Asymmetric Catalysis

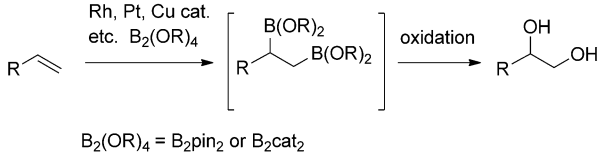
DOI: 10.1002/ange.201305181

Asymmetric Diboration of Terminal Alkenes with a Rhodium Catalyst and Subsequent Oxidation: Enantioselective Synthesis of Optically Active 1,2-Diols**

*Kenji Toribatake and Hisao Nishiyama**

Optically active 1,2-diols are an important class of organic compounds used for synthetic intermediates of bioactive or pharmaceutical compounds.[1] They have commonly been synthesized by direct asymmetric dihydroxylation of alkenes with osmium reagents,[2] asymmetric hydrogenation of α-hydroxyketones,[3] asymmetric hydrolytic kinetic resolution of epoxides,[4] and enzymatic reactions,[5] to name a few. However, efficient, reliable, and practical synthetic methods of optically active 1,2-diols are still in demand to solve challenging subjects such as expanding substrate scope, attaining a high level of enantioselectivity, lowering catalyst loading, or making the reaction environmentally benign. In that sense, direct dihydroxylation of alkenes with osmium-free catalysts has recently attracted attention.[6] Some iron catalysts such as non-heme iron enzyme mimics have also been explored.[7]

Alternatively, asymmetric 1,2-diboration of alkenes (ADA) and subsequent oxidation can provide optically active 1,2-diols (Scheme 1).[8,9] In 2003, Morken et al.



Scheme 1. Catalytic diboration of alkenes and subsequent oxidation to form 1,2-diols.

reported the first enantioselective 1,2-diboration of alkenes catalyzed by a rhodium catalyst with bis(catecholatodiboron) (B_2cat_2) in the presence of chiral phosphine ligands.[10] In their work, *trans* 1,2-disubstituted alkenes and terminal alkenes bearing tertiary alkyl groups were subjected to the catalytic diboration and subsequent oxidation to give optically active 1,2-diols with high enantioselectivities, whereas some *cis*-disubstituted alkenes and terminal alkenes only afforded moderate *ee* values. In 2009, Morken et al. also developed platinum-catalyzed asymmetric diboration of terminal alkenes to attain *ee* values of up to 94% for the corresponding 1,2-diol products.[11]

In this context, it should also be mentioned that monoboration of conjugated electron-deficient alkenes with diborons can be applied to the preparation of β-hydroxy carbonyl compounds, and it has been established as a reliable synthetic method.[12] Very recently, the asymmetric catalytic conjugate β-boration was carried out by metal-free organocatalysts such as chiral or nonchiral N-heterocyclic carbenes (NHCs) or phosphines.[13] Furthermore, catalytic diboration of non-activated alkenes using Lewis base chiral alkoxides was realized by Gulyás, Fernández, and co-workers.[14] Thus, catalytic di- and monoboration of alkenes are at the cutting and leading edge of organic synthesis.

As we studied the asymmetric conjugate monoboration of α,β-unsaturated carbonyl compounds with chiral rhodium-[bis(oxazolinyl)phenyl] complexes ([Rh(Phebox)]; **1**), and bis(pinacolato)diboron (B_2pin_2),[15] we became strongly intrigued by ADA (Figure 1). Herein, we report a highly

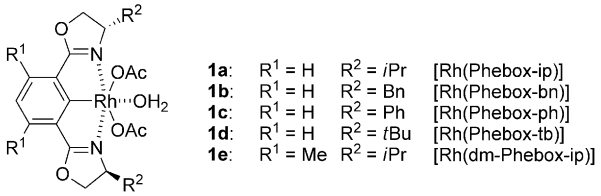


Figure 1. Chiral rhodium[bis(oxazolinyl)phenyl] complexes.

efficient ADA with a [Rh(Phebox)] catalyst and subsequent oxidation, thus producing optically active 1,2-diols.

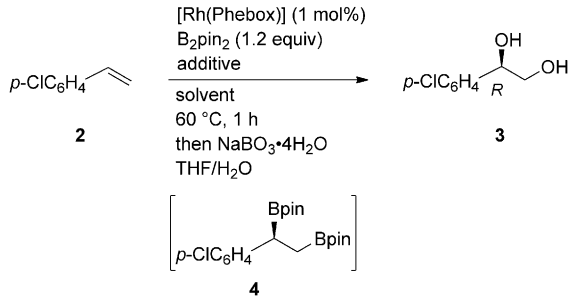
The mixture of *p*-chlorostyrene (**2**; 0.50 mmol) as a selected substrate and B_2pin_2 (1.2 equiv) in THF (1 mL) was treated at 60°C with 1 mol% of [Rh(Phebox-ip)] (**1a**), and subsequent oxidation with $NaBO_3{\cdot}4(H_2O)$ to give the 1,2-diol **3** in 20% yield with 66% *ee* (entry 1, Table 1). To our delight, the addition of NaO*t*Bu (5 mol%) promoted the diboration reaction smoothly to form the 1,2-diboration product in 1 hour, and subsequent oxidation (in the same pot) with sodium peroxoborate in THF and water at room temperature gave **3** in 94% yield with an *ee* value of more than 99% (entry 2). At 30°C, the addition of NaO*t*Bu was effective but resulted in a slight decrease in the *ee* value (entry 3). The reason of the decrease was not identified, and

[*] K. Toribatake, Prof. Dr. H. Nishiyama
Department of Applied Chemistry
Graduated School of Engineering
Nagoya University, Chikusa, Nagoya, 464-8603 (Japan)
E-mail: hnishi@apchem.nagoya-u.ac.jp
Homepage: http://www.apchem.nagoya-u.ac.jp/06-II-1/nisilab/index.html

[**] This research was partly supported by the Japan Society for the Promotion of Science (No. 2562007).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201305181.

Table 1: Asymmetric diboration and subsequent oxidation of *p*-chlorostyrene with the [Rh(Phebox)] catalysts **1a–e**.[a]



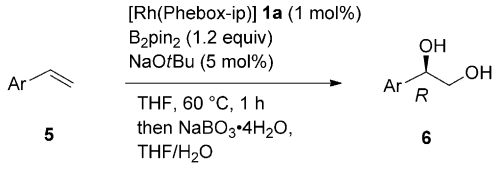
2 **3** **4**

Entry	Cat. **1**	Additive	Solvent	*T* [°C]	Yield [%]	*ee* [%]
1	**1a**	–	THF	60	20	66
2	**1a**	NaO*t*Bu	THF	60	94	>99
3	**1a**	NaO*t*Bu	THF	30	93	88[b]
4	**1a**	NaOEt	THF	60	92	93
5	**1a**	KO*t*Bu	THF	60	93	82
6	**1a**	NaOAc	THF	60	23	76
7	**1a**	Na_2CO_3	THF	60	29	77
8	**1a**	K_2CO_3	THF	60	20	55
9	**1a**	Cs_2CO_3	THF	60	91	76
10	**1a**	NaO*t*Bu	$C_6H_5CH_3$	60	50	61
11	**1a**	NaO*t*Bu	$C_6H_5CH_3$	80	79	96
12	**1a**	KO*t*Bu	$C_6H_5CH_3$	80	85	84
13	**1a**	NaO*t*Bu	Dioxane	80	46	61
14	**1b**	NaO*t*Bu	THF	60	95	95
15	**1c**	NaO*t*Bu	THF	60	91	94
16	**1d**	NaO*t*Bu	THF	60	23	12
17	**1e**	NaO*t*Bu	THF	60	88	99
18[c]	**1a**	NaO*t*Bu	THF	60	89	98

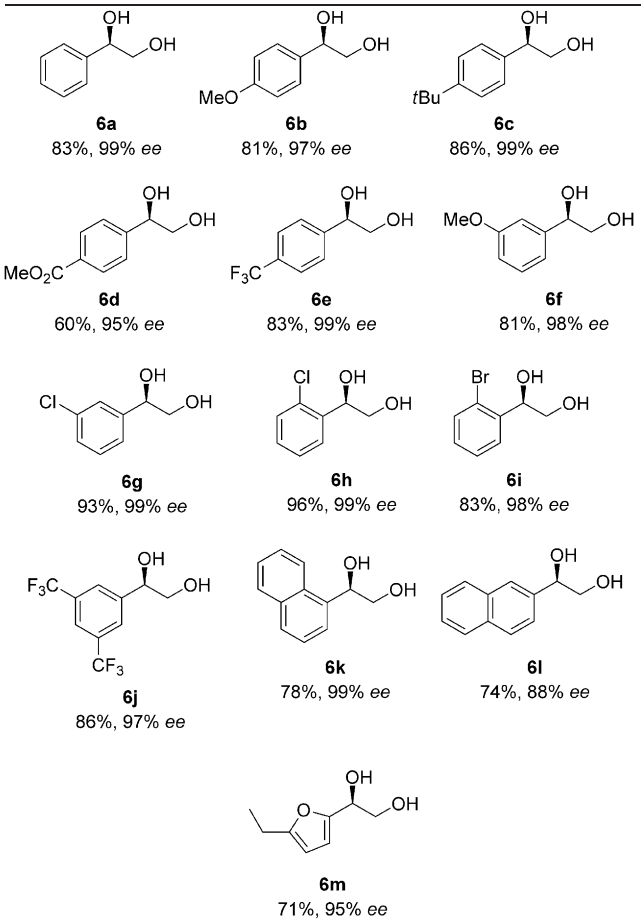
[a] Reaction conditions: *p*-Chlorostyrene (**2**; 0.50 mmol), [Rh(Phebox)] cat. (1.0 mol%), B_2pin_2 (1.2 equiv, 0.60 mmol), additive (5 mol%), THF (1.0 mL), reaction time (1 h). The diboration product was subsequently oxidized with $NaBO_3 \cdot 4H_2O$. [b] Average of three reactions; 87–93% yield, 88–90% *ee*. [c] *p*-Chlorostyrene (**2**; 1.38 g, 10.0 mmol), cat. **1a** (0.2 mol%), B_2pin_2 (1.2 equiv, 12.0 mmol), NaO*t*Bu (5 mol%), THF (20 mL), 60°C, 1 h, product **3** (1.53 g, 8.9 mmol).

the phenomenon was confirmed by running the reaction three times. NaOEt and KO*t*Bu worked efficiently to afford good yields and *ee* values (entries 4 and 5). Sodium acetate and carbonate and potassium carbonate decreased the yield to 20–29% with moderate *ee* values (entries 6–8). Cesium carbonate enhanced the diboration, but resulted in only 76% *ee* (entry 9). Toluene in place of THF required a slightly higher reaction temperature (80°C) to give 96% *ee* (entries 10–12). 1,4-Dioxane was not the solvent of choice (entry 13). Under the optimum reaction conditions (entry 2), several substituents on the oxazoline skeleton of the catalyst were examined, and the benzyl and phenyl substituents afforded the best results, thus affording **3** in over 90% yield with 94 and 95% *ee*, respectively (entries 14 and 15). However, a *tert*-butyl group resulted in a diminished reaction yield (entry 16). The catalyst **1e**,[15d] having dimethyl substituents on the phenyl skeleton, was also effective for producing a high yield with high enatioselectivity (entry 17). More noteworthy is that the reaction could also be practically manipulated on gram scale with respect to **2** by using a 0.2 mol% catalyst loading (substrate/catalyst = 500; entry 18).

Table 2: Asymmetric diboration and subsequent oxidation of aryl-substituted terminal alkenes using [Rh(Phebox-ip)] (**1a**).



5 **6**

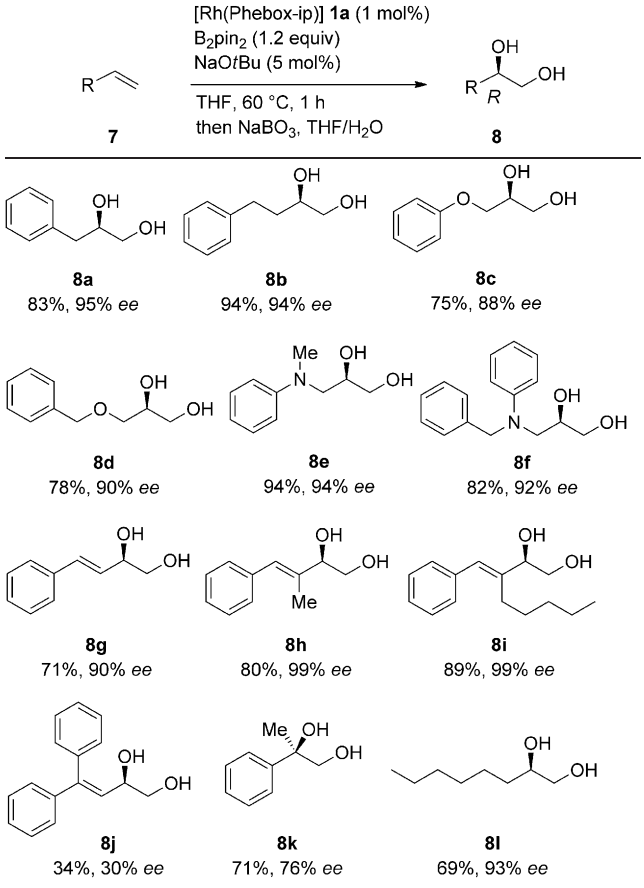


Reaction conditions: Aryl-substituted alkene (**5**; 0.50 mmol), [Rh(Phebox-ip)] (**1a**; 1.0 mol%), B_2pin_2 (1.2 equiv, 0.60 mmol), NaO*t*Bu (5 mol%), THF (1.0 mL), reaction time (1 h). The diboration product was subsequently oxidized with $NaBO_3 \cdot 4H_2O$. The yields are those of the isolated products and the *ee* values were determined by HPLC using a chiral stationary phase. Small amounts of pinacol contaminated **6h**, **6i**, and **6j**.

We next examined other aryl-substituted terminal alkenes as substrates and used the reaction conditions used in entry 2 of Table 1. The results are shown in Table 2. Styrene resulted in 99% *ee* for the diol **6a**. Substituted styrenes and naphthalene derivatives were borated in 60–96% yields with high enantioselectivities of up to 99%. The optically active diol **6j** derived from 3,5-bis(trifluoromethyl)styrene served as a precursor for production of the substance P antagonist as an antidepressant.[1b] A vinyl furan was nicely transformed into the corresponding diol **6m** in 95% *ee*.

Next, several functionalized terminal alkenes were subjected to the diboration under the standard reaction conditions (Table 3). 3-Phenylpropene and 4-phenyl-1-butene

Table 3: Asymmetric diboration and subsequent oxidation of substituted terminal alkenes using [[Rh(Phebox-ip)] (**1a**).



Reaction conditions: Substituted alkene (**7**; 0.50 mmol), [Rh(Phebox-ip)] (**1a**; 1.0 mol%), B_2pin_2 (1.2 equiv, 0.60 mmol), NaO*t*Bu (5 mol%), THF (1.0 mL), reaction time (1 h). The diboration product was subsequently oxidized with $NaBO_3 \cdot 4H_2O$. The yields are those of the isolated products and the *ee* values were determined by HPLC using a chiral stationary phase. For **8k**, the catalyst **1b** was used. Small amounts of pinacol contaminated **8i** and **8k**. The *ee* value of **8l** was determined from the corresponding dibenzoate.

produced the diols **8a** (95% *ee*) and **8b** (94% *ee*), respectively. The *ee* values and yields of the diols **8c** and **8d** derived from allylethers were slightly reduced. Interestingly, allylanilines were smoothly diborated to give the diols **8e** and **8f** in 94 and 92% *ee*, respectively. 1-Phenylbutadiene was converted into the 1,2-diol **8g** in 90% *ee*, and it is noteworthy that 2-methyl and 2-pentyl butadiene resulted in increased *ee* values of up to 99% for **8h** and **8i**. 1,1-Diphenylbutadiene unfortunately resulted in both a low yield and *ee* value. In terms of asymmetric diboration of dienes, Morken et al. used a chiral platinum catalyst to efficiently demonstrate selective 1,2-diol formation and its application to successive allylation.[11e,f] 1-Methylstyrene gave the diol **8k** with moderate *ee* value. A simple aliphatic alkene 1-octene was examined and resulted in a moderate yield and 93% *ee* of **8l**.

As a limitation of our method, 1,2-disubstituted alkenes such as β-methylstyrene, 1,2-dihydronaphthalene, or *trans*-stilbene could not be diborated under the standard reaction conditions.

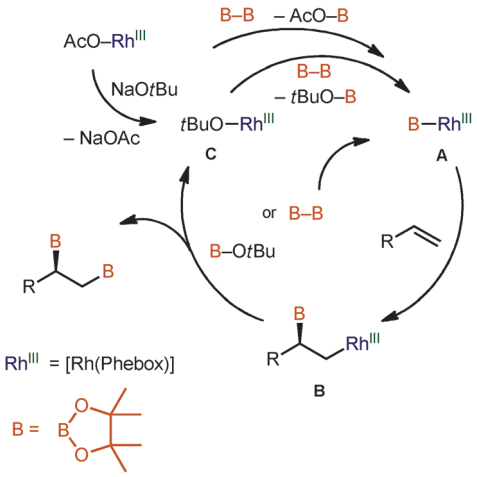


Figure 2. Proposed catalytic cycle.

Our proposed catalytic cycle is shown in Figure 2. We attempted to follow the reaction of the [Rh(Phebox)$(OAc)_2$-(H_2O)] complex and B_2pin_2 by ^1H NMR spectroscopy, but we could not confirm the corresponding boryl-rhodium species.[15] However, formation of a boryl acetate was confirmed, using ^{11}B NMR spectroscopy, by the reaction of [Rh(Phebox-*ip*) $(OAc)_2(H_2O)$] (**1a**) and B_2pin_2 at 60 °C for 30 minutes (see the Supporting Information). Therefore, on the basis of the fact that NaO*t*Bu accelerated the diboration, the σ-bond metathesis or the transmetallation is thought to be included in the catalytic cycle. The boryl–Rh^{III} species **A** coordinates to an alkene and subsequent insertion of the boryl group to form an alkyl–Rh species (**B**). Next, σ-bond metathesis or the transmetallation produces the diboration product and regenerates the active *t*BuO–Rh^{III} (**C**) or **A**. Recently, Bo, Fernández, and co-workers reported that Rh/NHC complexes mediate diboration of cyclic alkenes by a mechanism that includes an oxidative addition pathway to form a diboryl–Rh species without using a basic additive.[16] Therefore, the catalytic cycle may contain the generation of a Rh^I species and oxidative addition of diboron to form a $Rh^{III}B_2$ species.

Hypothetical transition-state model structures are also proposed (Figure 3). On the basis of the absolute configuration of the 1,2-diol product (*R*), the *Si* face of styrene binds to the rhodium atom to give the corresponding alkyl–Rh species, having the boryl group at the apical position, with subsequent *syn* diboration giving the product. The final oxidation treatment generates the 1,2-diol with retention. The structure **D** is likely to give the major enantiomer rather than the *Re*-face attack on the structure **E** because of steric hindrance. In the case of the boryl group in the equatorial position, the *Si*-face attack is more sterically encumebred for the structure **F** rather than for the structure **G**. Notably, **G** cannot give the desired chirality of the product diol.

In summary, we have found that chiral [Rh(Phebox)] acetate complexes can act as efficient catalysts for asymmetric catalytic diboration of terminal alkenes to afford high enantioselectivities. The diboration can provide a practical synthetic method for optically active 1,2-diols from a variety of substituted alkenes in high yields with high optical purities.

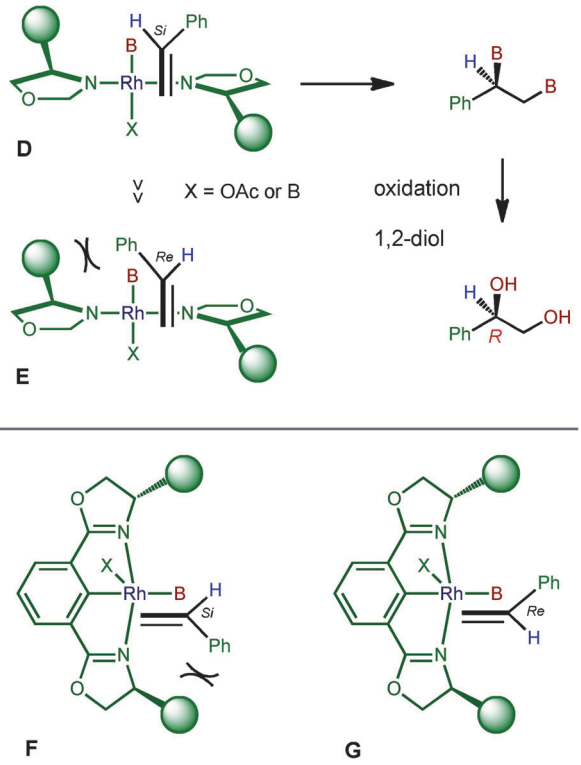


Figure 3. Proposed transition state. Boryl group at apical position and *syn* diboration to *Si* face of the α-carbon atom (**D** and **E**). The equatorial boryl structures **F** and **G**.

Application of this reaction for transformation of a variety of alkene substrates is currently underway in our laboratory.

Experimental Section

Typical procedure for asymmetric diboration and subsequent oxidation: Table 1, entry 2. [Rh(Phebox-ip)] **1a** (2.7 mg, 0.0050 mmol), bis(pinacolato)diboron (152 mg, 0.60 mmol), and NaO*t*Bu (2.5 mg, 0.026 mmol) were placed in a flask with a stirring bar. Under an argon atmosphere, 4-chlorostyrene (**2**; 69.3 mg, 0.50 mmol) and THF (1.0 mL) were added. The mixture was stirred at 60 °C for 1 h. At room temperature, $NaBO_3{\cdot}4H_2O$ (385 mg, 2.5 mmol), THF (1.5 mL), and water (2.5 mL) were added. The mixture was stirred for 1 h at room temperature and extracted with ethyl acetate (2 mL × 5). The extract was concentrated to give the crude reaction mixture, which was purified by silica gel column chromatography with ethyl acetate/*n*-hexane (1:7 to 3:1) as eluant. The corresponding diol **3**, *(R)*-1-(4-chlorophenyl)ethane-1,2-diol, was obtained in 94% yield (80.9 mg, 0.469 mmol) as a white solid; m.p. 84–86 °C. IR (KBr): $\tilde{\nu}$ =3388 (broad) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.11 (br s, 1H), 2.64 (br s, 1H), 3.57 (m, 1H), 3.69 (m, 1H), 4.75 (dd, J = 8.4, 3.3 Hz, 1H), 7.20–7.30 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 67.9, 74.0, 127.2, 128.5, 133.5, 138.6 ppm; Elemental Anal: calcd. (%) for $C_8H_9ClO_2$: C 55.67; H 5.26. Found: C 55.94; H 5.34. Chromatography: Daicel Chiralcel OD-H, *n*-hexane/2-propanol (98:2, 1.5 mL min^{-1}), retention time: 46.0 min (major), 52.8 (minor), 99.5% *ee* (*R*); $[\alpha]_D^{28}$ = −57.4 (c = 1.0, $CHCl_3$); Lit.[17,3a], $[\alpha]_D^{25}$ = −55.9 (c = 1.0, $CHCl_3$), 96% *ee* (*R*).

Received: June 17, 2013
Revised: July 23, 2013
Published online: September 2, 2013

Keywords: asymmetric catalysis · boron · diols · enantioselectivity · rhodium

[1] Selected papers: a) A. B. Smith III, S. S.-Y. Chen, F. C. Nelson, J. M. Reichert, B. A. Salvatore, *J. Am. Chem. Soc.* **1995**, *117*, 12013; b) P. J. Pye, K. Rossen, S. A. Weissman, A. Maliakal, R. A. Reamer, R. Ball, N. N. Tsou, R. P. Volante, P. J. Reider, *Chem. Eur. J.* **2002**, *8*, 1372; c) S. H. Kang, J. W. Jeong, Y. S. Hwang, S. B. Lee, *Angew. Chem.* **2002**, *114*, 1450; *Angew. Chem. Int. Ed.* **2002**, *41*, 1392; d) P. Gupta, S. V. Naidu, P. Kumar, *Tetrahedron Lett.* **2004**, *45*, 849; e) B. J. Edagwa, C. M. Taylor, *J. Org. Chem.* **2009**, *74*, 4132; f) B. B. Lohray, A. S. Reddy, V. Bhushan, *Tetrahedron: Asymmetry* **1996**, *7*, 2411; g) L. M. Schultze, H. H. Chapman, N. J. P. Dubree, R. J. Jones, K. M. Kent, T. T. Lee, M. S. Louie, M. J. Postich, E. J. Prise, J. C. Rohloff, R. H. Yu, *Tetrahedron Lett.* **1998**, *39*, 1853.

[2] a) H. C. Kolb, M. S. Van Nieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483; b) M. C. Noe, M. A. Letavic, S. L. Show, *Org. React.* **2005**, *66*, 109–625; c) A. B. Zaitsev, H. Adolfsson, *Synthesis* **2006**, 1725; d) S. Kobayashi, M. Sugiura, *Adv. Synth. Catal.* **2006**, *348*, 1496.

[3] For examples, asymmetric reduction of α-hydroxyketones: a) T. Ohkuma, N. Utsumi, M. Watanabe, K. Tsutsumi, N. Arai, K. Murata, *Org. Lett.* **2007**, *9*, 2565; b) R. Kadyrov, R. M. Koenigs, C. Brinkmann, D. Voigtlaender, M. Rueping, *Angew. Chem.* **2009**, *121*, 7693; *Angew. Chem. Int. Ed.* **2009**, *48*, 7556; c) T. Saito, T. Yokozawa, T. Ishizaki, T. Moroi, N. Sayo, T. Miura, H. Kumobayashi, *Adv. Synth. Catal.* **2001**, *343*, 264; d) M. Kitamura, T. Ohkuma, S. Inoue, N. Sayo, H. Kumobayashi, S. Akutagawa, T. Ohta, H. Takaya, R. Noyori, *J. Am. Chem. Soc.* **1988**, *110*, 629; e) S. Jeulin, N. Champion, S. Duprat de Paule, P. Dellis, V. Ratovelmanana-Vidal, J.-P. Genêt, *Synthesis* **2005**, 3666. For transfer hydrogenation of α-hydroxyketones, see f) D. J. Cross, J. A. Kenny, I. Houson, L. Campbell, T. Walsgrove, M. Wills, *Tetrahedron: Asymmetry* **2001**, *12*, 1801; g) D. S. Matharu, D. J. Morris, A. M. Kawamoto, G. J. Clarkson, M. Wills, *Org. Lett.* **2005**, *7*, 5489; h) T. Hamada, T. Torii, K. Izawa, T. Ikariya, *Tetrahedron* **2004**, *60*, 7411.

[4] a) M. Tokunaga, J. F. Larrow, F. Kakiuchi, E. N. Jacobsen, *Science* **1997**, *277*, 936; b) S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow, E. N. Jacobsen, *J. Am. Chem. Soc.* **2002**, *124*, 1307.

[5] For a review, see: a) N. Bala, S. S. Chimni, *Tetrahedron: Asymmetry* **2010**, *21*, 2879. Selected achievements of microbial reactions: b) Y. Nie, Y. Xu, X. Q. Mu, *Org. Process Res. Dev.* **2004**, *8*, 246; c) Z. Liu, J. Michel, Z. Wang, B. Witholt, Z. Li, *Tetrahedron: Asymmetry* **2006**, *17*, 47; d) S. Hwang, C. Y. Choi, E. Y. Lee, *Biotechnol. Lett.* **2008**, *30*, 1219; e) P. Mahajabeen, A. Chadha, *Tetrahedron: Asymmetry* **2011**, *22*, 2156.

[6] C. J. R. Bataille, T. J. Donohoe, *Chem. Soc. Rev.* **2011**, *40*, 114.

[7] For selected achievements: a) K. Suzuki, P. D. Oldenburg, L. Que, Jr., *Angew. Chem.* **2008**, *120*, 1913; *Angew. Chem. Int. Ed.* **2008**, *47*, 1887; b) T. W.-S. Chow, E. L.-M. Wong, Z. Guo, Y. Liu, J.-S. Huang, C.-M. Che, *J. Am. Chem. Soc.* **2010**, *132*, 13229.

[8] For reviews of catalytic diboration including asymmetric reactions, see: a) I. Beletskaya, C. Moberg, *Chem. Rev.* **2006**, *106*, 2320; b) H. E. Burks, J. P. Morken, *Chem. Commun.* **2007**, 4717.

[9] For achievements of catalytic diboration: a) R. T. Baker, P. Nguyen, T. B. Marder, S. A. Westcott, *Angew. Chem.* **1995**, *107*, 1451; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1336; b) C. Dai, E. G. Robins, A. J. Scott, W. Clegg, D. S. Yufit, J. A. K. Howard, T. B. Marder, *Chem. Commun.* **1998**, 1983; c) P. Nugyen, R. B. Coapes, A. D. Woodward, N. J. Taylor, J. M. Burke, J. A. K. Howard, T. B. Marder, *J. Organomet. Chem.* **2002**, *652*, 77; d) T. Ishiyama, M. Yamamoto, N. Miyaura, *Chem. Commun.* **1997**, 689; e) C. N. Iverson, M. R. Smith III, *Organometallics* **1997**, *16*,

2757; f) J. Ramírez, R. Corberán, M. Sanaú, E. Peris, E. Fernandez, *Chem. Commun.* **2005**, 3056; g) R. Corberán, J. Ramírez, M. Poyatos, E. Peris, E. Fernández, *Tetrahedron: Asymmetry* **2006**, *17*, 1759; h) V. Lillo, M. R. Fructos, J. Ramírez, A. A. C. Braga, F. Maseras, M. M. Díaz-Requejo, P. J. Pérez, E. Fernández, *Chem. Eur. J.* **2007**, *13*, 2614. For a theoretical approach, see: i) L. Dang, H. Zhao, Z. Lin, T. B. Marder, *Organometallics* **2007**, *26*, 2824; j) L. Dang, H. Zhao, Z. Lin, T. B. Marder, *Organometallics* **2008**, *27*, 1178. For asymmetric induction, see: k) T. B. Marder, N. C. Norman, C. R. Rice, *Tetrahedron Lett.* **1998**, *39*, 155.

[10] a) J. B. Morgan, S. P. Miller, J. P. Morken, *J. Am. Chem. Soc.* **2003**, *125*, 8702; b) S. Trudeau, J. B. Morgan, M. Shrestha, J. P. Morken, *J. Org. Chem.* **2005**, *70*, 9538; c) S. P. Miller, J. B. Morgan, F. J. Nepveux, J. P. Morken, *Org. Lett.* **2004**, *6*, 131.

[11] a) L. T. Kliman, S. N. Mlynarski, J. P. Morken, *J. Am. Chem. Soc.* **2009**, *131*, 13210; for dienes as substrates: b) N. F. Pelz, A. R. Woodward, H. E. Burks, J. D. Sieber, J. P. Morken, *J. Am. Chem. Soc.* **2004**, *126*, 16328; c) H. E. Burks, L. T. Kliman, J. P. Morken, *J. Am. Chem. Soc.* **2009**, *131*, 9134; d) K. Hong, J. P. Morken, *J. Org. Chem.* **2011**, *76*, 9102; e) L. T. Kliman, S. N. Mlynarski, G. E. Ferris, J. P. Morken, *Angew. Chem.* **2012**, *124*, 536; *Angew. Chem. Int. Ed.* **2012**, *51*, 521; f) G. E. Ferris, K. Hong, I. A. Roundtree, J. P. Morken, *J. Am. Chem. Soc.* **2013**, *135*, 2501.

[12] For reviews of catalytic conjugate boration including asymmetric reactions, see: a) V. Lillo, A. Bonet, E. Fernández, *Dalton Trans.* **2009**, 2899; b) L. Dang, Z. Lin, T. B. Marder, *Chem. Commun.* **2009**, 3987; c) J. A. Schiffner, K. Müther, M. Oestreich, *Angew. Chem.* **2010**, *122*, 1214; *Angew. Chem. Int. Ed.* **2010**, *49*, 1194; d) E. Hartmann, D. J. Vyas, M. Oestreich, *Chem. Commun.* **2011**, *47*, 7917; e) A. D. J. Calow, A. Whiting, *Org. Biomol. Chem.* **2012**, *10*, 5485. For other reviews of catalytic boration: f) T. Ohmura, M. Suginome, *Bull. Chem. Soc. Jpn.* **2009**, *82*, 29; g) J. Takaya, N. Iwasawa, *ACS Catal.* **2012**, *2*, 1993.

[13] a) K. Lee, A. R. Zhugralin, A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, *131*, 7253; b) A. Bonet, H. Gulyás, E. Fernández, *Angew. Chem.* **2010**, *122*, 5256; *Angew. Chem. Int. Ed.* **2010**, *49*, 5130; c) C. Pubill-Ulldemolins, A. Bonet, C. Bo, H. Gulyás, E. Fernández, *Chem. Eur. J.* **2012**, *18*, 1121; d) H. Wu, S. Radomkit, J. M. O'Brien, A. H. Hoveyda, *J. Am. Chem. Soc.* **2012**, *134*, 8277.

[14] a) A. Bonet, C. Pubill-Ulldemolins, C. Bo, H. Gulyás, E. Fernández, *Angew. Chem.* **2011**, *123*, 7296; *Angew. Chem. Int. Ed.* **2011**, *50*, 7158; b) A. Bonet, C. Sole, H. Gulyás, E. Fernández, *Org. Biomol. Chem.* **2012**, *10*, 6621.

[15] a) T. Shiomi, T. Adachi, K. Toribatake, L. Zhou, H. Nishiyama, *Chem. Commun.* **2009**, 5987; b) K. Toribatake, L. Zhou, A. Tsuruta, H. Nishiyama, *Tetrahedron* **2013**, *69*, 3551. For preparation of [Rh(Phebox)] catalysts, see: c) Y. Kanazawa, Y. Tsuchiya, K. Kobayashi, T. Shiomi, J. Itoh, M. Kikuchi, Y. Yamamoto, H. Nishiyama, *Chem. Eur. J.* **2006**, *12*, 63; d) J. Ito, T. Shiomi, H. Nishiyama, *Adv. Synth. Catal.* **2006**, *348*, 1235. For reviews on applications of [Rh(Phebox)] catalysts, see: e) H. Nishiyama, J. Ito, *Chem. Commun.* **2010**, *46*, 203; f) J. Ito, H. Nishiyama, *Synlett* **2012**, 509.

[16] C. Pubill-Ulldemolins, M. Poyatos, C. Bo, E. Fernández, *Dalton Trans.* **2013**, *42*, 746. Rh/NHC-catalyzed diboration and theoretical explanation.

[17] T. Shimada, K. Mukaide, A. Shinohara, J. W. Han, T. Hayashi, *J. Am. Chem. Soc.* **2002**, *124*, 1584.

