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Unexpected influence and its origin in rationally tuning the electronic effect of catalysts in the asymmetric borane reduction of ketones

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Abstract

Rationally tuning the electronic effect of catalysts is one of the most important strategies to improve stereoselectivity in asymmetric catalysis. (*S*)-2-aryl-3,1,2-oxazaborobicyclo[3.3.0]octanes, which can be considered as electronically tuned (*S*)-2-phenyl-3,1,2-oxazaborobicyclo[3.3.0]octane, were prepared and evaluated in the asymmetric borane reduction of ketones. An unexpected influence of the electronic effect of catalysts on the enantioselectivity was observed and attributed to the catalyst dimerization that was further confirmed experimentally. The unsuccessful tuning is accounted for by assuming that hydride transfer in the catalytic cycle is the rate-determining step in the reduction catalyzed by *B*-aryl catalysts.

Keywords: Asymmetric reduction; Borane; Electronic effect; Enantioselectivity; Ketone

1. Introduction

Factors governing the enantioselectivity of asymmetric catalysis have always been one of the crucial concentrations in organic chemistry. The asymmetric induction with enantiopure catalysts has been recognized to depend mainly on steric repulsion between the catalyst backbones (including substituents) and substrates [1]. However, more and more examples have been observed of the enantioselectivity being also dependent on the electronic effect of substrates, even with very similar structural features, for the same catalysts in asymmetric catalysis [2]. To understand and to solve this problem, alternatively, a strategy of "the electronic control" or "the electronic tuning" via variation of the electronic character of catalysts to optimize the stereoselectivity has been attempted and investigated in the last two decades [3]. Although prominent electronic-character-dependence of catalysts on the stereoselectivity was observed in some cases [4,5], the underlying reasons still remain obscure in most cases [6].

The catalytic enantioselective borane reduction of ketones catalyzed by the enantiopure oxazaborolidines shows not only a very broad range of practical applications [7], but also the insights into mechanistic details [8] and numerous factors affecting the enantioselectivity, such as the dimerization of catalysts [8a,9], the temperature [9b,10], the solvent [8a,9a,10], the borane source[11], and the electronic effects of ketones [12] and catalysts [13]. This would facilitate our investigation into the rational tuning of the electronic effect of catalysts in the asymmetric catalysis. Previously, almost all of examples on the electronic tuning of catalysts focused on the chiral ligand–metal complex-catalyzed asymmetric catalyses [3–5]. To the best of our knowledge, only a few examples on the electronic tuning of organocatalysts have been reported [5a,b,12b,13]. Although a few papers have considered the influence of the electronic effect of catalysts on the enantioselectivity in the asymmetric borane reduction of ketones, it is indicated that no obvious influence has been observed because most of the reported catalysts show very high enantioselectivities. All enantioselectivities are more than 95% e.e. so that no enough observation scope remains [5a,13]. Herein, we wish to present our results on the rational electronic

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tuning of catalysts in the oxazaborolidine-catalyzed asymmetric borane reduction of ketones.

2. Experimental

2.1. General methods

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 (300 MHz) spectrometer in $CDCl_3$ solution with TMS as an internal standard and ^{19}F NMR spectra were obtained on the same spectrometer in toluene solution with CF_3CO_2H as an external standard. HPLC analyses were performed on an HP1100 HPLC equipment. Arylboronic acids and borane-dimethyl sulfide complex were purchased from Acros Chemicals Co. Toluene and THF were heated under reflux over sodium benzophenone ketyl and distilled prior to use.

2.2. General procedure for the asymmetric reduction of ketones with catalysts 2

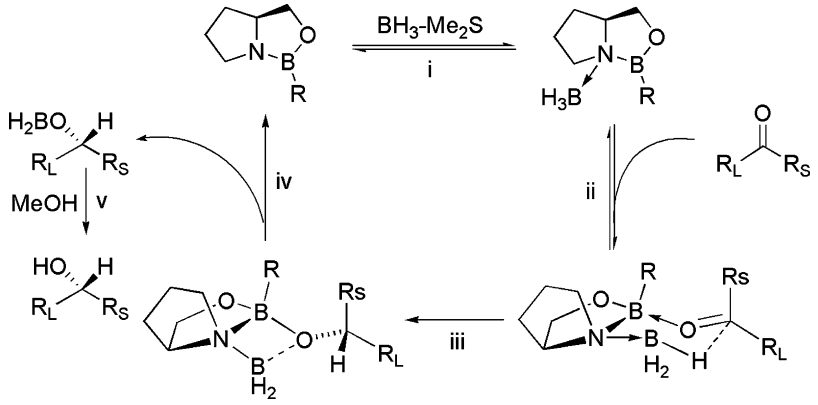
A 25 mL round-bottomed flask equipped with a stirring bar and a 10 mL pressure-equalizing addition funnel (containing a cotton plug and ca. 10 g of 5 A molecular sieves, and functioning as a Soxhlet extractor). A mixture of (*S*)-prolinol (0.05 mmol, 5.1 mg) and arylboronic acid (0.05 mmol) was dissolved in dry toluene (15 mL). The resulting solution was heated to reflux for 12 h. After most of the solvent was distilled off, the residue (ca. 3 mL) was cooled to room temperature (all solvent was removed for reductions in THF and dry THF (3 mL) was added). The addition funnel was removed and the flask was airproofed quickly to avoid moisture. The catalyst **2** was used directly without further purification.

To a solution of the freshly prepared catalyst **2** (0.05 mmol, 10 mol%) was added 2 mol/L borane-dimethyl sulfide complex in THF (0.25 mL, 0.5 mmol) under a nitrogen atmosphere at room temperature. The resulting solution was tuned to the desired temperature and stirred for 15 min. A solution of ketone **6** (0.5 mmol) in 4 mL of the desired solvent was then added dropwise over 1 h. After the addition, the resulting solution was stirred for 4 h and quenched with 0.5 mL of methanol in an ice bath. After concentration under reduced pressure, the residue was purified on a silica gel column with a mixture of petroleum ether (60–90 °C) and ethyl acetate (5:1, v/v) as an eluent to give chiral secondary alcohol as a colorless oil. The e.e. values were determined by chiral HPLC analysis.

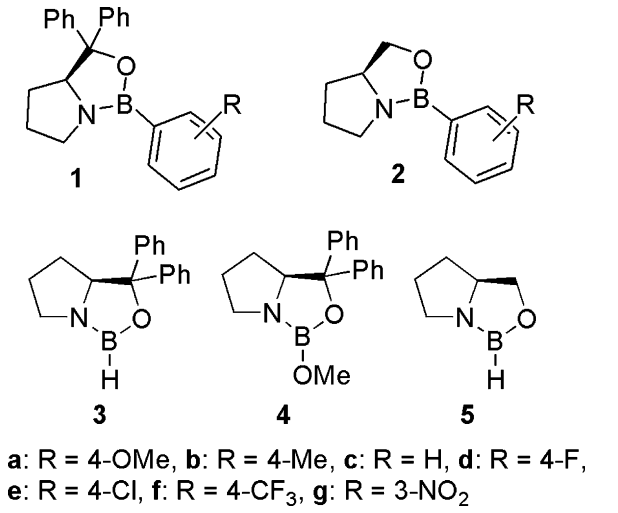
3. Results and discussion

It is generally accepted that the asymmetric borane reduction involves four key steps (Scheme 1) [8]: (1) coordination of borane to a catalyst, (2) complexation of a ketone to the endocyclic boron in the catalyst via the Lewis acid–base interaction, (3) hydride transfer to the carbonyl carbon of the ketone and (4) dissociation of an alkoxyborane moiety and regeneration of the catalyst. Some experimental and calculational results indicate that the rate-limiting step might be either the ketone–catalyst complexation or the hydride transfer step in the catalytic cycle [8c,12b,14]. In either case, especially for the first case, electron-deficient oxazaborolidines were assumed to accelerate the rate-limiting step. Moreover, we found that the non-catalytic reduction should take main responsibility for the generation of the racemic products [10]. Thus, we presumed that electron-deficient catalysts would show higher enantioselectivity than electron-rich ones, especially for electron-deficient ketones, because electron-deficient catalysts would favor the complexation with a ketone. It was partly proved in our previous experimental results although the enantioselectivity was not markedly different (10% e.e. was improved from catalysts **1a** to **1e** for 4-nitroacetophenone) [12b].

According to our previous results, electron-deficient substituted ketones show lower enantioselectivity than electron-rich ones under the catalysis of catalysts **3** and **4** (Scheme 2) [12b]. Recently we started a project on tuning the electronic effect of catalysts rationally to improve the enantioselectivity in the asymmetric catalysis. To tune the electronic effect of catalysts effectively, we used the *B*-aryl catalysts **1**, which can be considered as the electronically tuned *B*-phenyl catalyst **1c**. Although in previous explanation [5a,13], no obvious influence of the electronic effect of catalysts on the enantioselectivity was observed, we thought that only little extent of the e.e. value variation will remain because very high enantioselectivities were obtained with catalysts **1**.



Scheme 1. General accepted mechanism for the oxazoborolidine-catalyzed asymmetric reduction of ketones.



Scheme 2. Structures of the oxazoborolidine catalysts.

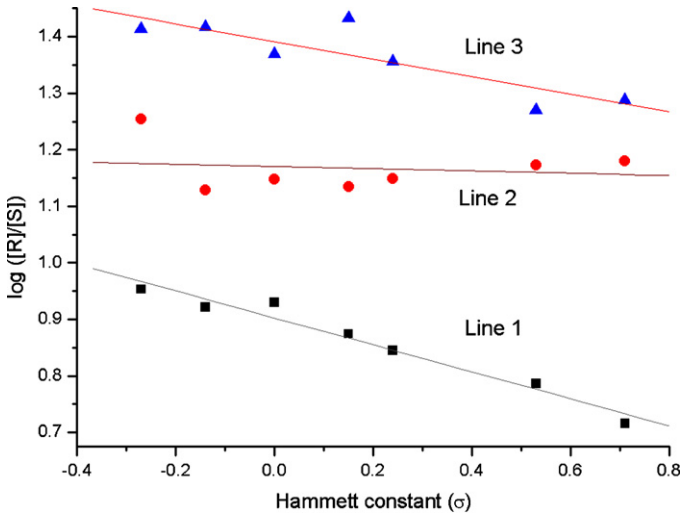


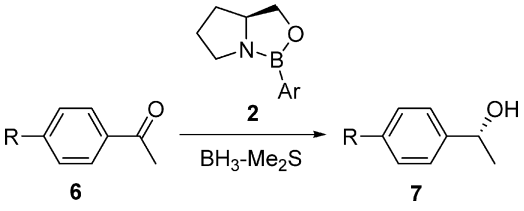
Fig. 1. Hammett plots of the asymmetric borane reduction of *p*-nitroacetophenone (**6g**) with catalysts **2**. Line 1, 30 °C in toluene; line 2, 110 °C in toluene; line 3, 60 °C in THF.

To give an enough extent of the e.e. value variation to observe an obvious influence, herein, we choose less efficient catalysts (*S*)-2-aryl-3,1,2-oxazaborobicyclo[3.3.0]octanes **2** (Scheme 2), which can be considered as electronically tuned (*S*)-2-phenyl-3,1,2-oxazaborobicyclo[3.3.0]octane **2c** via substitution for its phenyl group, to investigate the change of the enantioselectivity caused by variation in the electronic nature of the catalysts. With similar consideration, we selected *p*-nitroacetophenone (**6g**) as a substrate because electron-deficient ketones exhibited less enantioselectivity than electron-rich ones in our previous work [12b].

Initially, the catalysts **2a–g** were prepared and *in situ* evaluated in the asymmetric reduction of *p*-nitroacetophenone (**6g**) in toluene at 30 °C, optimal conditions in our previous studies [10]. We indeed observed an obvious influence of the electronic effect of catalysts on the enantioselectivity (Table 1, entries 1–7, columns 4 and 5). However, this is an unexpected influence. That is, electron-deficient catalysts show lower enantioselectivities than electron-rich ones. The data fit very good linearity ($R^2 = 0.96$) in the Hammett analysis [$\log([R]/[S]) = \rho\sigma + c$] with $\rho = -0.24$ and $c = 0.90$ (Fig. 1, line 1) [15].

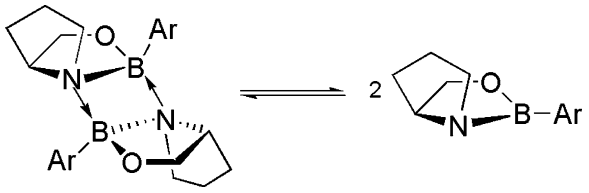
The negative slope of the Hammett plot (Fig. 1, line 1) invalidates our earlier assumption. It seems that some other factors determine the stereoselectivity instead of the rate of

Table 1
Asymmetric borane reduction of ketones catalyzed by different oxazaborolidine catalysts **2**



Entry	Catalyst (Ar)	Ketone (*R*)	30 °C in toluene		110 °C in toluene		60 °C in THF	
			Yield (%)[a]	e.e. (%)[b]	Yield (%)[a]	e.e. (%)[b]	Yield (%)[a]	e.e. (%)[b]
1	**2a** (4-MeOPh)	**6g** (O_2N)	87	80.0	87	89.5	87	92.5
2	**2b** (4-MePh)	**6g** (O_2N)	89	78.6	89	86.2	87	92.6
3	**2c** (H)	**6g** (O_2N)	93	78.9	84	86.7	99	90.8
4	**2d** (4-FPh)	**6g** (O_2N)	84	76.4	89	86.3	99	92.9
5	**2e** (4-ClPh)	**6g** (O_2N)	91	75.0	87	86.8	90	91.6
6	**2f** (4-CF_3Ph)	**6g** (O_2N)	89	71.9	98	87.4	93	89.8
7	**2g** (3-O_2NPh)	**6g** (O_2N)	93	67.7	93	87.6	88	90.2
8	**2a** (4-MeOPh)	**6b** (Me)	80	75.7[c]				
9	**2g** (3-O_2NPh)	**6b** (Me)	79	56.4[c]				
10	**2a** (4-MeOPh)	**6a** (MeO)	95	66.5[c]				
11	**2g** (3-O_2NPh)	**6a** (MeO)	95	52.9[c]				

[a] Isolated yields after the column chromatography.
[b] Determined by HPLC analysis, using AS chiral column (4.6 × 250 mm, Chiralpak) and a mixture of *n*-hexane and 2-propanol (90:10, v/v) as an eluent at a flow rate of 0.8 mL/min at monitoring wave 228 nm. Configuration was assigned as *R* by comparison of retention times (Refs. [4a,10b]).
[c] OB chiral column (4.6 mm × 250 mm Chiralcel) and *n*-hexane:2-propanol 95:5 (v/v) at a flow rate of 1.0 mL/min at 220 nm.



Scheme 3. Equilibrium between the monomers and dimers of the oxazaborolidine catalysts **2**.

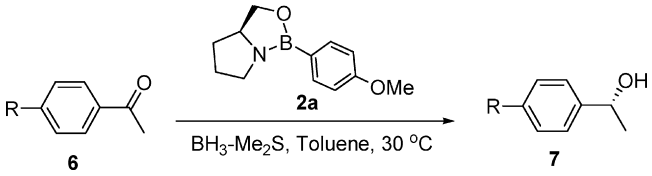
the catalyst–substrate complexation or hydride transfer. We previously found that the dimerization of *B*-unsubstituted (*S*)-3,1,2-oxazaborobicyclo[3.3.0]octane **5** decreases the enantioselectivity with decreasing reduction temperature [9b]. The electron-deficient catalysts should favor dimerization than their electron-rich counterparts (Scheme 3) since the electron-withdrawing substituents increase the Lewis acidity of the boron atom so that the tendency for the boron atom to coordinate with the nitrogen atom in another catalyst molecule increases. Thus, we presumed that the dimerization of catalysts might be the main factor influencing the enantioselectivities because the dimerization reduces efficient catalyst loading, increasing non-catalytic reduction to give rise more racemic alcohol products. If the variation in the extent of dimerization preponderates over those of catalyst–ketone complexation and hydride transfer, the rate of the catalytic reaction will vary with the extent of dimerization. In this way, the e.e. value will decrease with the decreasing ratio of catalytic reaction. The dissociation of the dimers may retard the catalytic reaction rate, affecting the enantioselectivity.

The above hypothesis was confirmed experimentally via determination of ^{19}F NMR spectra of catalyst **2d** at different temperatures in toluene. Its monomer indeed increases with increasing temperature (the monomer (at 41.1 ppm):dimer (at 37.6 ppm) ratio varies from 0.49:1.00 at 20 °C, 0.80:1.00 at 30 °C, 1.01:1.00 at 50 °C to 1.53:1.00 at 70 °C).

To inhibit the dimerization and to observe the original influence of the electronic effect of catalysts on the enantioselectivity, the same series of reactions were conducted in toluene at 110 °C (Table 1, entries 1–7, columns 6 and 7) and in THF at 60 °C (Table 1, entries 1–7, columns 8 and 9), respectively, because both high temperature [9b] and coordinative solvents can inhibit the dimerization. The results indicate that the enantiomeric excess values increased from 67–80% in toluene at 30 °C to 86–90% in toluene at 110 °C to 90–93% in THF at 60 °C. However, it should be noted that still no prominent and expected influence of the electronic effect of catalysts on the enantioselectivity was observed (Fig. 1, lines 2 and 3).

In the asymmetric reduction system, the catalyst dimerization could also be inhibited partially if the ketone possesses strong coordinative ability. Thus, two electron-rich ketones, *p*-methoxyacetophenone (**6a**) and *p*-methylacetophenone (**6b**), were reduced under the catalysis of two representative catalysts **2a** and **2g**. The results surprised us again. Rather than the expected higher e.e. values, lower e.e. values were obtained in comparison with *p*-nitroacetophenone (**6g**) (Table 1, entries 8–11). Although our previous investigation indicates that the coordination step in the catalytic cycle is the enantioselective

Table 2
Asymmetric borane reductions of substituted acetophenones **6** catalyzed by (*S*)-2-(4-methoxyphenyl)-3,1,2-oxazaborobicyclo[3.3.0]octane (**2a**)



Entry	Ketone	*R*	Yield[a] (%)	e.e.[b] (%)
1	**6a**	MeO	95	66.5
2	**6b**	Me	93	75.7
3	**6c**	H	92	75.9[c]
4	**6d**	F	76	77.8[d]
5	**6e**	Cl	96	78.5
6	**6f**	Br	74	77.8
7	**6g**	NO_2	76	80.0

[a] Isolated yields after the column chromatography.
[b] Determined by HPLC analysis, using OB chiral column (4.6 mm × 250 mm, Chiralcel) and a mixture of *n*-hexane and 2-propanol (95:5, v/v) as an eluent at an flow rate of 1.0 mL/min at monitoring wave 220 nm. Configuration was assigned as *R* by comparison of retention times (Refs. [4a,10b]).
[c] *n*-Hexane:2-propanol 90:10 (v/v).
[d] *n*-Hexane:2-propanol 98:2 (v/v).

and rate-determining step for reactions catalyzed by catalysts **3** and **4** (Scheme 2) [12b]. The current results seems to indicate that the coordination step is not the rate-determining step and the hydride transfer is in the reduction catalyzed by catalysts **2**.

To identify the rate-determining step in the catalytic cycle in the reduction catalyzed by catalysts **2**, we investigated the influence of the substrate electronic effect on the enantioselectivity in the reaction system through a series of *para*-substituted acetophenones **6a–g** as substrates and (*S*)-2-(4-methoxyphenyl)-3,1,2-oxazaborobicyclo[3.3.0]octane (**2a**) as the catalyst. The catalyst **2a** is the most unfavorable catalyst to form the complexes with ketones. If it still shows the hydride transfer as the rate-determining step, all of catalysts **2** should show the hydride transfer as the rate-determining step. The results are summarized in Table 2. When the substituent of acetophenone changed from nitro- to methoxy-group, the e.e. value dropped from 80% to 67%. The Hammett plot showed a positive slope of 0.10 with the correlation coefficient $R^2 = 0.89$ (Fig. 2) since the electron-donating substituents on ketones do not favor the hydride transfer. The ketone **3a** is excluded from the Hammett analysis because the competitive coordination of methoxy-group leads to extra racemic products as our previous report [16]. The results indeed reveal that the hydride transfer is the rate-determining step under the catalysis of catalysts **2**. This is the reason why no obvious influence of the electronic effect of catalysts on the enantioselectivity was observed. The unsuccessful rational tuning is accounted for by assuming that hydride transfer is actually the rate-determining step in the investigated reduction while the tuning is based on the assumption that the ketone–catalyst complexation is the rate-determining step. This also indicates that *B*-aryl-substituted oxazaborolidines are more electron-deficient than *B*-unsubstituted, *B*-alkyl, and *B*-methoxy ones. Therefore, the complexation step accelerates and

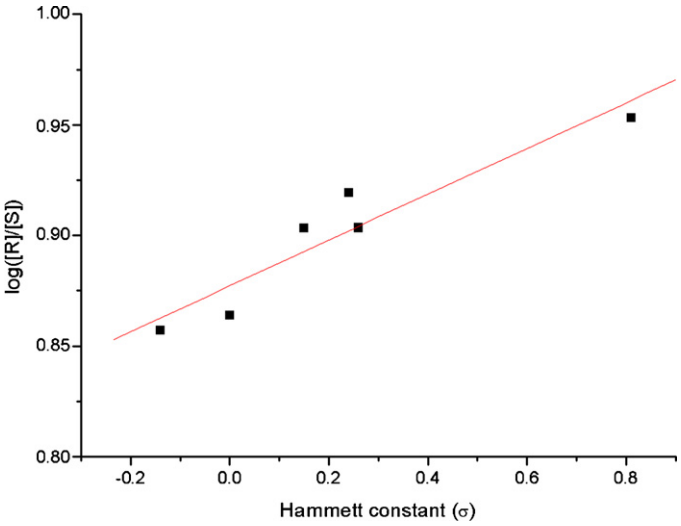


Fig. 2. Hammett plot of the catalyst **2a**-catalyzed borane reduction of *para*-substituted acetophenone.

the hydride transfer becomes the rate-limiting step under their catalysis.

Additionally, the kinetic isotope effect in the hydride transfer was measured previously by Corey et al. [14]. The low k_H/k_D ratio (1.7) indicates an early transition state for the highly exothermic hydride transfer [14a]. The similarity between the substrate–catalyst complex and the transition state of hydride transfer weakens the influence of the electronic effect of catalysts. This is in great accordance with the low slope (+0.10) of the Hammett plot in Fig. 2 (compared with −1.82 and −1.66 obtained with catalysts **3** and **4**, respectively [12b]). In a similar manner, the variation of the electronic nature of catalysts slightly affects the enantioselectivity.

With the experimental results so far, we can now depict a sketch of factors affecting the enantioselectivity in the asymmetric reduction of ketones catalyzed by enantiopure oxazaborolidines with different electronic natures. Rates of substrate–catalyst complexation and hydride transfer, together with the dimerization of catalysts, affect the enantioselectivity. In different reaction systems, the influence of each of factors varies and the dominant factor may change.

4. Conclusions

In summary, for rationally tuning the electronic effect of catalysts to improve their stereoselectivity in asymmetric catalysis, (*S*)-2-aryl-3,1,2-oxazaborobicyclo[3.3.0]octanes, which can be considered as electronically tuned (*S*)-2-phenyl-3,1,2-oxazaborobicyclo[3.3.0]octane, were prepared and evaluated in the asymmetric borane reduction of ketones. However, an unexpected influence was observed and attributed to the dimerization of the catalysts. The influence was weakened via raising reduction temperature and using coordinative solvent. The unsuccessful rational tuning is attributable to the fact that the hydride transfer step in the catalytic cycle is the rate-determining step in the asymmetric reduction catalyzed by (*S*)-2-aryl-3,1,2-oxazaborobicyclo[3.3.0]octanes, while the tuning is based on the assumption that the complexation of the catalyst and the substrate is the rate-determining step. We hope that the present study has addressed an important issue: although the rational regulation of the electronic effect of catalysts is one of important strategies to improve stereoselectivity in asymmetric catalysis, the electronic effect of catalysts is a complicated factor influencing the enantioselectivity in a different manner. The influence is affected by interactions between the catalyst and the substrate, the catalyst and solvent, even the catalyst itself, and the rate-determining step as well.

Acknowledgments

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