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Synergistic effect of achiral quaternary ammonium salt on asymmetric additions of diethylzinc to aldehydes

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Introduction

The demand of using asymmetric catalysis in the production of chiral compounds has been driving the development of excellent chiral catalytic systems to be the focus of intensive research in asymmetric chemistry.¹ Enantioselective catalytic transformations which involve carbon-carbon bond formation are probably one of the most attractive asymmetric reactions. Concerning this subject, the asymmetric additions of organometallic reagents, particularly organozinc reagent, to carbonyl groups have been extensively studied.² Various chiral catalysts have been developed which lead to alcohol products with excellent enantiomeric excesses in high vields for the asymmetric additions of organozinc reagents to aldehydes and ketones.³ Although chiral catalyst is the key factor for an efficient asymmetric reaction, additive is also important for the catalytic turnover and enantioselectivity. Many achiral additives, such as metal Lewis acids⁴ (Al, Ti, Cu, Ba etc.), polyethers⁵ (D*i*MPEG etc.), alcohols⁶ (MeOH, *i*PrOH etc.), borate ester,⁷ phosphine amine,⁸ and phosphine oxides⁹ etc. have also been reported to improve the reactivity and enantioselectivity of asymmetric additions of organozinc to carbonyl groups. However, for most of these developed chiral catalytic systems, high loading amounts of chiral catalysts over 1 mol %, normally in the range of 10-20 mol %, are required to achieve synthetically useful results. Highly efficient catalytic systems for the asymmetric additions of organozinc with carbonyl groups giving excellent yields and enantioselectivities of addition products with very low chiral catalyst loadings

ABSTRACT

Our investigation has shown that achiral quaternary ammonium salt has a significant synergistic effect on the asymmetric additions of diethylzinc to aldehydes catalyzed by chiral phosphoramide–Zn(II) complex. The addition of 10 mol % NBu₄X can dramatically reduce the loading amount of chiral ligand without sacrificing the excellent reactivity and enantioselectivity of the asymmetric reaction.

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(<1 mol %) are still rare.¹⁰ Thus, in terms of catalyst loading, significant progress is still desirable.

Successful examples have been reported using quaternary ammonium salts as stoichiometric or catalytic additives in asymmetric reactions which involve Pd, Ru, Ir etc.¹¹ but no report of using an achiral quaternary ammonium salt as an additive in the asymmetric addition of organozinc to a carbonyl group has been found despite the fact that it has been used to promote the non-asymmetric addition of organozinc to aldehyde.¹² We have been interested in investigating the effects of achiral quaternary ammonium salts on the addition reactions of carbonyl compounds.¹³ Herein, we report a highly efficient catalytic system for the asymmetric additions of dialkylzinc to aldehydes using an achiral quaternary ammonium salt and a chiral phosphoramide as cocatalysts. The significant synergistic effect of achiral guaternary ammonium salt and chiral phosphoramide results in the dramatic decrease of the loading amount of the chiral catalyst needed for the asymmetric reaction to achieve high efficiency.

Results and discussion

In our previous study, we developed a new chiral 1,2-amino phosphoramide **L1** derived from (1R,2R)-1,2-cyclohexyl diamine (Scheme 1), which catalyzed the asymmetric addition of diethylzinc to benzylaldehyde to afford 99% yield and 94% ee value of addition product **2a**, but at least 10 mol % of **L1** was needed for the reaction to achieve such high efficiency.¹⁴

Reducing the chiral catalyst loading amount dramatically decreased both the yield and ee value of **2a**. However, we have found that this chiral phosphoramide catalyzed asymmetric reaction can be benefited by adding achiral quaternary ammonium salts. As can





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Scheme 1. The chiral ligand L1 derived from (1R,2R)-1,2-cyclohexyl diamine.

Table 1

The effects of NBu₄Br on the asymmetric additions of diethylzinc to benzylaldehydes^a

0	L1 (x mol%) Bu ₄ NBr (10 mol%)	ŌН
Ph + Et ₂ Z 1a 2.0 eq 1.0 equiv	n uiv hexane: toluene = 1:1 0 °C ~ r.t., 6 h	Ph 2a

Entry	<i>x</i> (mol %)	With Bu ₄ NBr (without)	
		Yield ^b (%)	ee ^c (%)
1	10	99 (99)	96 (94)
2	5.0	98 (81)	95 (92)
3	3.0	98 (65)	95 (72)
4	1.0	96 (52)	94 (58)
5	0.5	95 (32)	93 (38)
6	0.3	92 (27)	93 (34)
7	0.1	84, 90 ^d (18)	90, 92 ^d (30)
8	0.05	40 (16)	76 (11)

^a The reactions were carried out at 1.0 mmol scales and repeated three times for each.

^b Isolated yields.

^c Determined by chiral GC analysis.

^d Reaction time is 24 h.

be seen from viewing the data in Table 1, the synergistic effect of Bu₄NBr on this asymmetric reaction increases significantly with the decrease of the loading amount of L1. In the presence of 10 mol % L1, the ee value of 2a was improved slightly from 94% without Bu₄NBr to 96% with Bu₄NBr (Table 1, entry 1). However, compared with only 32% yield and 38% ee value of 2a obtained in the presence of 0.5 mol % L1 alone, the yield and ee value of 2a were dramatically enhanced to 95% and 93%, respectively, using 10 mol % Bu₄NBr as an additive (Table 1, entry 5), which is comparable with the use of 10 mol % L1 in reaction. Further decreasing the loading amount of L1 to 0.1 mol % still gave us 87% yield and 90% ee value of 2a for 6 h and 90% yield and 92% ee value of 2a for 24 h when 10 mol % NBu₄Br was present, while 0.1 mol % L1 used alone only afforded 18% yield and 30% ee value of 2a (Table 1, entry 7). Even for only 0.05 mol % of L1 used in the asymmetric reaction, the synergistic effect of Bu₄NBr was still significant enough as shown in Table 1, entry 8.

Encouraged by our initial study, we next evaluated the effectiveness of various achiral quaternary ammonium salts on the asymmetric addition of diethylzinc to benzylaldehyde catalyzed by 1.0 mol % L1 (Table 2). As shown in Table 2, entries 2-6, the alkyl chain length plays an important role for the effect of a tetraalkylammonium salt. (CH₃)₄NCl containing the shortest alkyl chain has the least effect for the asymmetric addition. The less solubility in hydrocarbon solvent, which results in a dilute solution of chloride anions, and the less steric hindrance of the short alkyl chain of (CH₃)₄NCl might be the reasons for (CH₃)₄NCl to give only 86% vield and 87% ee value of 2a. However, tetraalkylammonium salts with a medium alkyl chain length, such as Et₄NCl, Et₃NBnCl, and Bu₄NCl gave excellent yields and enantioselectivities of 2a and Bu₄NCl is the best one among them. In contrast, the bulky long aliphatic carbon chain of C₁₈H₃₇N(CH₃)₃Cl slowed down the addition reaction providing 2a with 77% yield only. No significant differences in product yields and enantioselectivities were observed in the presence of tetraalkylammonium salts with different halide ions (Table 2, entries 6–9), but the reaction with Bu₄NBr gave a

Table 2

Effects of different achiral quaternary ammonium salts on the asymmetric catalytic addition of ethylzinc to benzylaldehyde^a

	L1 (1.0 mol%) Additive (y mol%)	ŌН
Ph ² `H ⁺ Et ₂ 2n ⁻ 1a 2.0 equiv	hexane: toluene = 1:1 0 °C ~ r.t., 6 h	Ph 2a

Entry	Additive	y (mol %)	Yield ^b (%)	ee ^c (%)
1	None	None	52	58
2	N(CH ₃) ₄ Cl	10	86	87
3	C18H37N(CH3)3Cl	10	77	92
4	NEt ₄ Cl	10	96	92
5	NEt ₃ BnCl	10	96	90
6	NBu ₄ Cl	10	97	92
7	NBu ₄ Br	10	96	94
8	NBu ₄ I	10	95	94
9	NBu ₄ ClO ₄	10	62	89
10	Bu ₄ PBr	10	93	92
11	ZnCl ₂	10	62	<1
12	MgBr ₂	10	23	28
13	NBu ₄ Br	5	87	94
14	NBu ₄ Br	20	97	88
15	NBu ₄ Br	30	92	76
16	NBu ₄ Br	50	88	59
17	NBu ₄ Br	70	84	47
18	NBu ₄ Br	100	78	16

 $^{\rm a}\,$ The reactions were carried out at 1.0 mmol scales and repeated three times. $^{\rm b}\,$ Isolated yields.

^c Determined by chiral GC analysis.

slightly higher yield and ee value. In contrast, 2a was obtained in dramatically lower yield along with decreased enantioselectivity when perchlorate anion was the counter anion (Table 2, entry 9). Interestingly, phosphonium salt also shows the similar positive effect as ammonium salt. Using Bu₄PBr as the additive gave 2a with 93% yield and 92% ee values (Table 2, entry 10). It is noteworthy that using a metal Lewis acid as the additive has negative effect for the asymmetric addition reaction. The addition of 10 mol % ZnCl₂ or MgBr₂ dramatically decreased the ee value of the desired product 2a with only low to medium vield (Table 2, entries 11 and 12). Further investigation of the loading amount of Bu₄NBr in the reaction showed that changing the amount of Bu₄NBr from 10 mol % to 5 mol % decreased the yield of 2a from 96% to 87% but still gave excellent enantioselectivity of 94% (Table 2, entry 13). Owing to the background reaction caused by Bu₄NBr,¹² increasing the amount of Bu₄NBr resulted in the decrease of the activity and enantioselectivity of the asymmetric addition reaction (Table 2, entries 14–18).

Because halide effect in metal catalyzed reactions has been well recognized by the coordination of halide anion to metal,^{13b,15} we proposed a plausible transition state for NBu₄X/chiral L1 co-catalyzed asymmetric addition reaction on the basis of Ishihara's conjugate Lewis acid-Lewis base double activated transition state mode¹⁶ (Scheme 2). Without NBu₄X, the asymmetric reaction is catalyzed by chiral L1-zinc(II) complex via transition state A. The chiral L1-zinc(II) complex serves as a Lewis acid while concomitantly increasing the nucleophilicity of diethylzinc by P=O moiety of L1 and *Re*-face attack leading to (*R*)-product should be highly preferred without steric repulsion between the *i*-Pr group of chiral metallic complex and the R group of aldehyde.¹⁶ In the presence of NBu₄X, halide anion can coordinate with diethylzinc to form complex.^{12b,17} Therefore, the nucleophilicity of diethylzinc is increased by not only P=O moiety of L1, but also the coordinated halide anion. Thus, transition states **B** and **C** are possible. As shown in Table 2, entries 5-7, the differences in product yields and enantioselectivities with different halide anions (Cl, Br and I) are slight. Furthermore, the differences in product enantioselectivities are also not obvious between perchlorate anion and halide anions, but the dif-



Scheme 2. The proposed transition states for NBu₄X/chiral L1 co-catalyzed asymmetric addition of diethylzinc to aldehyde.

Table 3 Enantioselective addition of diethylzinc to aldehydes employing L1 and ${\rm Bu}_4{\rm NBr}$

0	Et 7 2	L1 (0.5 mol%) Bu ₄ NBr (10 mol%)	ŌH
R H 1.0 equiv 1a-j	2.0 equiv	hexane: toluene = 1:1 0 °C ~ r.t., 6 h	R

Entry	Product, R = With Bu ₄ NBr (with		Br (without)	
			Yield ^a (%)	ee ^b (%)
1	Ph	2a	95 (32)	93 (38)
2	4-MeO-C ₆ H ₄	2b	89 (29)	91 (77)
3	4-Cl-C ₆ H ₄	2c	98 (25)	91 (60)
4	$4-CF_3-C_6H_4$	2d	99 (19)	90 (9)
5	2-Me-C ₆ H ₄	2e	99 (31)	96 (77)
6	2- MeO-C ₆ H ₄	2f	99 (55)	93 (81)
7	1-Naph	2g	94 (10)	90 (21)
8	2-Naph	2h	94 (23)	89 (67)
9	2-Thienyl	2i	98 (23)	93 (55)
10	Cyclohexyl	2j	79 (31)	94 (89)

^a Isolated yields.

^b Determined by chiral GC analysis.

ferences in product yields are significant (Table 2, entries 5–8). These results indicate that the halide anion (Cl, Br and I) coordinated to diethylzinc does not further bridge the chiral zinc center to cause the change of the Zn(II) coordination environment in the chiral L1-zinc(II) complex. Therefore, the addition of NBu₄X can improve the catalytic turnover by enhancing the ethyl group transfer from diethylzinc to aldehyde, but has little influence on the enantioselectivity of alcohol product, which should be determined only by the chiral ligand L1. Thus, the transition state **B** is excluded and the transition state **C** is preferred. Additional evidence for the role of halide anion in the asymmetric reaction can be given by the fact that the synergistic effect of achiral quaternary ammonium salt is weak with high loading amount of chiral L1, but is improved dramatically by lowering the catalyst loading amount (Table 1).

The general applicability of this catalytic system, probed by utilizing a variety of aldehydes was demonstrated by the data displayed in Table 3. Thus, by using 10 mol % NBu₄Br and 0.5 mol % L1 as co-catalysts, asymmetric addition of diethylzinc to diverse aldehydes (aryl or alkyl, electron withdrawing or donating group substituted, and steric hindered) occurred in excellent yields and ee values. In contrast, the reactions carried out in the absence of Bu₄NBr had only normally poor to moderate efficiencies for both yields and ee values. Particularly, for aromatic aldehyde **1d** containing an electron-withdrawing group CF₃ at 4-position of the aromatic ring, the synergistic effect of Bu₄NBr was very obvious. In the absence of Bu₄NBr, very poor yield and ee value of **2d** were obtained, but the yield and enantioselectivity of this process jumped to 99% and 90%, respectively, when Bu₄NBr was present (Table 3, entry 3).

Conclusion

We have demonstrated that the significant synergistic effect of achiral quaternary ammonium salt on chiral phosphoramide catalyzed asymmetric additions of diethylzinc to aldehydes. Various achiral quaternary ammonium salts are effective, but Bu₄NBr is the best. In the presence of 10 mol % Bu₄NBr, only 0.5 mol % chiral phosphoramide is enough for the asymmetric reaction to achieve the same high efficiency as 10 mol % chiral phosphoramide used alone.

Experimental

General procedure for enantioselective additions of diethylzinc to aldehydes

Method A (without additive)

$$\begin{array}{c} O \\ R \\ H \\ 1.0 \text{ equiv} \end{array} + \begin{array}{c} \text{Et}_2 \text{Zn} \\ 2.0 \text{ equiv} \\ 0 \text{ °C} \\ \hline \end{array} + \begin{array}{c} \text{L1 (10 mol\%)} \\ 0 \text{ equiv} \\ 0 \text{ °C} \\ \hline \end{array} \\ \begin{array}{c} O \\ \text{r.t.} \\ 0 \text{ fm} \end{array}$$

To a solution of chiral ligand **L1** (35.6 mg, 0.10 mmol, 10 mol %) in dry toluene (2.0 mL), Et₂Zn (1.0 M in hexane, 2.0 mL, 2.0 mmol, 2.0 equiv) was added dropwise at 0 °C via a syringe under nitrogen atmosphere. After being stirred for 30 min, aldehyde (**1a**, 106 mg, 101.4 μ L, 1.0 mmol) was added dropwise to the solution at 0 °C via a syringe. The mixture was stirred for 6 h at room temperature and quenched by addition of aqueous HCl (1.0 M, 5 mL). Extraction with EtOAc (10 mL × 3) gave combined organic layers that were washed with brine (10 mL), dried over MgSO₄, and concentrated in vacuo to give a residue that was subjected to silica gel column chromatography (EtOAc/hexane = 1/10), which afforded the corresponding enantio-enriched secondary alcohol (**2a**) as a colorless oil. The ee value of the secondary alcohol was determined by Chiral GC. The absolute configuration of the alcohol was assigned as (*R*) by comparison of the optical rotation with reported data.

Method B (with additive)



To a well-dried Schlenk tube charged with Bu_4NBr (32.2 mg, 0.10 mmol, 10 mol %), a solution of chiral ligand L1 (1 mL,

0.5 mol %, 0.5×10^{-2} M in toluene) and dry toluene (1.0 mL) was added, then diethylzinc (1.0 M in hexane, 2.0 mL, 2.0 mmol, 2.0 equiv) was slowly added at 0 °C via a syringe under nitrogen atmosphere. After being stirred for 30 min, aldehyde (**1a**, 106 mg, 101.4 µL, 1.0 mmol) was added dropwise to the mixture at 0 °C. The mixture was stirred for 6 h at room temperature and quenched by addition of aqueous HCl (1.0 M, 5 mL). Extraction with EtOAc (10 mL × 3) gave combined organic layers that were washed with brine (10 mL), dried over MgSO₄, and concentrated in vacuo to give a residue that was subjected to silica gel column chromatography (EtOAc/hexane = 1/10), which afforded the corresponding enantio-enriched secondary alcohol (**2a**) as a colorless oil. The ee value of the secondary alcohol was determined by Chiral GC. The absolute configuration of the alcohol was assigned as (*R*) by comparison of the optical rotation with reported data.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.03.066.

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