9:91; Table 3, entry 9). Finally, <sup>Cl</sup>IPr<sup>CPh<sub>3</sub></sup>, which contained Cl substituents on the N-heterocycle ring and CPh<sub>3</sub> substituents on the phenyl rings,<sup>[13]</sup> was the most effective ligand, giving compound **5a** in 99% yield with high selectivity ((Z)-4a/5a,2:98; Table 3, entry 10). The selectivity was further improved by using THF as a solvent (Table 3, entry 11), from which compound 5a was isolated in its pure form by column chromatography on silica gel in 94% yield. Thus, the catalyst system shown in Table 3, entry 11 (with <sup>Cl</sup>IPr<sup>CPh<sub>3</sub></sup> as the ligand) was determined to be the best for the preparation of compounds 5.

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Thus, we have established the optimal catalyst system for the two alkenylborane derivatives, that is, compounds (*Z*)-4 (Table 3, entry 5) and **5** (Table 3, entry 11). The structures of  $[(^{Me}IMes)CuCl]$  and  $[(^{CI}IPr^{CPh_3})CuCl]$  were determined in their monomeric forms by X-ray crystallography, as shown in Figure 2, which were similar to those of other [(NHC)CuCl] complexes.<sup>[14]</sup>



Figure 2. Crystal structures of a) [( $^{\rm Me}IMes)CuCl]$  and b) [( $^{\rm Cl}IPr^{\rm CPh_3})$ -CuCl]-CHCl\_3.

The hydroboration of various allenes to afford compounds (Z)-4 was achieved with  $B_2(pin)_2$  in the presence of [(MeIMes)CuCl] as a catalyst (Table 4). Very recently, Yuan and Ma reported that a  $CuCl/P(p-MeOC_6H_4)_3$  catalytic system afforded compound (Z)-4 by the hydroboration of monosubstituted allenes with  $B_2(pin)_2^{[11b]}$  (see above). However, with this catalyst system, only aryl-substituted allenes were applicable; alkyl-substituted allenes could not be used owing to the poor selectivities for the products. In sharp contrast, by using our catalyst system, monosubstituted allenes that contained primary alkyl (Table 4, entries 1 and 2) or secondary alkyl substituents (Table 4, entry 3), as well as aromatic ones (Table 4, entries 4-6), selectively gave compounds (Z)-4b-4h in good-to-high yields. With arylallenes 1 f-1h, the reactions proceeded smoothly with a more-acidic alcohol, CF<sub>3</sub>CH(OH)CF<sub>3</sub> (4.0 equiv), in place of MeOH (Table 4, entries 4–6) as the proton source.

On the other hand, alkenylboranes **5** were selectively produced with  $[(^{CI}IPr^{CPh_3})CuCl]$  as the catalyst (Table 5). Allenes that contained primary (Table 5, entries 1 and 2), secondary (Table 5, entry 3), and tertiary alkyl groups (**1b–1e**; Table 5, entry 4) provided the corresponding products in good-to-high yields with high selectivities. The reactions of

Table 4. Copper-catalyzed hydroboration of various allenes to afford al-kenylboranes ((Z)-4).<sup>[a]</sup>

j		[( <sup>Me</sup> IMes)CuCl] (2.0 mol %) NaO <i>t</i> Bu (12 mol %)	P	
	1b-d, 1f-h	$B_2(pin)_2$ (1.1 equiv) MeOH (8.0 equiv) toluene, -20 °C, 2 h	B(pin) (Z)-4b-d, (Z)-4f-h	
Entry	Substrate	Product	Yield [%] <sup>[b]</sup>	$(Z)-4/5^{[c]}$
1	Ph 1b	PhB(pin) (Z)- <b>4b</b>	90	93:7
2	TBSO	TBSO (Z)- <b>4c</b>	89	91:9
3	1d	(Z)- <b>4d</b> B(pin)	90	97:3
4 <sup>[d]</sup>	Ph 1f	PhB(pin) (Z)- <b>4f</b>	83	95:5
5 <sup>[e]</sup>	MeO	MeO B(pi	n) 56	97:3
	1g	(Z)- <b>4g</b>		
6 <sup>[f]</sup>	CI	B(pin)	81	91:9
	1h	(Z)- <b>4h</b>		

[a] Reaction conditions: Allene (0.50 mmol),  $B_2(pin)_2$  (0.53 mmol), [(<sup>Me</sup>IMes)CuCl] (0.010 mmol, 2.0 mol%), NaOrBu (0.060 mmol, 12 mol%), toluene (1.0 mL), -20°C, 2 h. [b] Yield of the isolated product. [c] Ratio of compounds (*Z*)-**4/5**, as determined by GC. [d]  $B_2(pin)_2$ (0.75 mmol), [(<sup>Me</sup>IMes)CuCl] (0.038 mmol, 7.5 mol%), CF<sub>3</sub>CH(OH)CF<sub>3</sub> (2.0 mmol). [e]  $B_2(pin)_2$  (0.75 mmol), [(<sup>Me</sup>IMes)CuCl] (0.025 mmol, 5.0 mol%), CF<sub>3</sub>CH(OH)CF<sub>3</sub> (2.0 mmol). [f]  $B_2(pin)_2$  (0.60 mmol), [(<sup>Me</sup>IMes)CuCl] (0.025 mmol, 5.0 mol%), CF<sub>3</sub>CH(OH)CF<sub>3</sub> (2.0 mmol).

arylallenes **1**f–**1**h also proceeded in high yields and selectivities (Table 5, entries 5–7). The presence of electron-donating and -withdrawing groups on the aryl ring did not affect the yields or selectivities. Not only 1-substituted allenes but also 1,1-disubstituted (**1i**) and 1,3-disubstituted allenes (**1j**) gave their corresponding products (**5i** and **5j**) with high selectivities (Table 5, entries 8 and 9).

Mechanism of the hydroboration reaction: The mechanism of the hydroboration reaction to provide allylboranes (2) must be similar to that of alkynes<sup>[5]</sup> and a possible catalytic cycle is shown in Scheme 4. In this cycle, copper hydride would be generated by the reaction between a copper alkoxide and HB(pin). We had previously confirmed that  $[(^{C1}IPr)CuH]$  was obtained quantitatively by a stoichiometric reaction of  $[(^{C1}IPr)Cu(OtBu)]$  with HB(pin).<sup>[5]</sup> The copper hydride inserts into an allene from the sterically less-encumbered face of the allene to give the (*Z*)- $\sigma$ -allyl copper species as a kinetic product (Scheme 4, step a), which isomerizes into the corresponding thermodynamically stable (*E*)- $\sigma$ allyl copper species.  $\sigma$ -Bond metathesis between an (*E*)- $\sigma$ allyl copper species and HB(pin) gives compounds (*E*)-2 and LCuH<sup>[15]</sup> (Scheme 4, step b).

Table 5.	Copper-catalyzed	hydroboration	of vario	us allenes	to	afford	al
kenylbo	ranes (5). <sup>[a]</sup>						

	R <sup>1</sup> R <sup>3</sup>	[( <sup>CI</sup> IPr <sup>CPh</sup> 3)CuCI] (2.0 mol %) NaO <i>t</i> Bu (12 mol %)	B(pin) B <sup>1</sup> ⊥	
_	Ƴ R <sup>2</sup> 1b-j	B₂(pin)₂ (1.2 equiv) MeOH (2.0 equiv) THF, 28 ºC, 2 h	R <sup>2</sup> R <sup>3</sup> 5b-j	
Entry	Substrate	Product	Yield [%] <sup>[b]</sup>	$5/(Z)-4^{[c]}$
1	Ph	B(pin)	88	97:3
2	TBSO	B(pin) TBSO	90	98:2
3	1d	B(pin) 5d	88	98:2
4	Ph1e	Ph B(pin)	94	100:0
5	Ph 1f	B(pin) Ph	82	98:2
6	MeO	MeO B(pin)	80	99:1
7	CI	Cl B(pin)	90	97:3
8	1h Li	5h B(pin) 5i	56	100:0 <sup>[d]</sup>
9	PhC <sub>3</sub> H <sub>7</sub> 1j	B(pin) Ph C <sub>3</sub> H <sub>7</sub> (Z)- <b>5j</b>	85	100:0 <sup>[e]</sup>

[a] Reaction conditions: Allene (0.50 mmol),  $B_2(pin)_2$  (0.60 mmol), [(<sup>C1</sup>Pr<sup>CPh<sub>3</sub></sup>)CuCl] (0.010 mmol, 2.0 mol%), NaOtBu (0.060 mmol, 12 mol%), THF (2.0 mL), 28 °C, 2 h. [b] Yield of the isolated product. [c] Ratio of compounds 5/(Z)-4, as determined by GC. [d] 5i/2i, 93:7. [e] (Z)-5j/(E)-5j, 83:17.



Scheme 4. Plausible reaction mechanism that employs HB(pin).

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With regards to the mechanism of the hydroboration reaction to afford alkenylboranes (4 or 5), some stoichiometric reactions were performed by employing MeIMes and CIIPr as the ligands. In the catalytic reactions, MeIMes was an effective ligand for preparing compounds (Z)-4 (Table 3, entry 5) and <sup>CI</sup>IPr was a suitable ligand for preparing compounds 5 (Table 3, entry 9). First, two boryl copper complexes, [(<sup>Me</sup>IMes)CuB(pin)] (6a) and [(<sup>CI</sup>IPr)CuB(pin)] (6b), were prepared in good yields by the reaction of [(NHC)Cu-(OtBu)<sup>[16]</sup> with B<sub>2</sub>(pin)<sub>2</sub> (Scheme 5 a and b), according to a literature procedure for [(IPr)CuB(pin)].<sup>[17]</sup> Isolated complexes 6a and 6b were stable in the solid state under a N<sub>2</sub> atmosphere. In toluene solution, compound 6a decomposed at room temperature, whilst compound 6b was stable at room temperature for a few hours. The crystal structure of compound **6b** was determined by X-ray crystallography (Figure 3). The copper atom has an almost-linear geometry



Figure 3. Crystal structure of compound 6b.

with a carbon atom on the NHC ligand and a boron atom. The C-Cu-B bond angle is 165.51(15)° which is comparable to that of [(IPr)CuB(pin)] (168.07(10)°).

Boryl copper complexes 6a and 6b smoothly reacted with compound  $\mathbf{1a}^{[18]}$  and the formation of (Z)- $\sigma$ -allyl copper species 7a and 7b was confirmed by <sup>1</sup>H NMR and NOESY measurements (Scheme 6a and b). All attempts to grow single crystals of compounds 7a and 7b that were suitable for X-ray crystallographic analysis failed. On the other hand, a similar  $\sigma$ -allyl copper complex (7c) was prepared from compounds 6b and 1f in 61% yield (Scheme 6c) and they afforded good-quality single crystals. Notably, the (Z)- $\sigma$ -allyl structure of compound **7c** was confirmed by X-ray crystallographic analysis (Figure 4). In the unit cell, there are two independent complexes, one of which is shown in Figure 4. The average length of the C1-C2 bond (1.361(4) Å) is considerably shorter than that of the C2-C3 bond (1.492(4) Å), which clearly indicates the  $\sigma$ -allyl structure of compound 7c.

When compound **7a** was protonated with MeOH at -20 °C, the ratio of compounds (Z)-**4a/5a** was 47:53 (Scheme 6a), which was not as selective as the reaction with



Scheme 5. Synthesis of boryl copper complexes 6a and 6b.



Scheme 6. Stoichiometric reactions between compound 1a and  $[(^{Me}IMes)CuB(pin)]$  (6a) or  $[(^{CI}IPr)CuB(pin)]$  (6b).

C1<sub>C2</sub>C3

Figure 4. Crystal structure of compound 7c.

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[(<sup>Me</sup>IMes)CuCl] as the catalyst (Table 3, entry 5). The <sup>1</sup>H NMR spectra of compound 7a at 20°C, -10°C, -30°C, and -50°C almost did not change (for details, see the Supporting Information). However, protonation at -80°C provided compounds (Z)-4a/5a in a 99:1 ratio (Scheme 6a), which was comparable to that in the catalytic reaction. On the other hand, similar protonation of compound 7b with MeOH selectively provided compound **5a** ((Z)-4a/5a, 6:94) in a  $S_{\rm F}2'$ fashion at both room temperature and at -20°C (Sche-

me 6b). This selectivity is reminiscent of the selectivity in the hydroboration reaction catalyzed by [(<sup>CI</sup>IPr)CuCl] (Table 3, entry 9).

From these results in the stoichiometric reactions, a possible catalytic cycle for the hydroboration reaction with  $B_2(pin)_2$  is shown in Scheme 7. First, a boryl copper species



Scheme 7. Probable reaction mechanism that employs  $B_2(pin)_2$ .

is generated from the reaction between a copper alkoxide and  $B_2(pin)_2$ . The boryl copper species (6) inserts into an allene (1) from the sterically less-encumbered face of the allene, thus exclusively affording a (*Z*)- $\sigma$ -allyl copper intermediate (Scheme 7). In the case of bulky NHC ligands, such as <sup>CI</sup>IPr and <sup>CI</sup>IPr<sup>CPh<sub>3</sub></sup>, the (*Z*)- $\sigma$ -allyl copper species is preferentially protonated in a S<sub>E</sub>2' fashion to afford compounds **5** (Scheme 7, step b). On the other hand, with the less-bulky <sup>Me</sup>IMes as the ligand, the (*Z*)- $\sigma$ -allyl copper is preferentially protonated in a S<sub>E</sub>2 fashion, thus giving compounds (*Z*)-**4** (Scheme 7, step b'). To the best of our knowledge, as clearly indicated in Scheme 6, we first show that the site of protona-

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tion of the  $\sigma\mbox{-allyl}$  copper species could be controlled by the choice of ligands.  $^{[19]}$ 

**Hydroboration of 1,3-diene derivatives**: The hydroboration of 1,3-dienes is a useful reaction for synthesizing allylboranes and homoallylboranes, which are important intermediates in organic synthesis.<sup>[20,21]</sup> We anticipated that analogous catalytic systems for allenes could be applicable to the selective hydroboration of 1,3-diene derivatives (Scheme 8). By



Scheme 8. Copper-catalyzed hydroboration of 1,3-dienes.

employing 1,3-cyclohexadiene (**8a**) as a substrate and HB-(pin) as a hydroboration reagent, an allylborane (**9a**) was selectively isolated in 81 % yield with DTBMAr-Xan (for the structure, see Figure 1) as the ligand (Scheme 8a). On switching the boron source from HB(pin) to  $B_2(pin)_2$ , a homoallylborane (**10a**) was selectively isolated in 77 % yield with ClAr-Xan as the ligand in THF at 60 °C (Scheme 8b). Notably, when 1-phenyl-1,3-butadiene (**8b**) was used as the substrate, an allylborane (**9b**) and a homoallylborane (**10b**) were selectively isolated in high yields by employing HB-(pin) and  $B_2(pin)_2$  as the boron source, respectively (Scheme 8c and d). Moreover, by employing  $B_2(pin)_2$  as the boron source and [(IMes)CuCl] as the catalyst, a 1,4-hydroborated allylborane (**9b**') was isolated with high selectively (Scheme 8e).

### Conclusion

We have developed a highly selective copper-catalyzed hydroboration of allenes to give an allylborane (2) and two alkenylboranes (4 and 5). The key to the success of this selective reaction is controlling the generation of the catalytic species (Cu-H or Cu-B), as well as the selective protonation of the allyl copper species. An analogous catalytic system was also applicable to the selective hydroboration of 1,3-dienes, which gave allylboranes (9) and homoallylboranes (10), respectively. This method should be widely applicable to other catalytic reactions.

#### **Experimental Section**

General procedure for the reactions shown in Table 2: CuCl (0.99 mg, 0.010 mmol, 2.0 mol%), CF<sub>3</sub>Ar-Xan (11.2 mg, 0.010 mmol, 2.0 mol%), and NaOtBu (5.77 mg, 0.060 mmol, 12 mol%) were placed in an ovendried Schlenk flask (20 mL). The flask was evacuated and backfilled with argon three times. 1,4-Dioxane (1.0 mL) was added and the mixture was stirred for 15 min at RT under an argon atmosphere. HB(pin) (87  $\mu L,$ 0.60 mmol) was added to the resulting solution at 0°C and the mixture was stirred at 0°C for 5 min. An allene (0.50 mmol) was added to the mixture at 0°C and the mixture was stirred at 28°C for 2 h. After the reaction had reached completion, the selectivity of the product was determined by GC analysis. The mixture was filtered through a pad of silica gel and the volatile compounds were removed in vacuo. The products were purified by column chromatography on silica gel (n-hexane/Et<sub>2</sub>O). General procedure for the reactions shown in Table 4: [(MeIMes)CuCl] (4.31 mg, 0.010 mmol, 2.0 mol%) and NaOtBu (5.77 mg, 0.060 mmol, 12 mol %) were placed in an oven-dried Schlenk flask (20 mL). The flask was evacuated and backfilled with argon three times. Toluene (1.0 mL) was added and the mixture was stirred for 15 min at RT under an argon atmosphere. B<sub>2</sub>(pin)<sub>2</sub> (133 mg, 0.53 mmol) was added to the resulting solution and the mixture was stirred at RT for 5 min. Then, MeOH (168 µL, 4.0 mmol) and an allene (0.50 mmol) were added successively at -20 °C and the mixture was stirred at -20 °C for 2 h (in the cases of Table 4, entries 4-6, CF3CH(OH)CF3 (208 µL, 2.0 mmol) was used instead of MeOH). After the reaction, the selectivity of the product was determined by GC analysis. The mixture was filtered through a pad of Celite and silica gel. All of the volatile compounds were removed in vacuo. The products were obtained by column chromatography on silica gel (nhexane/Et<sub>2</sub>O).

General procedure for the reactions shown in Table 5:  $[(^{CI}Pr^{CPh_3})CuCl]$ (10.4 mg, 0.010 mmol, 2.0 mol%) and NaOtBu (5.77 mg, 0.060 mmol, 12 mol%) were placed in an oven-dried Schlenk flask (20 mL). The flask was evacuated and backfilled with argon three times. THF (2.0 mL) was added and the mixture was stirred for 15 min at RT under argon atmosphere. B<sub>2</sub>(pin)<sub>2</sub> (152 mg, 0.60 mmol) was added to the resulting solution and the mixture was stirred at RT for 5 min. Then, MeOH (42 µL, 1.0 mmol) and an allene (0.50 mmol) were added successively at 28 °C and the mixture was stirred at 28 °C for 2 h. After the reaction, the selectivity of the product was determined by GC analysis. The mixture was filtered through a pad of Celite and silica gel. All of the volatile compounds were removed in vacuo. The products were obtained by column chromatography on silica gel (*n*-hexane/Et<sub>2</sub>O).

**Crystallographic data**: CCDC-926626 ([( $^{Me}$ IMes)CuCl]), CCDC-926627 ([( $^{CI}$ IPr $^{CPh_3}$ )CuCl]), CCDC-926628 (**6b**), and CCDC-926629 (**7c**). contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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