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Enantioselective 1,4-addition of cyclopropylboronic acid catalyzed by rhodium/chiral diene complexes†

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Rhodium-catalyzed asymmetric addition of cyclopropylboronic acids to electron-deficient alkenes such as alkenylsulfones, enones, enoates, and nitroalkenes proceeded to give high yields of the corresponding 1,4-addition products with high enantioselectivity.

Asymmetric conjugate addition of organometallic reagents to electron-deficient alkenes catalyzed by Rh complexes is now well-recognized to be one of the most reliable methods for carbon–carbon bond formation introducing aryl and alkenyl groups with high enantioselectivity.[1,2] On the other hand, asymmetric conjugate addition of alkyl groups has been developed using Ni and Cu catalysts,[3] and thus both catalytic systems perform a complementary role in the transition metal-catalyzed asymmetric conjugate addition reactions.[4] The catalytic conjugate addition of simple alkyl metal reagents under the rhodium catalysis using organometallic reagents is difficult because an intermediate alkylrhodium(I) species having a β-hydrogen readily undergoes elimination to give a hydridorhodium species and an alkene.[4] As rare examples of the rhodium-catalyzed addition reaction of alkyl metal reagents, we reported asymmetric methylation of imines by the use of Me_2Zn or trimethylboroxine as a methylating reagent, where the β-hydrogen to be eliminated does not exist.[5,6] von Zezschwitz and co-workers reported asymmetric 1,2- or 1,4-addition of Me_3Al to cyclic enones catalyzed by a rhodium/binap complex.[7] The stereoselective alkyl transfer from potassium benzylic trifluoroborates to aldehydes was also reported by Aggarwal and co-workers, where it is proposed that the reaction proceeds by direct migration of the benzylic group to the aldehyde without formation of a benzylrhodium species.[8] In this context, we focused on the use of a cyclopropylrhodium(I) species for the conjugate addition, which may avoid the β-hydrogen elimination leading to the formation of a highly strained cyclopropene. The asymmetric addition of dicyclopropylzinc to aldehydes was reported by the use of a chiral amino alcohol.[9] The diastereoselective addition of cyclopropyllithium or magnesium bromide to imines is achieved using a chiral auxiliary on the nitrogen.[10] The Cu-catalyzed enantioselective addition of dicyclopropylzinc to a β-disubstituted nitroalkene was reported to give the addition product in low yield with low enantioselectivity.[11,12] Here we report that the asymmetric addition of cyclopropylboronic acid to electron-deficient alkenes catalyzed by Rh/chiral diene complexes. To the best of our knowledge, this is the first example of the metal-catalyzed asymmetric conjugate addition of cyclopropylboronic acids.[13]

We found that a Rh complex coordinated with a diene ligand has high catalytic activity in the addition of cyclopropylboronic acid to an alkenylsulfone (Table 1). Thus, treatment of alkenylsulfone **1a** with cyclopropylboronic acid (**2**, 2.5 equiv.) in the presence of $[RhCl(cod)]_2$ (3 mol% of Rh) and K_3PO_4 (1 equiv.) in toluene at 60 °C for 12 h gave the addition product **3a** in 60% yield (entry 1, Table 1). An enantioselective addition was achieved by the use of chiral diene ligands.[14] A Rh complex coordinated with a ferrocenyl (Fc)-substituted diene ligand based on the tetrafluorobenzobarrelene (tfb) framework,[15] which is a superior catalyst in the asymmetric addition of arylboronic acids to alkenyl sulfonyl compounds,[16,17] displayed a high catalytic activity and enantioselectivity to give **3a** in 96% yield with 97% ee (entry 2). Other tfb ligands substituted with phenyl (Ph) and benzyl (Bn), and bicyclo[2.2.2]octadienes **L1** and **L2**,[18] which are derived from a natural product, were less effective in the present addition reaction (entries 3–6). The use of a rhodium-bisphosphine complex $[RhCl((R)\text{-binap})]_2$[19] did not give the addition product at all (entry 7). Cyclopropylboronic acid neopentylglycolate **2′** can also be used to give a 99% yield of **3a** with 94% ee, although the reaction requires a higher reaction temperature (80 °C, entry 8). The absolute configuration of product **3a** formed by the use of (*S*,*S*)-Fc-tfb* was determined to be *S* by X-ray crystallographic analysis.

The results obtained for the enantioselective addition of cyclopropylboronic acid (**2**) to several alkenyl sulfonyl compounds **1**

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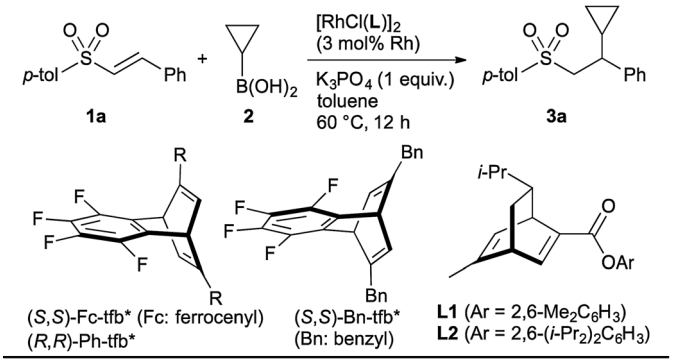
Table 1 Rh-catalyzed addition of cyclopropylboronic acid **2** to alkenylsulfone **1a**[a]

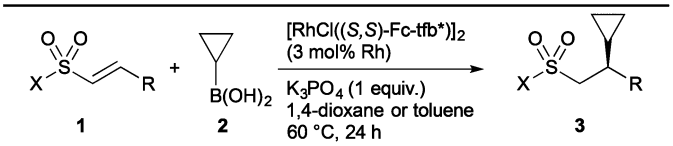


Entry	L	Yield[b] (%)	ee[c] (%)
1	cod (1,5-cyclooctadiene)	60	—
2	(*S*,*S*)-Fc-tfb*	96[d]	97
3	(*R*,*R*)-Ph-tfb*	43	93
4	(*S*,*S*)-Bn-tfb*	24	60
5	(*R*)-**L1**	10	—[e]
6	(*R*)-**L2**	4	—[e]
7	(*R*)-Binap	0	—
8[f]	(*S*,*S*)-Fc-tfb*	99	94

[a] Reaction conditions: alkenylsulfone **1a** (0.10 mmol), **2** (0.25 mmol), the Rh catalyst (3 mol% of Rh), K_3PO_4 (1 equiv.) in toluene (0.4 mL) at 60 °C for 12 h. [b] Determined by ^1H NMR analysis using 1,4-dimethoxybenzene as an internal standard. [c] Determined by chiral HPLC analysis. [d] Isolated yield. [e] Not determined. [f] Cyclopropylboronic acid neopentylglycolate **2′** was used instead of **2** in the presence of methanol (3 equiv.) at 80 °C.

are summarized in Table 2.[20] The reaction of alkenyl sulfones having 2-furyl (**1b**) and 2-thienyl (**1c**) at the β-position proceeded to give the corresponding addition products **3b** and **3c**, respectively, in high yields with high enantioselectivity (entries 1 and 2). A pyridyl group on alkenyl sulfone **1d** slowed the reaction to give **3d** in 51% yield at 80 °C for 12 h, but the enantioselectivity was high (96% ee, entry 3). Alkenyl sulfones substituted with 2-methyl-1-propenyl (**1e**), butyl (**1f**), and benzyl (**1g**)[21] are also good substrates

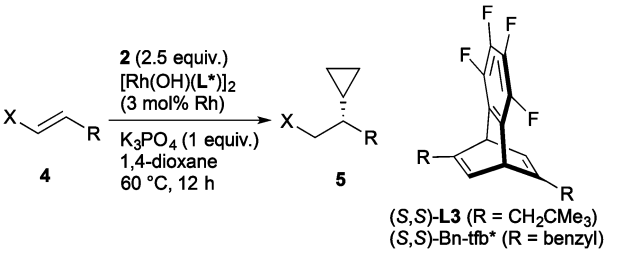
Table 2 Asymmetric cyclopropylation of alkenylsulfonyl compounds **1**[a]



Entry	X	R	Yield[b] (%)	ee[c] (%)
1	*p*-Tolyl	2-Furyl (**1b**)	97 (**3b**)	93
2	*p*-Tolyl	2-Thienyl (**1c**)	97 (**3c**)	93
3[d,e,f]	*p*-Tolyl	3-Pyridyl (**1d**)	51 (**3d**)	96
4	*p*-Tolyl	CH=CMe$_2$ (**1e**)	78 (**3e**)	83
5[g]	*p*-Tolyl	Butyl (**1f**)	94 (**3f**)	96
6[g,h]	*p*-Tolyl	Benzyl (**1g**)	92 (**3g**)	97
7[d,e]	2,6-Me$_2$C$_6$H$_3$O	Ph (**1h**)	80 (**3h**)	98
8	EtO	Ph (**1i**)	86 (**3i**)	92
9	*N*-Morpholyl	Ph (**1j**)	96 (**3j**)	98

[a] Reaction conditions: alkenylsulfone **1** (0.20 mmol), **2** (0.50 mmol), [RhCl((*S*,*S*)-Fc-tfb*)]$_2$ (3 mol% of Rh), K_3PO_4 (1 equiv.) in 1,4-dioxane (for **1b–d**, **1f**, **1h**; 0.8 mL) or toluene (for **1e**, **1g**, **1i**, **1j**; 0.8 mL) at 60 °C for 24 h. [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] At 80 °C. [e] Performed with 3.5 equiv. of **2**. [f] Performed with 5 mol% of Rh. [g] For 12 h. [h] Na_3PO_4 was used instead of K_3PO_4.

Table 3 Asymmetric cyclopropylation of enones, enoates, and nitroalkenes[a]



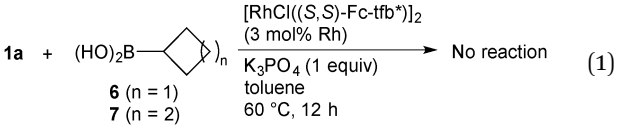
Entry	L*	X	R	Yield[b] (%)	ee[c] (%)
1[d,e]	**L3**	COPh	Ph (**4a**)	80 (**5a**)	84
2	**L3**	COPh	4-ClC$_6$H$_4$ (**4b**)	89 (**5b**)	84
3	**L3**	COPh	4-CF$_3$C$_6$H$_4$ (**4c**)	95 (**5c**)	86
4[d,e]	Bn-tfb*	CO_2Et	Ph (**4d**)	63 (**5d**)	81
5	**L3**	$CO_2CH(CF_3)_2$	Ph (**4e**)	70 (**5e**)	84
6	**L3**	CO_2(*t*-Bu)	CO_2(*t*-Bu) (**4f**)	99 (**5f**)	81
7	Bn-tfb*	NO_2	*p*-Tolyl (**4g**)	92 (**5g**)	89
8[e]	Bn-tfb*	NO_2	4-ClC$_6$H$_4$ (**4h**)	80 (**5h**)	89
9[e,f]	Bn-tfb*	NO_2	4-MeOC$_6$H$_4$ (**4i**)	70 (**5i**)	89

[a] Reaction conditions: **4** (0.20 mmol), **2** (0.70 mmol), [Rh(OH)(**L***)]$_2$ (3 mol% of Rh), K_3PO_4 (for **4a–f**; 1 equiv.) in 1,4-dioxane (0.8 mL) or KHF_2 (for **4g–i**; 1 equiv.) in toluene (0.8 mL) at 60 °C for 12 h. [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] 5 mol% of Rh was used. [e] For 24 h. [f] At 80 °C.

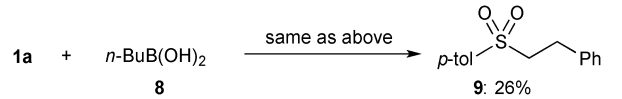
to give the corresponding addition products in good to high yields with high enantioselectivity (entries 4–6). Not only alkenyl sulfones, but also sulfonates (**1h** and **1i**) and a sulfonamide (**1j**) can be applicable with high enantioselectivity (entries 7–9).

The enantioselective addition of cyclopropylboronic acid proceeded toward the other electron-deficient alkenes than alkenyl sulfones, where the higher enantioselectivity was observed with alkyl-substituted tfb ligands than that with Fc-tfb* (Table 3). In the presence of hydroxorhodium/chiral tfb catalysts,[22] the addition to α,β-unsaturated ketones **4a–c**, esters **4d** and **4e**, and di-*tert*-butyl fumarate (**4f**) proceeded to give the corresponding addition products in good yields with 81–86% ee (entries 1–6), where ligand **L3** substituted with neopentyl groups displayed good enantioselectivity, except for the addition to ethyl ester **4d**. Nitroalkenes **4g–i** were also applicable acceptors by the use of KHF_2 as a base[23] instead of K_3PO_4 to give the corresponding addition products with 89% ee (entries 7–9).

The addition of cyclobutylboronic acid (**6**) or cyclopentylboronic acid (**7**) to alkenylsulfone **1a** under the same reaction conditions as for cyclopropylboronic acid (**2**) did not take place and **1a** was recovered intact (eqn (1)). On the other hand, the use of n-butylboronic acid (**8**) gave only saturated sulfone **9** in 26% yield, indicating that the reduction of **1a** proceeds *via* the formation of a hydridorhodium generated by β-hydrogen elimination of a n-butylrhodium species (eqn (2)). The results also imply that the transmetalation of the Rh with cyclobutyl- and cyclopentylboronic acid does not take place under the present reaction conditions.

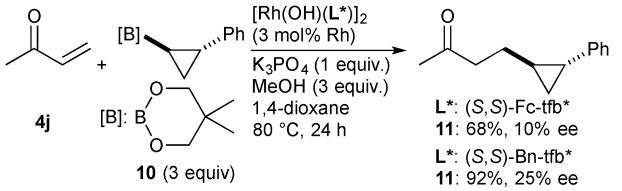


(1)

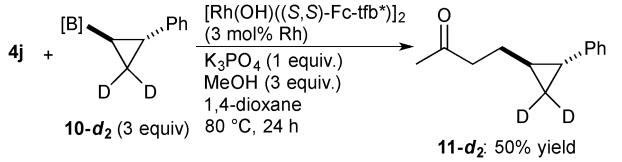


(2)

Transfer of a substituted cyclopropyl group also took place under the rhodium catalysis (eqn (3) and (4)). Thus, the addition of a racemic cyclopropylboronate **10** having *trans*-2-phenyl to methyl vinyl ketone (**4j**) in the presence of [Rh(OH)((*S*,*S*)-Fc-tfb*)]$_2$ proceeded to give the addition product **11** in 68% yield (eqn (3)). The relative configuration of **11** was determined to be *trans*, indicating that the transmetalation and the following insertion took place with retention of the configuration.[24] A kinetic resolution of the racemic **10** was also observed (10% ee with Fc-tfb* and 25% ee with Bn-tfb*). In the reaction of deuterated **10**-d_2, migration of deuterium, which should be due to the β-hydrogen elimination, was not observed (eqn (4)). Shintani and Nozaki reported that the polymerization of 3,3-diarylcyclopropenes catalyzed by a rhodium complex, where 1,4-rhodium migration of a cyclopropylrhodium(I) species *cis* to an aromatic ring takes place to form an arylrhodium(I) intermediate.[25] In the reaction of cyclopropylboronate **10**, such a 1,4-rhodium migration was not observed, and thus the result also supports that the intermediate cyclopropylrhodium(I) is *trans* to the phenyl group.



(3)



(4)

In summary, we have developed Rh-catalyzed asymmetric addition of cyclopropylboronic acids to electron-deficient alkenes. The Rh complexes coordinated with chiral diene ligands based on a tetrafluorobenzobarrelene framework displayed high catalytic activity and enantioselectivity. The addition of a substituted-cyclopropyl group proceeded with the stereoretention, indicating that the transmetalation and the subsequent carborhodation proceed with the retention of the configuration.

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22 The hydroxorhodium complexes displayed higher catalytic activity than the corresponding chlororhodium complexes. The absolute configuration of the products was assigned by consideration of the stereochemical reaction pathway. Therefore, the products obtained with (*S*,*S*)-R-tfb* ligands in Table 3 have the opposite configuration to those in Table 2.

23 The use of KHF_2 as an effective base was reported in the arylation of nitroalkenes, see: (*a*) Z.-Q. Wang, C.-G. Feng, S.-S. Zhang, M.-H. Xu and G.-Q. Lin, *Angew. Chem., Int. Ed.*, 2010, **49**, 5780; (*b*) K.-C. Huang, B. Gopula, T.-S. Kuo, C.-W. Chiang, P.-Y. Wu, J. P. Henschke and H.-L. Wu, *Org. Lett.*, 2013, **15**, 5730.

24 In Pd-catalyzed cross coupling of cyclopropylboronic acids, the stereoretention was observed, see: ref. 13*a*–*c*. The coupling reaction with inversion of the configuration of benzylboron reagents was also reported. T. Ohmura, T. Awano and M. Suginome, *J. Am. Chem. Soc.*, 2010, **132**, 13191.

25 R. Shintani, R. Iino and K. Nozaki, *J. Am. Chem. Soc.*, 2014, **136**, 7849.