Enantioselective addition of dialkylzincs to *N*-diphenylphosphinylimines using polymer-supported *N*,*N*-dialkylnorephedrines as chiral ligands

Takefumi Suzuki, Takanori Shibata and Kenso Soai*

Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162 Japan

Chiral *N*,*N*-dialkylnorephedrines supported on polystyrene resin catalyse the enantioselective addition of dialkylzincs to *N*-diphenylphosphinylimine, affording optically active *N*-diphenylphosphinylamines with high enantiomeric excess. The influence on the enantioselectivity of the carbon-chain spacer between the chiral function and polymer resin has been examined. Reaction temperature- and solvent-dependency on the chiral polymer-catalysed reaction has also been examined.

Introduction

Chiral polymers are attractive materials in their utility as chiral catalysts in asymmetric synthesis.[1] Polymer catalysts unite the advantages of homogeneous and heterogeneous catalyst; they possess high catalytic activity in organic solvents and are conveniently recovered and recycled. However, only a handful of those show high enantioselectivity in asymmetric carbon–carbon bond-forming reactions.[2] We have reported that dialkylzincs react enantioselectively with aromatic and aliphatic aldehydes using polymeric chiral ligands, that is, chiral β-amino alcohols supported on polystyrene resin, to afford the corresponding optically active secondary alcohols in high enantiomeric excesses up to 89% ee.[3]

On the other hand, the development of asymmetric syntheses of optically active amines is of importance in the preparation of compounds for therapeutic use, since partial structures of physiologically active substances such as amino acids and alkaloids frequently contain optically active amines.[4] Although one of the simpler methods for the synthesis of chiral amines is by asymmetric alkylation of imines, there have been few reports of enantioselective alkylation of imines.[5]

We have reported that dialkylzincs enantiomerically add to *N*-diphenylphosphinylimines using chiral β-amino alcohols as chiral ligands to afford the corresponding optically active phosphinamides in high enantiomeric excess (up to 95% ee).[6] Such optically active phosphinamides readily undergo acid hydrolysis to give the corresponding optically active amines without racemization.

We here disclose the full detail of an enantioselective addition of dialkylzincs to *N*-diphenylphosphinylimines using chiral β-amino alcohols supported on polystyrene resin as a chiral ligand.[7]

Results and discussion

Synthesis of polymer-supported and the corresponding monomeric *N*,*N*-dialkylnorephedrines as chiral ligands

In considering how the structure of the connection between the polystyrene and the asymmetric auxiliary might influence the chiral environment of the catalyst, we thought that the reactivity and enantioselectivity could possibly be altered by introducing spacers between the resin and the chiral amino alcohol. We have, therefore, synthesized[3b,c] the chiral polymers as shown in Fig. 1; in **1ap**[3c] and **1bp**[3c] the chloromethylated polystyrene resin (chlorine content 0.8 mmol g^{-1}) and the chiral amino alcohol are connected directly, whilst in **2ap**[3c] and **2bp**[3c] the polystyrene resin and the chiral entity are connected with a carbon straight chain as a spacer. A chiral polymer **1ap***, containing more of the chiral reactive site, was also prepared from chloromethylated polystyrene resin (chlorine content 4.3 mmol g^{-1}) and (1*R*,2*S*)-ephedrine.

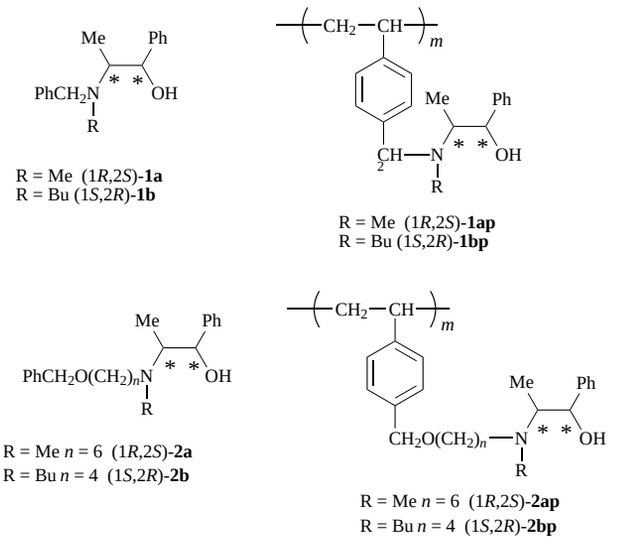


Fig. 1

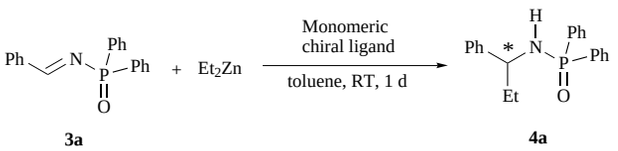
In order to examine the catalytic activity, the corresponding monomeric chiral amino alcohols **1a**,[2a] **1b**,[3c] and **2a**,[3c] **2b**[3c] were also synthesized.

Enantioselective addition of diethylzinc to *N*-diphenylphosphinylimine using monomeric or polymeric chiral ligands

As a preliminary experiment, asymmetric ethylation of *N*-diphenylphosphinylimine **3a** using diethylzinc using monomeric chiral amino alcohols **1a**, **1b**, **2a** and **2b** as chiral ligands was examined (Table 1). In each entry, optically active phosphinamide **4a** was obtained in high enantiomeric excess. Among them **1a** was found to be the most effective ligand for the enantioselective alkylation. Interestingly, the presence of a carbon spacer decreased the catalytic activity when the nitrogen atom of the chiral ligand was substituted when a methyl group (Entries 1 and 3), while it increased with a butyl substituent (Entries 2 and 4).

Next we examined the enantioselective addition of Et_2Zn to *N*-diphenylphosphinylimine using polymer-supported *N*,*N*-dialkylnorephedrines **1ap**, **1bp**, **2ap** and **2bp** (Table 2).

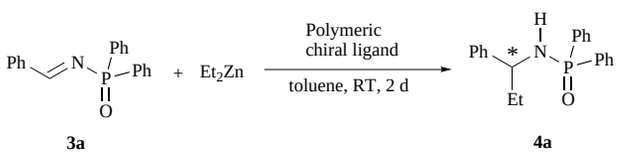
Table 1 Enantioselective ethylation of imine **3a** using monomeric chiral ligands



3a **4a**

Entry	Ligand	Yield (%)	Ee (%)	Config'n
1	(1*R*,2*S*)-**1a**	91	91	*R*
2	(1*S*,2*R*)-**1b**	39	78	*S*
3	(1*R*,2*S*)-**2a**	47	81	*R*
4	(1*S*,2*R*)-**2b**	75	83	*S*

Table 2 Enantioselective ethylation of the imine **3a** using polymeric chiral ligands



3a **4a**

Entry	Ligand[a]	Yield (%)	Ee (%)	Config'n
1	(1*R*,2*S*)-**1ap**	70	84	*R*
2[b]	(1*S*,2*R*)-**1bp**	10	6	*S*
3	(1*R*,2*S*)-**2ap**	31	69	*R*
4	(1*S*,2*R*)-**2bp**	52	65	*S*
5[c]	(1*R*,2*S*)-**1ap**	45	81	*R*
6	(1*R*,2*S*)-**1ap***[d]	55	62	*R*

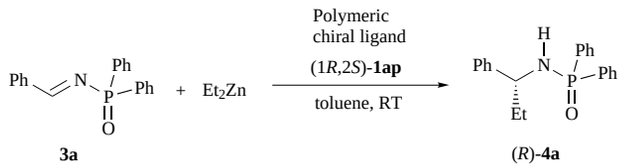
[a] Unless otherwise noted, polymeric chiral ligands were prepared using chloromethylated polystyrene resin (1% divinylbenzene; chlorine content 0.8 mmol g^{-1}; 100–200 mesh). [b] Reaction time is 5 d. [c] Recycled chiral ligand **1ap** was used. [d] Polymeric chiral ligand **1ap*** was prepared using chloromethylated polystyrene resin (2% divinylbenzene; chlorine content 4.3 mmol g^{-1}; 200–400 mesh).

The order of catalytic activity was in accordance with that of the corresponding monomeric chiral catalyst and optically active (*R*)-**4a** was obtained using the polymeric chiral ligand (1*R*,2*S*)-**1ap** in good yield (70%) and with high enantiomeric excess (84%; Entry 1). Further, when polymeric chiral ligands are used, the influence of a carbon spacer on the catalytic activity varies with the substituent on the nitrogen atom; the differences noted were larger than those for monomeric ligands; **1bp** possesses almost no catalytic activity (10%, 6% ee), while **2bp**, which is different from **1bp** only in the existence of carbon spacer, has moderate catalytic activity (52%, 65% ee) (Entries 2 and 4). These results suggest that the bulky butyl group on the nitrogen atom decreases the catalytic activity when the chiral moiety is directly connected to the polymer resin but that the spacer enables the substrate to approach the chiral moiety.

One of the advantages of a polymeric chiral ligand over a monomeric chiral ligand is its easier separation from the reaction mixture. Thus, filtration of the reaction mixture readily separated insoluble polymeric chiral ligand, with subsequent recycling of chiral ligand and purification of the product being facilitated. In Entry 5, recycled chiral polymeric ligand which had been used in Entry 1, recovered by filtration and washed with acid and base, was examined. As a result, **4a** was obtained with almost the same ee as that in Entry 1, although the chemical yield was diminished. These results imply that in this system the facile recycling of the polymeric ligand is possible by the appropriate treatment of the used ligand.

Use of **1ap*** for the addition of diethylzinc to **3a** gave a much decreased ee (62% ee; Entry 6), a result probably explained in terms of a higher degree of polymer loading of ephedrine in **1ap*** than in **1ap**. A high degree of loading may give rise to active site interactions, which interfere with the formation of an appropriate transition state.

Table 3 Effect of reaction temperature on the reaction using the polymeric ligand (1*R*,2*S*)-**1ap**



3a (*R*)-**4a**

Entry	Temp. (°C)	Time (h)	Yield (%)	Ee (%)
1	40	12	40	57
2	RT	48	70	84
3	0	48	19	79
4	− 10	12	9.5	59

It was found that use of polymeric ligands gave rise to a need for longer reaction times and resulted in generally lower chemical yields than those found with monomeric ligands. This reduced catalytic activity is a result of the partial insolubility of polymeric chains that may fail to operate as a chiral ligand in the asymmetric reaction, and thus result in a decrease of the active sites for polymeric ligands.

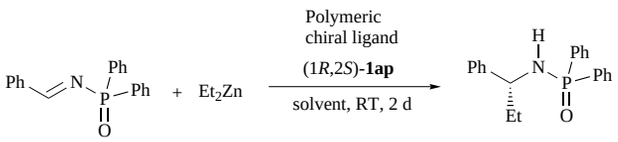
Screening of the reaction conditions using the polymeric chiral ligand 1ap

In order to improve the chemical and optical yield, we optimized the reaction conditions of the enantioselective ethylation of *N*-diphenylphosphinylimine **3a** using the polystyrene-supported norephedrine derivative (1*R*,2*S*)-**1ap** which had been shown to give the best results of the compounds tested.

Effect of temperature. We examined the effect of temperature on the reaction using the catalysts (1*R*,2*S*)-**1ap** (Table 3). At room temperature the alkylated product (*R*)-**4a** was given with the highest enantiomeric excess (84% ee) and chemical yield (70%; Entry 2). At 0 °C, only a slight decrease in the enantiomeric excess was observed, but there was a considerable decline in the chemical yield (Entry 3). At 40 °C, the enantiomeric excess decreased markedly (Entry 1). These results suggested that although the catalytic reaction fails to proceed smoothly at 0 °C, direct ethylation by diethylzinc proceeds at 40 °C regardless of the use or not of a chiral catalyst. Moreover, it is noticeable that temperature dependency is much increased in reactions using a polymeric chiral ligand than those using a monomeric chiral ligand (*N*,*N*-dialkylnorephedrine at RT, 0 °C and −13 °C affords **4a** with 86, 89 and 88% ees, respectively);[8] this may indicate that the degree of the swelling of the polymers has a potent influence on the catalytic activity.

Examination of solvent. On examining the effect of various solvents (Table 4) on the enantioselective addition of diethylzinc to **3a**, we found that the product (*R*)-**4a** was given in high enantiomeric excess (80–85% ee) in toluene, diethyl ether, *o*- or *m*-xylene or isopropylbenzene (Entries 1–3, 6, 7, 11); it was found that toluene was the best solvent. In hexane or benzene, both enantiomeric excesses and chemical yields remained low (Entries 4, 5). It is noted that a more significant solvent effect was observed in the reactions with polymeric asymmetric catalysts than with monomeric ones [monomeric *N*,*N*-dibutylnorephedrine (DBNE) shows the same enantioselectivity of 84% ee both in toluene and hexane].[8] It is thought that the degree of swelling of the polymeric ligand varied with different solvents. Thus, it probably gives rise to a significant solvent effect in the asymmetric alkylation, *e.g.* benzene was adsorbed by the polymeric catalyst, and thus, for the reaction mixture to be stirred smoothly double the volume of solvent was required to that required of others; little swelling of the polymeric asymmetric catalysts was observed in hexane, the optimum amount of swelling was observed on use of toluene as solvent. On the other hand, in the enantioselective addition of dialkyl-

Table 4 Effect of solvent on the reaction using polymeric ligand (1*R*,2*S*)-**1ap**

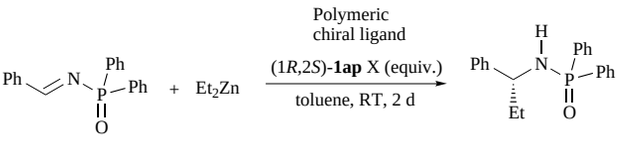


3a (*R*)-**4a**

Entry[a]	Solvent	Yield (%)	Ee (%)
1	Toluene	70	84
2[b]	Toluene	80	80
3	Diethyl ether	50	83
4	Hexane	55	2
5[c]	Benzene	4	22
6	*o*-Xylene	56	85
7	*m*-Xylene	43	85
8	*p*-Xylene	28	78
9	Ethylbenzene	56	62
10	Mesitylene	49	75
11	Isopropylbenzene	20	82
12	Acetonitrile	15	55

[a] Unless otherwise noted, a hexane solution of diethylzinc was used. [b] A toluene solution of diethylzinc was used. [c] Reaction time is 5 d.

Table 5 Effect of the amount of polymeric ligand (1*R*,2*S*)-**1ap**



3a (*R*)-**4a**

Entry	X (equiv.)	Yield (%)	Ee (%)
1	0.4	50	61
2	0.6	55	71
3	0.8	60	80
4	1.0	70	84
5	2.0	54	88

zincs to aldehydes using polymeric chiral catalysts (**1ap**), hexane as well as toluene affords the products (*sec*-alcohols) with high ees.[3]

Because diphenylphosphinylimine **3a** is bulkier than aldehydes, such as benzaldehyde, the enantioselectivities of the addition to imine using polymeric ligand seems to be affected by the environment of active site more drastically than those of the addition to aldehydes. The appropriate swelling of polymeric chiral ligand seems to be essential, *i.e.* too little swelling in hexane and too much swelling in benzene.

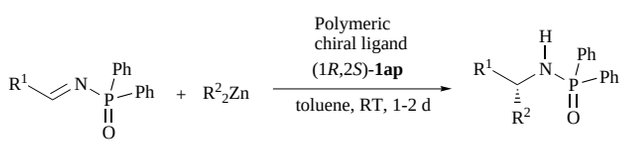
Examination of the amount of chiral catalyst

The optimal amount of the polymeric asymmetric catalyst (1*R*,2*S*)-**1ap** was determined (Table 5). With the other reaction conditions fixed (reaction time = 2 d, reaction temperature = RT, solvent = toluene), the amount of **1ap** was varied in the range 0.4–2.0 equiv. compared with the phosphinylimine **3a**. The enantiomeric excesses increased with increasing amounts of **1ap**. The chemical yield was at a maximum with equivalent amounts of **1ap** and substrate (Entry 4).

Enantioselective addition of dialkylzincs to various *N*-diphenylphosphinylimines

In order to evaluate the generality of this asymmetric reaction, the enantioselective alkylation of various *N*-diphenylphosphinylimines **3a–d** having phenyl, naphthyl or furyl groups on the carbon atom of the imines were carried out in the presence of (1*R*,2*S*)-**1ap** under the optimum reaction conditions as mentioned above (Table 6). The corresponding ethylated products

Table 6 Enantioselective ethylation of various imines **3a–d** with dialkylzincs using (1*R*,2*S*)-**1ap**



3a–d **4a–e**

Entry	R^1	R^2		Yield (%)	Ee (%)
1	Phenyl	Et	**4a**	70	84
2	1-Naphthyl	Et	**4b**	65	62
3	2-Naphthyl	Et	**4c**	61	85
4	2-Furyl	Et	**4d**	31	69
5	Phenyl	Me	**4e**	46	86

4a–d were given in good or high enantiomeric excesses. In the enantioselective addition of diethylzinc, phosphinylimine **3c** possessing a 2-naphthyl group gave the corresponding phosphinamide **4c** in the optical yield of 85% ee (Entry 3). The generality of the reaction for other dialkylzincs was exemplified with dimethylzinc: enantioselective addition of dimethylzinc to **3a** afforded the corresponding compound **4e** with an ee as high as 86% (Entry 5).

In conclusion, enantioselective addition of dialkylzincs to *N*-diphenylphosphinylimine in the presence of a chiral amino alcohol supported on polystyrene resin as a chiral ligand affords optically active phosphinamides with high ee. The solvent effect on the enantioselectivity is significant, and toluene is the best solvent. The chiral polymer ligand easily separated from the product by filtration, can be re-used without any significant decline in its enantioselectivity.

Experimental

General

^{1}H NMR and IR spectra, and optical rotations (given in units of 10^{-1} deg cm^2 g^{-1}) were recorded with an HITACHI R-1200 spectrometer, an HITACHI 260-10(30) spectrophotometer, and a JASCO DIP-360 polarimeter, respectively. HPLC analyses were performed using SHIMADZU LC-6A or 8A with a Daicel chiral column.

Materials

Diethylzinc in hexane was purchased from Kanto Chemical Co. Chloromethylated polystyrene resins (1% divinylbenzene; chlorine content 0.8 mmol g^{-1}; 100–200 mesh and 2% divinylbenzene; chlorine content 4.3 mmol g^{-1}; 200–400 mesh) were purchased from Kokusan Chemical Works and Fluka Chemika, respectively. Compounds **1a**,[2a] **1b**,[3c] **1ap**,[3c] **1bp**,[3c] **2a**,[3c] **2b**,[3c] **2bp**[3c] and **3a–c**[9] were prepared according to the literature procedures. Compound **3d** was synthesized from 2-furaldehyde and *P*,*P*-diphenylphosphinamide by a literature procedure.[9]

***N*-(2-Furylmethylidene)-*P*,*P*-diphenylphosphinamide 3d.** White solid, mp 151 °C; ν_{max}(KBr disk)/cm^{-1} 1625 and 1205; δ_H 6.59 (m, 1H), 7.18–8.30 (m, 12H) and 9.10 (d, 1H, *J* 35.4) [Found: *m*/*z* (HRMS) 295.0769. Calc. for $C_{17}H_{14}NO_2P$: *M*, 295.0762].

General procedure for the enantioselective addition of diphenylphosphinylimines 3 by using a polymeric chiral ligand (1*R*,2*S*)-1ap

To a toluene solution (3 ml) of the polymeric asymmetric catalyst (1*R*,2*S*)-**1ap** (0.2 mmol, 0.2597 g) and the imine **3** (0.2 mmol) at 0 °C under an argon atmosphere, diethylzinc was added dropwise. After completion of the addition and removal of the ice bath the mixture was stirred at room temperature for 2 days. After this, the reaction was quenched by the addition of saturated aqueous ammonium chloride to the reaction mixture

which was then filtered under reduced pressure to remove the precipitates and then extracted with dichloromethane (10 ml × 3). The combined extracts were dried (Na_2SO_4), filtered and evaporated under reduced pressure. TLC purification [hexane–acetone 3:2 (v/v), developed twice] of the residue gave the corresponding optically active diphenylphosphinamide **4**, the enantiomeric excess of which was determined by HPLC analysis using DAICEL Chiralcel OD (4.6 × 250 mm; 254 nm UV detector; eluent: 3% propan-2-ol in hexane; flow rate: 1.0 ml min^{-1}; column temperature: *ca*. 20 °C).

(*R*)-*N*-(1-Phenylpropyl)-*P*,*P*-diphenylphosphinamide 4a. Yield 70%, ee 84% (R_t/min 15 for *R* isomer, 24 for *S* isomer); ν_{max}(KBr disk)/cm^{-1} 3150 and 1210; δ_H 0.80 (3H, t), 1.93 (2H, m), 3.48 (1H, m), 4.14 (1H, m) and 7.10–8.20 (15H, m) [Found: *m*/*z* (HRMS) 335.1442. Calc. for $C_{21}H_{22}NOP$: *M*, 335.1439]; mp 129.0 °C (recrystallized from hexane–ethyl acetate, 98% ee); $[\alpha]_D^{32}$ −42.3 (*c* 2.0, MeOH, 98% ee).

***N*-[1-(1-Naphthyl)propyl]-*P*,*P*-diphenylphosphinamide 4b.** Yield 65%, ee 62% (R_t/min 27 for *R* isomer, 41 for *S* isomer); ν_{max}(KBr disk)/cm^{-1} 3150 and 1185; δ_H 0.84 (3H, t), 2.05 (2H, m), 3.95 (1H, br s), 4.95 (1H, m) and 6.85–8.40 (17H, m) [Found: *m*/*z* (HRMS) 385.1598. Calc. for $C_{25}H_{24}NOP$: *M*, 385.1596]; mp 133.5–134.0 °C (recrystallized from hexane–dichloromethane, 65% ee); $[\alpha]_D^{32}$ −21.5 (*c* 2.0, MeOH, 65% ee).

***N*-[1-(2-Naphthyl)propyl]-*P*,*P*-diphenylphosphinamide 4c.** Yield 61%, ee 85% (R_t/min 27 for *R* isomer, 44 for *S* isomer); ν_{max}(KBr disk)/cm^{-1} 3200 and 1190; δ_H 0.83 (3H, t), 2.01 (2H, m), 3.37 (1H, br s), 4.25 (1H, m) and 7.05–8.15 (17H, m) [Found: *m*/*z* (HRMS) 385.1596. Calc. for $C_{25}H_{24}NOP$: *M*, 385.1596]; mp 150.5 °C (recrystallized from hexane–dichloromethane, 91% ee); $[\alpha]_D^{27}$ −50.6 (*c* 3.8, MeOH, 91% ee).

***N*-[1-(2-Furyl)propyl]-*P*,*P*-diphenylphosphinamide 4d.** Yield 31%, ee 69% (R_t/min 38 for *R* isomer, 46 for *S* isomer); ν_{max}(KBr disk)/cm^{-1} 3140 and 1210; δ_H 0.87 (3H, t), 1.94 (2H, q), 3.37 (1H, br), 4.18 (1H, m), 6.14 (2H, m) and 7.10–8.15 (11H, m) [Found: *m*/*z* (HRMS) 325.1224. Calc. for $C_{19}H_{20}NO_2P$: *M*, 325.1232]; mp 98 °C (recrystallized from hexane–dichloromethane, 76% ee); $[\alpha]_D^{27}$ −40.0 (*c* 4.07, MeOH, 76% ee).

Recycling of the chiral polymer (1*R*,2*S*)-1ap

The used polymer **1ap** (2.2 g), recovered from the quenched mixture by filtration, was stirred first in a mixture of THF (16 ml), 6 M aq. HCl (2 ml) and water (4 ml) and then after being filtered off was stirred again for 4 h in a mixture of THF (16 ml) and 2 M aqueous sodium hydroxide (4 ml). The polymer **1ap** was then filtered off and washed successively with 50 ml portions of water, methanol, THF, aq. THF, THF and methanol. After being dried at 40 °C *in vacuo* for 5 h, it was recycled and used for enantioselective ethylation (Recovery: 1.6 g).

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