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Enantioselective Synthesis of *anti*-1,2-Oxaborinan-3-enes from Aldehydes and 1,1-Di(boryl)alk-3-enes Using Ruthenium and Chiral Phosphoric Acid Catalysts

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ABSTRACT: A cationic ruthenium(II) complex catalyzes double-bond transposition of 1,1-di(boryl)alk-3-enes to generate in situ 1,1-di(boryl)alk-2-enes, which then undergo chiral phosphoric acid-catalyzed allylation of aldehydes producing homoallylic alcohols with a (*Z*)-vinylboronate moiety. 1,2-*Anti* stereochemistry is installed in an enantioselective manner. The (*Z*)-geometry forged in the products allows their isolation in a form of 1,2-oxaborinan-3-enes, upon which further synthetic transformations are operated.

■ INTRODUCTION

The allylation reaction of aldehydes with γ-substituted allylboron reagents [1-(boryl)alk-2-enes] offers a convenient and reliable method to stereoselectively construct homoallylic alcohols with contiguous chiral centers. Many useful methods for the preparation of γ-substituted allylboron reagents have been developed.[1,2] For example, Roush has reported that enantioenriched (*S*)-(*E*)-γ-substituted α-stannyl allylic boranes are generated from allenylstannane and diisopinocampheylborane.[3] The following allylation reaction with aldehydes forms (*E*)-δ-stannyl-substituted *anti*-homoallylic alcohols with high enantioselectivity [Figure 1(a)].[4] On the other hand, we have investigated an in-situ generation of allylboron species from 1-(boryl)alkenes by way of double-bond transposition, which is catalyzed by transition-metal catalysts.[5,6] The arising allylboron species immediately add to the aldehydes, also in the reaction mixture, through a six-membered chair-like transition state, where a high enantioselectivity can be induced by a chiral phosphoric acid.[7] Transition-metal catalysts, which are effective for double-bond transposition, are potentially active in geometrical *E*/*Z*-isomerization of double bonds as well.[8] When 1,1-di(boryl)alk-3-enes are reacted with aldehydes mediated by a catalytic palladium(I) species,[5d] the initially produced δ-boryl-substituted *anti*-homoallylic alcohols contain a (*Z*)-vinylboronate moiety, which is more difficult to shape than an (*E*)-vinylboronate moiety in general.[9] Unfortunately, this stereochemistry is not preserved under the reaction conditions, instead isomerization occurs to the (*E*)-geometry [Figure 1(b)]. With this scenario in mind we have been searching for a transition-metal catalyst which is more specifically effective for double-bond transposition of 1,1-di(boryl)alk-3-enes to allow the preservation of the product with (*Z*)-geometry. We now report a cationic ruthenium(II) complex that specifically catalyzes double-bond transposition without touching the (*Z*)-geometry of the allylated product [Figure 1(c)].

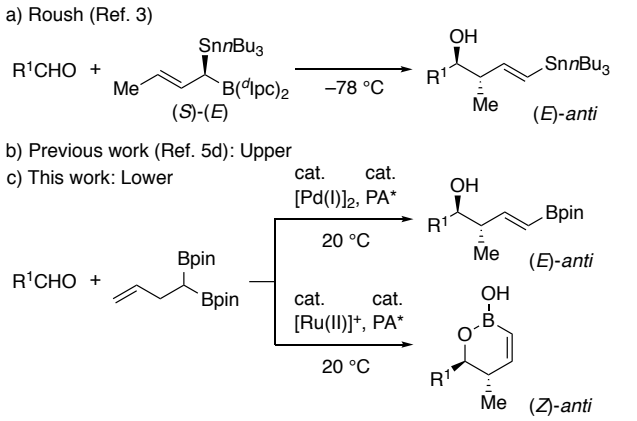
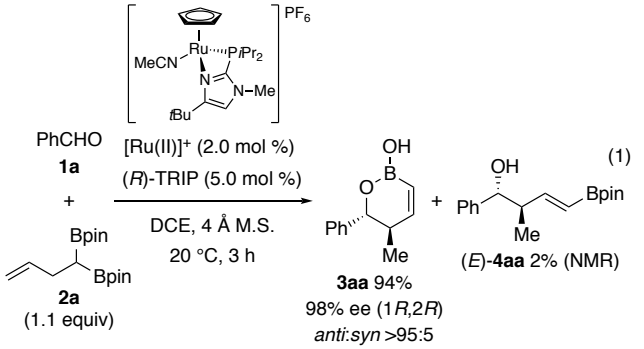


Figure 1. Diastereo- and enantioselective synthesis of δ-substituted homoallylic alcohols. a) (*E*)-geometry on the stannyl group. b) (*E*)-geometry on the boryl group. c) (*Z*)-geometry on the boryl group. ^{d}Ipc = *d*-isopinocampheyl. Bpin = pinacolatoboronate. PA* = chiral phosphoric acid.

■ RESULTS AND DISCUSSION

Grotjahn et al. reported that the cationic ruthenium(II) complex, [CpRu(P–N)(MeCN)]PF_6 (P–N: 2-P*i*Pr_2-4-*t*Bu-1-Me-imidazole) promotes double-bond transposition by way of a π-allyl intermediate.[10] We found that the ruthenium(II) complex performed as specifically as we desired: A mixture of benzaldehyde (**1a**, 0.20 mmol) and 1,1-di(boryl)but-3-ene **2a** (0.22 mmol)[11] in 1,2-dichloroethane (DCE) was stirred at 20 °C in the presence of [CpRu(P–N)(MeCN)]PF_6 (2.0 mol %), (*R*)-TRIP (5.0 mol %; TRIP = 3,3'-Bis(2,4,6-triisopropylphenyl)-1,1'-binaphthyl-2,2'-diyl hydrogen phosphate),[12] and 4 Å molecular sieves (4 Å M.S.) (eq 1). After 3 hours, aldehyde **1a** was completely consumed and the reaction mixture was subjected to aqueous workup. The following chromatographic purification on silica gel afforded *anti*-1,2-oxaborinan-3-ene **3aa** in 94% isolated yield in 98% ee.[13] No *syn* isomer was detected by ^{1}H NMR (400 MHz), proving the *anti*/*syn* selectivity is >95:5. It is likely that an acyclic homoallylic alcohol having (*Z*)-geometry is initially formed and then cyclizes into

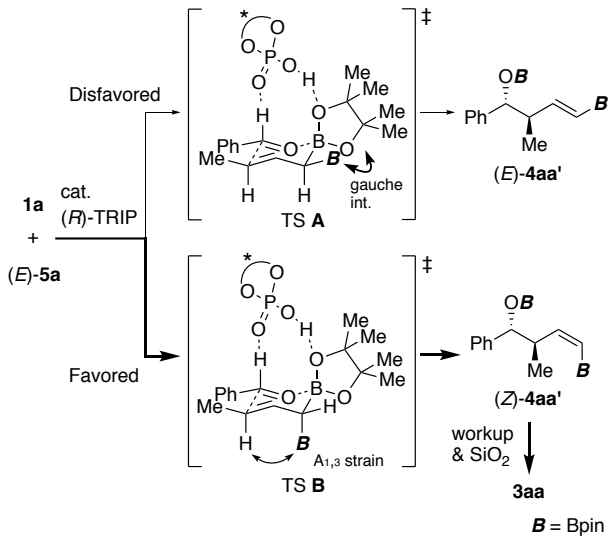
a six-membered ring structure during workup/purification.[14] The corresponding (*E*)-isomer **4aa** remaining in the acyclic form was observed in ca. 2% (NMR yield). Thus, **1a** and **2a** were coupled by C–C bond formation with installation of two chiral centers and a double bond in a stereoselective fashion.[15] A larger scale experiment using 849 mg (8.0 mmol) of **1a** also gave a comparable result [96% yield, 96% ee (1.44 g of **3aa**)].



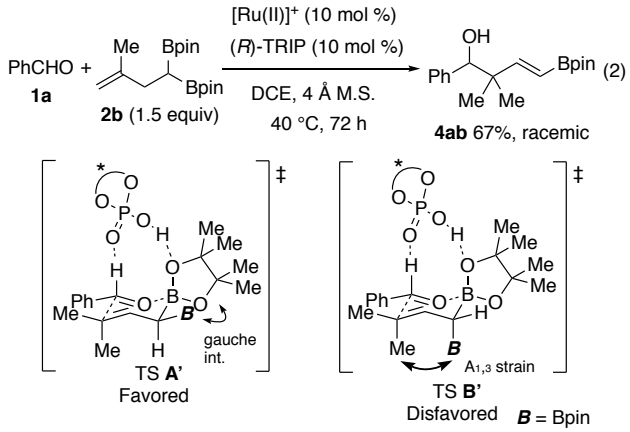
We presume the following stepwise scenario brings about this transformation: Initially, (*E*)-1,1-di(boryl)but-2-ene **5a** is generated from 1,1-di(boryl)but-3-ene **2a** through double-bond transposition. As soon as (*E*)-**5a** is generated, it undergoes (*R*)-TRIP-catalyzed enantioselective addition to aldehyde **1a** via TS **B**, as mentioned in Scheme 1 (vide infra), to form the (*Z*)-isomer of *anti*-homoallylic alcohol **4aa'**, which cyclizes to **3aa** upon workup.

The six-membered chair-like transition-state structures TS **A** and **B** depicted in Scheme 1 are assumed to account for the selective formation of the (*Z*)-isomer of *anti*-homoallylic alcohol **4aa'**, as with the palladium(I)-catalyzed case we have previously reported.[5d] One of the two boryl groups (represented as ***B***) takes an exocyclic position, either pseudo-equatorial one leading to *E* isomer, or pseudo-axial one leading to *Z* isomer. The boryl group located in a pseudo-equatorial position in TS **A** suffers from gauche interactions with the pinacolato ligand of the other boryl group, whereas the boryl group located in a pseudo-axial position in TS **B** suffers from 1,3-allylic strain to an adjacent hydrogen atom. The gauche interactions is more significant than that by the 1,3-allylic strain, inducing the *Z* selectivity.

Scheme 1. Proposed Pathway for the Formation of 3aa from 1a and (*E*)-5a

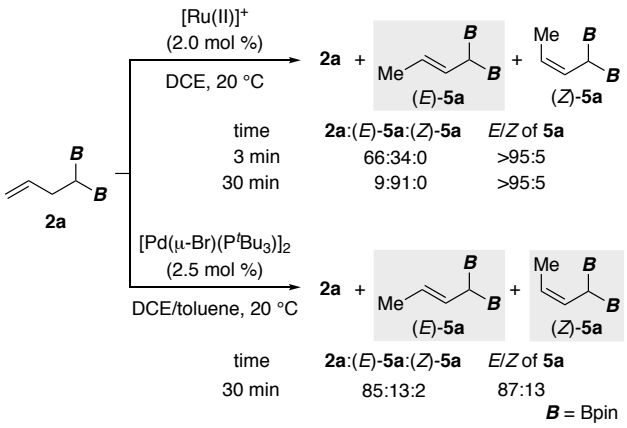


Interestingly, the double-bond geometry of the product reversed from *Z* to *E* when 1,1-di(boryl)-3-methylbut-3-ene **2b** was used in place of α-olefin **2a**. The (*E*)-isomer of *anti*-homoallylic alcohol **4ab** was obtained in 67% yield in a racemic form from **2b** (eq 2). The corresponding 1,2-oxaborinan-3-ene was not detected. The alkene **2b** structurally differs from **2a** in that it possesses an additional methyl group at the 3-position. Six-membered transition states TS **A'** and TS **B'** which are analogous to TS **A** and TS **B** are postulated. In this second example, the 1,3-allylic strain between the additional methyl group and the boryl group both located in pseudo-axial positions in TS **B'** governs the outcome of this reaction. This destabilizing interaction would be significant enough to reverse the energetic balance between TS **A'** and TS **B'**. Thus, the contrast in the double-bong geometry observed with **2a** and **2b** endorses the afore-mentioned stereochemical explanation (Scheme 1).



Following this, the process of double-bond transposition from 1,1-di(boryl)but-3-ene **2a** to 1,1-di(boryl)but-2-ene **5a** was monitored by ^{1}H NMR in the absence of an aldehyde, and the ruthenium(II) and palladium(I) catalysts were compared (Scheme 2). 1,1-Di(boryl)but-3-ene **2a** was simply treated with 2.0 mol % of the ruthenium(II) complex or 2.5 mol % of the palladium(I) dimer at 20 °C. In the case of ruthenium(II), double-bond transposition proceeded expeditiously and 91% of **2a** isomerized to **5a** after 30 min. The *E*/*Z* ratio of the arising **5a** had been constantly over 95:5 from the early stage of

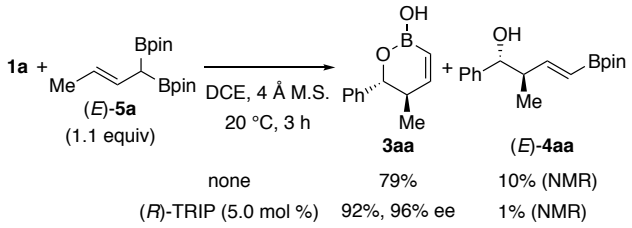
Scheme 2. A Control Experiment in the Absence of Aldehydes



transposition. In the case of palladium(I), only 15% of **2a** isomerized to **5a** after 30 min and the *E*/*Z* ratio was 87:13. Thus, the ruthenium(II) catalyst proved to be both more active and stereoselective for the double-bond transposition of **2a**.

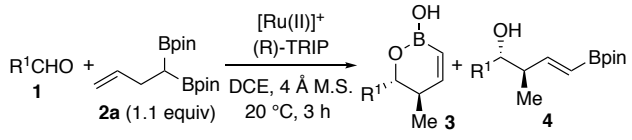
The (*E*)-**5a** was prepared by the afore-mentioned Ru(II)-catalyzed reaction and isolated by florisil column chromatography. The isolated (*E*)-**5a** was reacted with benzaldehyde (**1a**) at 20 °C for 3 hours[16] both in the *absence* and *presence* of (*R*)-TRIP (5.0 mol %) (Scheme 3). In the absence of (*R*)-TRIP, racemic **3aa** was formed in 79% yield together with 10% (NMR) of (*E*)-*anti*-homoallylic alcohol **4aa**. In the presence of (*R*)-TRIP, **3aa** was formed in 92% yield, 96% ee, accompanied by only an insignificant amount (1%) of **4aa**. We presume that the energy difference between TS **A** and TS **B** is reflected into a higher *Z*/*E* selectivity when accelerated by the phosphoric acid.[17]

Scheme 3. The Allylation Reaction of Benzaldehyde (1a) with (*E*)-5a in the *Absence* and *Presence* of (*R*)-TRIP



This allylation reaction could be carried out using a wide scope of aldehydes (Table 1). Enantioselectivities over 90% ee were observed in all cases. The *anti*-1,2-oxaborinan-3-enes **3aa**–**3ea** were obtained in yields ranging from 91% to 97% each derived from an electronically and sterically diverse array of aromatic aldehydes **1a**–**1e** (entries 1–5). Heteroaromatic aldehyde **1f** and α,β-unsaturated aldehyde **1g** could also be applied to this reaction (entries 6 and 7). Not only aromatic aldehydes but aliphatic ones such as 2-phenylacetaldehyde (**1h**) and cyclohexanecarbaldehyde (**1i**) successfully participated in the reaction (entries 8 and 9). On the whole, the yields of the allylated products in the Ru(II)-catalyzed reactions are relatively higher than those by using Pd(I).

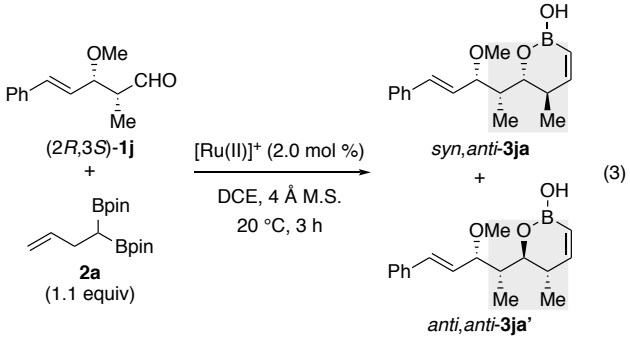
Table 1. Asymmetric Allylation Reactions of Various Aldehydes 1a–1i with 2a[a]



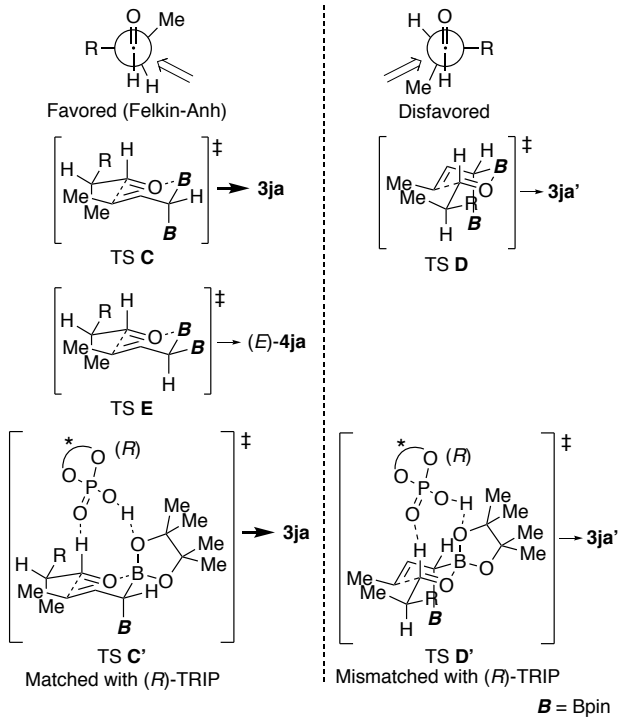
entry	R^1 (**1**)	**3**	cat. Ru(II) yield of **3** (%)[b,c]	cat. Ru(II) ee of **3** (%)[d]	cat. Pd(I)[j] yield of **4** (%)	cat. Pd(I)[j] ee of **4** (%)
1	Ph (**1a**)	*ent*-**3aa**[e]	91	97[f]	80	98
2	4-ClC_6H_4 (**1b**)	**3ba**	95	98	90	99
3	4-$MeOC_6H_4$ (**1c**)	**3ca**	97	97	80	98
4	4-MeC_6H_4 (**1d**)	**3da**	96	97	82	98
5	2-MeC_6H_4 (**1e**)	**3ea**	93	96	78	97
6	2-furyl (**1f**)	**3fa**	93	96	67	91
7	PhCH=CH (**1g**)	**3ga**	88	97	68	97
8	$PhCH_2$ (**1h**)	**3ha**	69[g,h]	93	72	92
9	Cy (**1i**)	**3ia**	78[g,i]	90	71	96

[a]On a 0.20 mmol scale. See eq 1 for reaction conditions. [b]Isolated yield after chromatographic purification. [c]*Anti*/*syn* ratio of **3** and product ratio (**3**/**4**) were determined to be >95:5 by ^{1}H NMR in all cases. [d]As determined by chiral HPLC of phenylated products. [e](*S*)-TRIP was used. [f](1*S*,2*S*). [g]10 mol % of (*R*)-TRIP was used. [h]NMR yield. [i]10 °C, 5 h. [j]Data reported in Ref. 5d. Reaction conditions: **1** (0.20–0.40 mmol), **2a** (2.0 equiv), $[Pd(\mu\text{-}Br)(P\textit{t}Bu_3)]_2$ (2.5 mol %), (*R*)-TRIP (5.0 mol %), DCE/toluene, 4 Å M.S., 20 °C, 17 h.

The allylation reaction of α-branched chiral aldehyde (2*R*,3*S*)-**1j**[3b,18] with **2a** was carried out in the *absence* and *presence* of TRIP (5.0 mol %) (eq 3). In the absence of TRIP, *syn*,*anti*-**3ja** (highlighted in gray) was formed in 42% total yield with 88:12 diastereoselectivity (**3ja**/**3ja'**) together with 24% (NMR) of (*E*)-*syn*,*anti*-homoallylic alcohol **4ja**. In the presence of (*R*)-TRIP, *syn*,*anti*-**3ja** was formed in 69% total yield, and higher diastereoselectivity (**3ja**/**3ja'** >95:5) and *Z*/*E* selectivity (**3ja**/**4ja**) were observed. On the other hand, a lower diastereoselectivity (**3ja**/**3ja'** = 55:45) and *Z*/*E* selectivity (**3ja**/**4ja**) were observed in the presence of (*S*)-TRIP. These



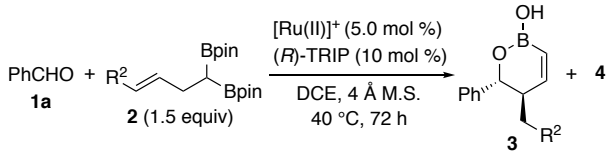
none **3ja** 42% total yield (**3ja**/**3ja'** = 88:12), (*E*)-**4ja** 24% (NMR)
(*R*)-TRIP **3ja** 69% total yield (**3ja**/**3ja'** >95:5), (*E*)-**4ja** 2% (NMR)
(*S*)-TRIP **3ja** 48% total yield (**3ja**/**3ja'** = 55:45), (*E*)-**4ja** 13% NMR



results suggest that, in the absence of phosphoric acid, the reaction proceeds via TS **C** and TS **E** which accord with the Felkin-Anh model. (*R*)-TRIP has the matched stereochemical orientation to assist in TS **C'** by the chelation through the pinacolato oxygen and aldehyde proton.

A variety of 1,1-di(boryl)alk-3-enes **2c**–**2g** having Me, Et, *i*Pr, CF_3, and Ph groups as the R^2 substituent[11] were subjected to the allylation reaction with benzaldehyde (**1a**) (Table 2). More forcing conditions were applied in those cases ($[Ru]^+$ (5.0 mol %), (*R*)-TRIP (10 mol %), 40 °C, 72 hours) because double-bond transposition was slower. Yet, the yields of **3ac**–**3af** were good and the enantioselectivities were over >90% ee (entries 1–4)). The phenyl-substituted derivative **2g** failed to undergo the double-bond transposition even at 80 °C (entry 5).

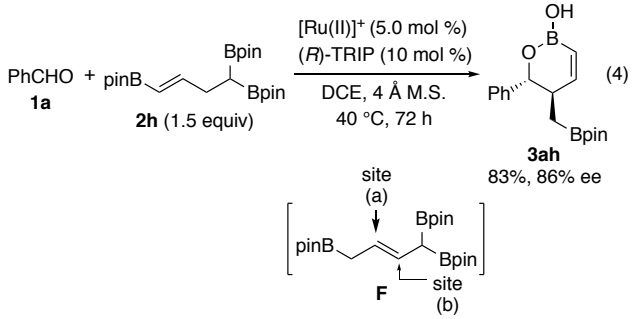
Table 2. Asymmetric Allylation Reactions of Benzaldehyde (1a) with Various 1,1-Di(boryl)alk-3-enes 2b–2e[a]



entry	R^2 (**2**)	**3**	cat. Ru(II) yield of **3** (%)[b,c]	cat. Ru(II) ee of **3** (%)[d]	cat. Pd(I)[g] yield of **4** (%)	cat. Pd(I)[g] ee of **4** (%)
1	Me (**2c**)[e]	**3ac**	90	95	85	96
2	Et (**2d**)	**3ad**	93	93	67	97
3	*i*Pr (**2e**)	**3ae**	82	90	85	95
4	CF_3 (**2f**)	**3af**	76	91	77	96
5	Ph (**2g**)	**3ag**	0[f]	–	82	92

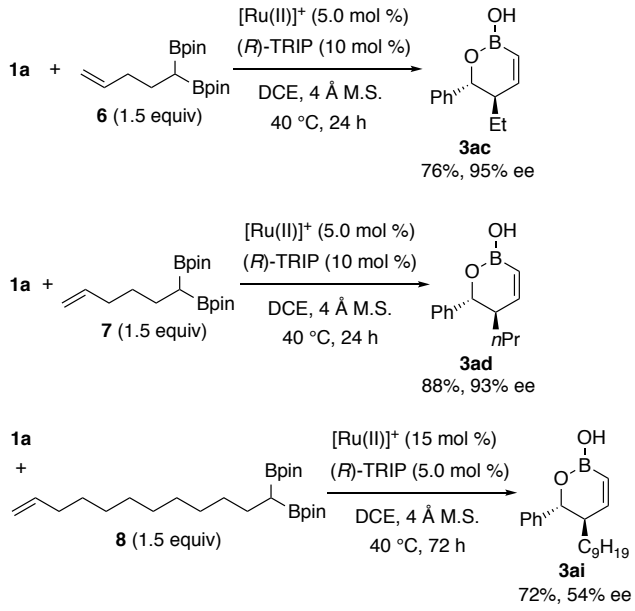
[a]On a 0.20 mmol scale. [b]Isolated yield after chromatographic purification. [c]*Anti*/*syn* ratio of **3** and product ratio (**3**/**4**) were determined to be >95:5 by ^{1}H NMR in all cases. [d]As determined by chiral HPLC of phenylated products. [e]*E*/*Z* = 79:21. [f]80 °C. [g]Data reported in Ref. 5d except for entry 2 (R^2 = Et). Reaction conditions: **1** (0.20 mmol), **2a** (2.0 equiv), $[Pd(\mu\text{-Br})(P\textit{t}Bu_3)]_2$ (2.5 mol %), (*R*)-TRIP (5.0 mol %), DCE/toluene, 4 Å M.S., 20–30 °C, 17–41 h.

4-Boryl-substituted 1,1-di(boryl)but-3-ene **2h** was newly prepared by an S_N2 reaction of bis(pinacolatoboryl)methane with (*E*)-1-boryl-3-bromoprop-1-ene under basic conditions. It was subjected to the allylation reaction with benzaldehyde (**1a**). The allylboronate intermediate **F** having two reactive sites (a) and (b) was expected to be generated in situ from **2h**. The *anti*-1,2-oxaborinan-3-ene **3ah** was selectively obtained in 83% yield and 86% ee (eq 4). Thus, the intermediate **F** is more reactive at (a) than at (b).

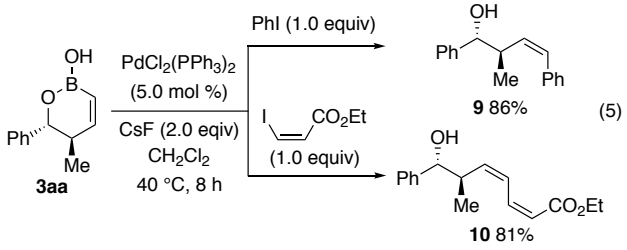


Under these conditions, a carbon–carbon double bond could also transpose itself from a more remote position to an allylic position relative to boron (Scheme 4).[10a,19] 1,1-Di(boryl)pent-4-ene **6** and 1,1-di(boryl)hex-5-ene **7** both successfully acted as the allylboron precursor. In these examples, *anti*-1,2-oxaborinan-3-enes **3ac** and **3ad** were formed in 76% and 88% yields respectively both with high enantioselectivities. In the extreme case of 1,1-di(boryl)dodec-11-ene **8**, the double-bond transposition took place nine times to give the corresponding product **3ai** in 72% yield and 54% ee along with a small amount of (*E*)-isomer **4ai** (7% NMR yield).

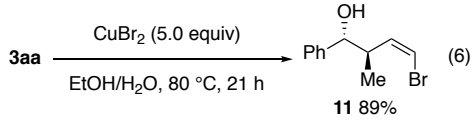
Scheme 4. The Utilization of 1,1-Di(boryl)alk-*n*-enes 5–7 (*n* = 4, 5, 11) as the Allylboron Precursors

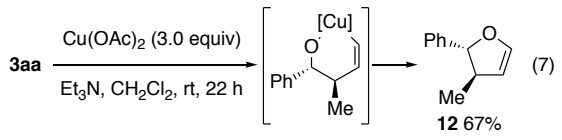


The synthetic utility of the boryl-substituted product **3aa** was exemplified by further transformations. The Suzuki-Miyaura cross-coupling reaction with iodides (iodobenzene and ethyl (*Z*)-3-iodoacrylate) was executed using $PdCl_2(PPh_3)_2$ as the catalyst. Importantly, the coupled alkenes **9** and **10** were formed with retention of the double-bond geometry (*Z*/*E* >95:5) (eq 5).

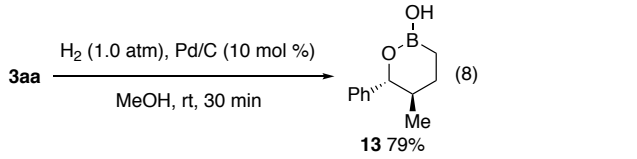


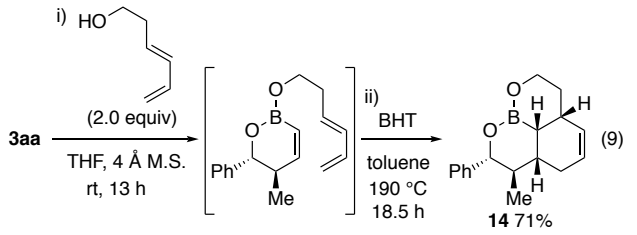
Treatment with $CuBr_2$ resulted in the formation of the bromide **11** again without a loss of geometrical purity (*Z*/*E* >95:5) (eq 6).[20] An intramolecular Chan-Lam coupling reaction of **3aa** afforded the 2,3-dihydrofuran **12** (eq 7).[21]



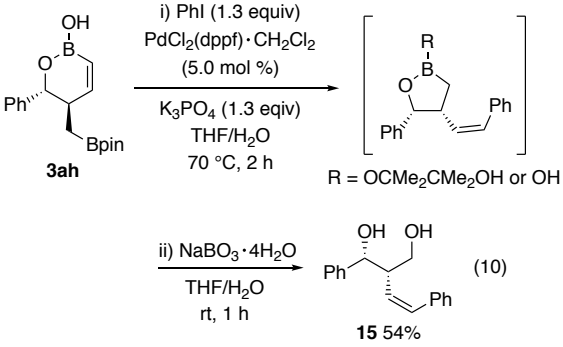


Hydrogenation of the double bond moiety contained within **3aa** was carried out (H_2, Pd/C), yielding 1,2-oxaborinan-2-ol **13** (eq 8). A boron-tethered intramolecular Diels-Alder reaction using (*E*)-3,5-hexadiene-1-ol[22] proceeded well to give tricycle **14** with high diastereoselectivity (>95:5) (eq 9).

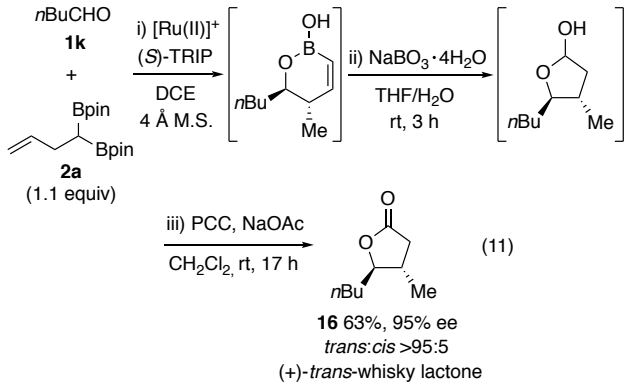




The product **3ah** containing two boryl groups was subjected to the palladium-catalyzed cross-coupling reaction with iodobenzene. Coupling occurred selectively at the boryl group on the sp^2 carbon with retention of the double-bond geometry with the B–C(sp^3) bond intact. The crude coupling product was next treated with sodium peroxoborate to oxidize the remaining B–C(sp^3) bond. 1,3-Diol **15** was isolated in 54% yield (eq 10). Thus, it was easy to differentiate the two B–C bonds in further synthetic transformations.



(+)-*trans*-Whisky lactone **16** was stereoselectively synthesized through three steps of the allylation reaction of pentanal (**1k**) with **2a**, B–C bond oxidation to a hemiacetal with sodium peroxoborate, and oxidation to the lactone with pyridinium



chlorochromate (eq 11).[23]

■ CONCLUSION

In summary, we have developed a new relay system consisting of the cationic ruthenium(II) and phosphoric acid catalysts for the diastereo- and enantioselective synthesis of *anti*-1,2-oxaborinan-3-enes starting from aldehydes and 1,1-di(boryl)alk-3-enes. This new system complements the previously reported system using palladium(I)[5d] to make both stereochemical options available for the double-bond geometry of the allylated products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization of the new compounds, and spectroscopic data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Hall, D. G. *Boronic Acids*, Wiley-VCH, Weinheim, **2011**. (b) Hall, D. G.; Lachance, H. *Allylboration of Carbonyl Compounds*, Wiley, Hoboken, New Jersey, **2012**. (c) Yus, M.; González-Gómez, J. C.; Foubelo, F. *Chem. Rev.* **2013**, *113*, 5595. (d) Diner, C.; Szabó, K. J. *J. Am. Chem. Soc.* **2017**, *139*, 2. See also: (e) Feng, J.; Kasun, Z. A.; Krische, M. J. *J. Am. Chem. Soc.* **2016**, *138*, 5467.

(2) For the synthesis and reactions of enantioenriched γ,α-disubstituted allylboron reagents, see: (a) Fang, G. Y.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2007**, *46*, 359. (b) Althaus, M.; Mahmood, A.; Suárez, J. R.; Thomas, S. P.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2010**, *132*, 4025. (c) Chen, J. L.-Y.; Scott, H. K.; Hesse, M. J.; Willis, C. L.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2013**, *135*, 5316. (d) Luo, Y.; Roy, I. D.; Madec, A. G. E.; Lam, H. W. *Angew. Chem. Int. Ed.* **2014**, *53*, 4186. (e) Chen, J. L.-Y.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2014**, *53*, 10992. (f) Yamamoto, E.; Takenouchi, Y.; Ozaki, T.; Miya, T.; Ito, H. *J. Am. Chem. Soc.* **2014**, *136*, 16515. (g) Potter, B.; Szymaniak, A. A.; Edelstein, E. K.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 17918. (h) Zhou, Q.; Srinivas, H. D.; Zhang, S.; Watson, M. P. *J. Am. Chem. Soc.* **2016**, *138*, 11989. (i) Edelstein, E. K.; Namirembe, S.; Morken, J. P. *J. Am. Chem. Soc.* **2017**, *139*, 5027. For the synthesis and reactions of enantioenriched α-substituted allylboron reagents, see: (j) Carosi, L.; Hall, D. G. *Angew. Chem. Int. Ed.* **2007**, *46*, 5913. (k) Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 14856. (l) Fernández, E.; Pietruszka, J.; Frey, W. *J. Org. Chem.* **2010**, *75*, 5580. (m) Hesse, M. J.; Essafi, S.; Watson, C. G.; Harvey, J. N.; Hirst, D.; Willis, C. L. Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2014**, *53*, 6145. (n) Brauns,

M.; Muller, F.; Gülden, D.; Böse, D.; Frey, W.; Breugst, M.; Pietruszka, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 1548. (o) Allais, C.; Roush, W. R. *Org. Lett.* **2017**, *19*, 2646.

(3) (a) Chen, M.; Roush, W. R. *J. Am. Chem. Soc.* **2011**, *133*, 5744. (b) Chen, M.; Roush, W. R. *J. Am. Chem. Soc.* **2012**, *134*, 3925. See also: (c) Chen, M.; Ess, D. H.; Roush, W. R. *J. Am. Chem. Soc.* **2010**, *132*, 7881.

(4) For asymmetric allylation using chiral allylboron reagents functionalized with another semi-metal element, see: [B] (a) Chen, M.; Handa, M.; Roush, W. R. *J. Am. Chem. Soc.* **2009**, *131*, 14602. (b) Ferris, G. E.; Hong, K.; Roundtree, I. A.; Morken, J. P. *J. Am. Chem. Soc.* **2013**, *135*, 2501. (c) Zhao, T. S. N.; Zhao, J.; Szabó, K. J. *Org. Lett.* **2015**, *17*, 2290. [Si] (d) Peng, F.; Hall, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 3070. (e) Chen, M.; Roush, W. R. *Org. Lett.* **2013**, *15*, 1662.

(5) (a) Shimizu, H.; Igarashi, T.; Miura, T.; Murakami, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 11465. (b) Miura, T.; Nishida, Y.; Morimoto, M.; Murakami, M. *J. Am. Chem. Soc.* **2013**, *135*, 11497. (c) Miura, T.; Nishida, Y.; Murakami, M. *J. Am. Chem. Soc.* **2014**, *136*, 6223. (d) Miura, T.; Nakahashi, J.; Murakami, M. *Angew. Chem. Int. Ed.* **2017**, *56*, 6989.

(6) For related reactions using olefinic organoboron compounds, see: (a) Moriya, T.; Suzuki, A.; Miyaura, N. *Tetrahedron Lett.* **1995**, *36*, 1887. (b) Ohmura, T.; Oshima, K.; Suginome, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 12501. (c) Lin, L.; Yamamoto, K.; Matsunaga, S.; Kanai, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 10275. (d) Hemelaere, R.; Carreaux, F.; Carboni, B. *Chem. Eur. J.* **2014**, *20*, 14518. (e) Weber, F.; Ballmann, M.; Kohlmeyer, C.; Hilt, G. *Org. Lett.* **2016**, *18*, 548. (f) Trost, B. M.; Cregg, J. J.; Quach, N. *J. Am. Chem. Soc.* **2017**, *139*, 5133.

(7) (a) Jain, P.; Antilla, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 11884. (b) Grayson, M. N.; Pellegrinet, S. C.; Goodman, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 2716. (c) Fustero, S.; Rodríguez, E.; Lázaro, R.; Herrera, L.; Catalán, S.; Barrio, P. *Adv. Synth. Catal.* **2013**, *355*, 1058. (d) Barrio, P.; Rodriguez, E.; Saito, K.; Fustero, S.; Akiyama, T. *Chem. Commun.* **2015**, *51*, 5246. (e) Koukal, P.; Ulč, J.; Nečas, D.; Kotora, M. *Eur. J. Org. Chem.* **2016**, 2110. (f) Grayson, M. N.; Yang, Z.; Houk, K. N. *J. Am. Chem. Soc.* **2017**, *139*, 7717.

(8) Gauthier, D.; Lindhardt, A. T.; Olsen, E. P. K.; Overgaard, J.; Skrydstrup, T. *J. Am. Chem. Soc.* **2010**, *132*, 7998 and references therein.

(9) Cross-metathesis of vinylboronate with terminal alkenes offers an attractive strategy for the synthesis of (*Z*)-alkenylboronates. See: (a) Kiesewetter, E. T.; O'Brien, R. V.; Yu, E. C.; Meek, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2013**, *135*, 6026. (b) Quigley, B. L.; Grubbs, R. H. *Chem. Sci.* **2014**, *5*, 501.

(10) (a) Grotjahn, D. B.; Larsen, C. R.; Gustafson, J. L.; Nair, R.; Sharma, A. *J. Am. Chem. Soc.* **2007**, *129*, 9592. (b) Erdogan, G.; Grotjahn, D. B. *J. Am. Chem. Soc.* **2009**, *131*, 10354. (c) Erdogan, G.; Grotjahn, D. B. *Org. Lett.* **2014**, *16*, 2818. See also: (d) Higman, C. S.; de Araujo, M. P.; Fogg, D. E. *Catal. Sci. Technol.* **2016**, *6*, 2077. (e) Jana, A.; Misztal, K.; Zak, A.; Grela, K. *J. Org. Chem.* **2017**, *82*, 4226.

(11) 1,1-Di(boryl)alk-3-enes were easily prepared by an S_N2 reaction of commercially available bis(pinacolatoboryl)methane with allylic halides under basic conditions (LDA). See: Zhang, Z.-Q.; Yang, C.-T.; Liang, L.-J.; Xiao, B.; Lu, X.; Liu, J.-H.; Sun, Y.-Y.; Marder, T. B.; Fu, Y. *Org. Lett.* **2014**, *16*, 6342.

(12) For TRIP as the chiral phosphoric acid catalyst, see: (a) Akiyama, T. WO 2004096753, 2004; *Chem. Abstr.* **2004**, *141*, 411087. (b) Hoffmann, S.; Seayad, A. M.; List, B. *Angew. Chem. Int. Ed.* **2005**, *44*, 7424. For seminal work on chiral phosphoric acids, see: (c) Akiyama, T.; Itoh, J.; Yokota, K.; Fuchibe, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1566. (d) Uraguchi, D.; Terada, M. *J. Am. Chem. Soc.* **2004**, *126*, 5356.

(13) The absolute configuration of **3aa** was assigned as (1*R*,2*R*) based on the optical rotation data of the phenylated product **9**.[2a]

(14) For synthesis of 1,2-oxaborinan-2-ol derivatives, see: (a) Micalizio, G. C.; Schreiber, S. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 3272. (b) Hansen, E. C.; Lee, D. *J. Am. Chem. Soc.* **2006**, *128*, 8142. (c) McNulty, L.; Kohlbacher, K.; Borin, K.; Dodd, B.; Bishop, J.; Fuller, L.; Wright, Z. *J. Org. Chem.* **2010**, *75*, 6001.

(15) For recent reviews on sequential processes involving double-bond transposition, see: (a) Larionov, E.; Li, H.; Mazet, C. *Chem. Commun.* **2014**, *50*, 9816. (b) Vasseur, A.; Bruffaerts, J.; Marek, I. *Nature Chem.* **2016**, *8*, 209.

(16) The progress of the reaction was monitored after 10 min by ^{1}H NMR. Whereas 38% of **1a** was converted in the absence of (*R*)-TRIP, **1a** was already fully converted in the presence of (*R*)-TRIP (5 mol %), demonstrating acceleration of the allylboration by TRIP.

(17) (a) Carosi, L.; Lachance, H.; Hall, D. G. *Tetrahedron Lett.* **2005**, *46*, 8981. (b) Incerti-Pradillos, C. A.; Kabeshov, M. A.; Malkov, A. V. *Angew. Chem. Int. Ed.* **2013**, *52*, 5338.

(18) Chen, M.; Roush, W. R. *Org. Lett.* **2012**, *14*, 1880.

(19) For a recent example of functional group transposition from a remote position for C–C bond formation, see: Juliá-Hernández, F.; Moragas, T.; Cornella, J.; Martin, R. *Nature* **2017**, *545*, 84.

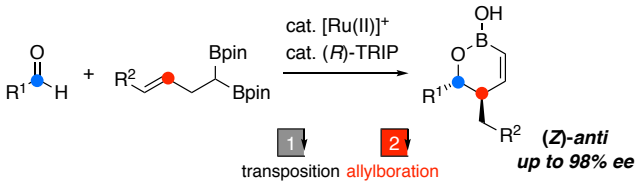
(20) Murphy, J. M.; Liao, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 15434.

(21) Körner, C.; Starkov, P.; Sheppard, T. D. *J. Am. Chem. Soc.* **2010**, *132*, 5968.

(22) Batey, R. A.; Thadani, A. N.; Lough, A. J. *J. Am. Chem. Soc.* **1999**, *121*, 450.

(23) For similar transformation via hemiacetals, see: Liang, T.; Zhang, W.; Chen, T.-Y.; Nguyen, K. D.; Krische, M. J. *J. Am. Chem. Soc.* **2015**, *137*, 13066.

TOC Graphic:


cat. [Ru(II)]+
cat. (R)-TRIP
Bpin
Bpin
OH
B
O
R1
R2
H
O
R1
R2
1
2
transposition
allylboration
(Z)-anti
up to 98% ee