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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 $[\text{RhCl}(\text{cod})]_2$ (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 tetrafluorobenzobarrelele (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 $[\text{RhCl}((R)\text{-binap})]_2$ 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 alkenyl-sulfone **1a**^a

Reaction scheme for Table 1: Alkenyl sulfone **1a** reacts with cyclopropylboronic acid **2** in the presence of [RhCl(L)]₂ (3 mol% Rh) and K₃PO₄ (1 equiv.) in toluene at 60 °C for 12 h to form product **3a**.

Structures of ligands L1 and L2 are shown: L1 (Ar = 2,6-Me₂C₆H₃) and L2 (Ar = 2,6-(*i*-Pr)₂C₆H₃).

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

^a Reaction conditions: alkenylsulfone **1a** (0.10 mmol), **2** (0.25 mmol), the Rh catalyst (3 mol% of Rh), K₃PO₄ (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

Reaction scheme for Table 2: Alkenyl sulfone **1** reacts with cyclopropylboronic acid **2** in the presence of [RhCl((*S,S*)-Fc-tfb*)]₂ (3 mol% Rh) and K₃PO₄ (1 equiv.) in 1,4-dioxane or toluene at 60 °C for 24 h to form product **3**.

Entry	X	R	Yield ^b (%)	ee ^c (%)
1	<i>p</i> -Tolyl	2-Furyl (1b)	97 (3b)	93
2	<i>p</i> -Tolyl	2-Thienyl (1c)	97 (3c)	93
3 ^{d,e,f}	<i>p</i> -Tolyl	3-Pyridyl (1d)	51 (3d)	96
4	<i>p</i> -Tolyl	CH=CMe ₂ (1e)	78 (3e)	83
5 ^g	<i>p</i> -Tolyl	Butyl (1f)	94 (3f)	96
6 ^{g,h}	<i>p</i> -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	<i>N</i> -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), K₃PO₄ (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 Na₃PO₄ was used instead of K₃PO₄.

Table 3 Asymmetric cyclopropylation of enones, enoates, and nitroalkenes^a

Reaction scheme for Table 3: Enone **4** reacts with cyclopropylboronic acid **2** (2.5 equiv.) in the presence of [Rh(OH)(L*)]₂ (3 mol% Rh) and K₃PO₄ (1 equiv.) in 1,4-dioxane at 60 °C for 12 h to form product **5**.

Structures of ligands L3 and L2 are shown: L3 (R = CH₂CMe₃) and L2 (R = benzyl).

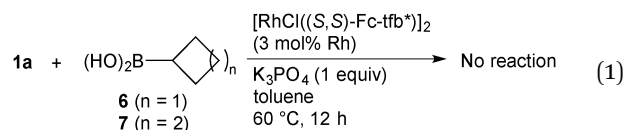
Entry	L*	X	R	Yield ^b (%)	ee ^c (%)
1 ^{d,e}	L3	COPh	Ph (4a)	80 (5a)	84
2	L3	COPh	4-ClC ₆ H ₄ (4b)	89 (5b)	84
3	L3	COPh	4-CF ₃ C ₆ H ₄ (4c)	95 (5c)	86
4 ^{d,e}	Bn-tfb*	CO ₂ Et	Ph (4d)	63 (5d)	81
5	L3	CO ₂ CH(CF ₃) ₂	Ph (4e)	70 (5e)	84
6	L3	CO ₂ (<i>t</i> -Bu)	CO ₂ (<i>t</i> -Bu) (4f)	99 (5f)	81
7	Bn-tfb*	NO ₂	<i>p</i> -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

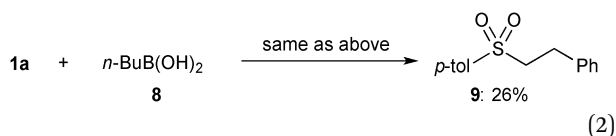
^a Reaction conditions: **4** (0.20 mmol), **2** (0.70 mmol), [Rh(OH)(L*)]₂ (3 mol% of Rh), K₃PO₄ (for **4a–f**; 1 equiv.) in 1,4-dioxane (0.8 mL) or KHF₂ (for **4g–i**; 1 equiv.) in toluene (0.8 mL) at 60 °C for 12 h. ^b Isolated yields. ^c Determined by chiral HPLC analysis. ^d 5 mol% of Rh was used. ^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).

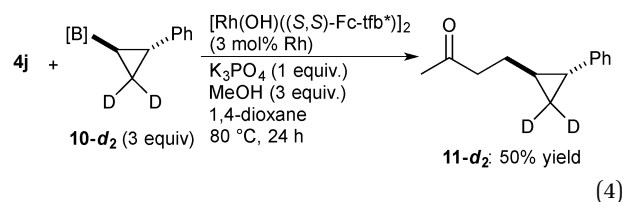
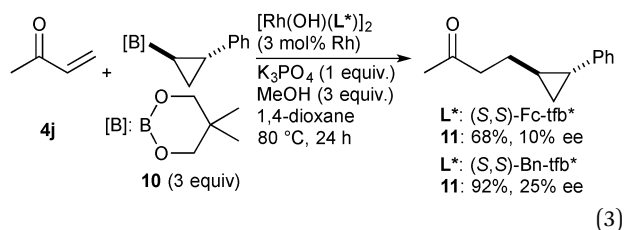
The enantioselective addition of cyclopropylboronic acid proceeded toward the other electron-deficient alkenes than alkenyl sulfones, where the higher enantioselectivity was observed with alkyl-substituted tfb ligands than that with Fc-tfb* (Table 3). In the presence of hydroxorhodium/chiral tfb catalysts,²² 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 KHF₂ as a base²³ instead of K₃PO₄ 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.





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-d₂**, 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-diaryl-cyclopropenes 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.



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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