DOI: 10.1002/adsc.200505221

Enantioselective Addition of Organozinc Reagents to Aldehydes Catalyzed by 3,3′-Bis(diphenylphosphinoyl)-BINOL

Manabu Hatano, Takashi Miyamoto, Kazuaki Ishihara*

Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan
Fax: (+81)-52-789-3331/(+81)-52-789-3222, e-mail: ishihara@cc.nagoya-u.ac.jp

Received: March 3, 2005; Accepted: August 1, 2005

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de/home/

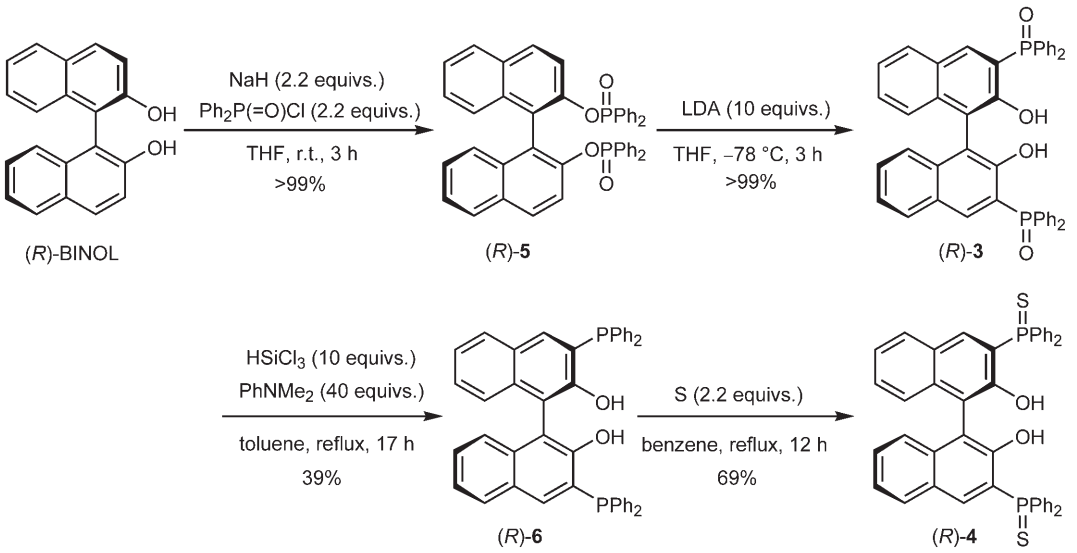
Abstract: The enantioselective addition of organozinc reagents to aromatic and aliphatic aldehydes **1** gives secondary alcohols **2** with excellent enantioselectivities in high yields through the catalytic use of (*R*)-3,3′-bis(diphenylphosphinoyl)-BINOL (**3**) or (*R*)-3,3′-bis(diphenylthiophosphinoyl)-BINOL (**4**) without Ti(IV) complexes. The coordination of the *O* or *S* atom of a (thio)phosphinoyl group bearing a BINOL backbone to organozinc reagents can efficiently increase the nucleophilicity of the organozinc reagents.

Keywords: asymmetric catalysis; binaphthol; diethylzinc; enantioselective addition; phosphine oxides; secondary alcohols

For carbon-carbon bond-forming reactions, the catalytic enantioselective addition to aldehydes of organozinc reagents is a versatile method for synthesizing optically active secondary alcohols.[1,2] Chiral zinc and titanium complexes can catalyze this reaction through the combined use of amino alcohols (N,O ligands), diamines (N,N ligands), or diols (O,O ligands) as excellent chiral auxiliaries.[3,4] In particular, 1,1′-bi-2-naphthol (BINOL) is highly effective in the diethylzinc addition to aldehydes, although more than a stoichiometric amount of Ti(O-*i*-Pr)$_4$ is necessary to achieve both excellent enantiomeric excess and chemical yield within a short reaction time.[5,6] The use of a 'chiral/achiral activator' as an additive to BINOL-Zn(II) catalyst has been effective for enhancing the catalytic activity without Ti(IV) complexes.[7] On the other hand, 3,3′-disubstituted BINOLs[8] have been designed to establish the catalytic asymmetric addition of organozinc reagents without any other 'activators' such as Ti(IV) complexes.[9] However, these efficient 3,3′-functionalized BINOL analogues are sometimes difficult to synthesize in satisfactory yields because of the multi-step transformations from the starting BINOL. We report here the highly enantioselective addition of organozinc to aldehydes without any other activators, catalyzed by (*R*)-3,3′-bis(diphenylphosphinoyl)-BINOL [(*R*)-**3**], which can be derived from (*R*)-BINOL quantitatively. To the best of our knowledge, this is the first example of the catalytic asymmetric addition of organozinc reagents to aldehydes in the presence of phosphine oxide (P=O)[10] or phosphine sulfide (P=S) moieties in chiral O,O ligands.[11]

(*R*)-3,3′-Bis(diphenylphosphinoyl)-BINOL [(*R*)-**3**] was prepared almost quantitatively from commercially available (*R*)-BINOL in two steps (Scheme 1).[12] (*R*)-BINOL in THF was treated with NaH (2.2 equivs.) followed by the dropwise addition of diphenylphosphinic chloride (2.2 equivs.), to give the corresponding phosphinates (*R*)-**5** quantitatively without further purification.[13] The rearrangement proceeded with LDA (10 equivs.) in THF at $-78\,^{\circ}C$ to give (*R*)-**3** quantitatively as colorless crystals after recrystallization from toluene/hexane (*ca.* 1/5).[14] An X-ray analysis of (*R*)-**3** is shown in Fig. 1. Hydrogen bonding, which was observed in Naph-O-*H*···O=P (1.863 Å) to form a six-membered ring, brings us to the assumption that the chelation to Zn (instead of *H*) is in this manner, unlike BINOLate(κ^2*O*,*O*′)-Zn(II) chelation (*vide infra*). This hydrogen bonding of (*R*)-**3** was responsible for the observed downfield shift, such as 10.57 ppm, in the ^{1}H NMR. Moreover, for the synthesis of (*R*)-3,3′-bis(diphenylthiophosphinoyl)-BINOL [(*R*)-**4**] as a new chiral auxiliary, two consecutive steps were carried out from (*R*)-**3**. Reduction[15] of (*R*)-**3** to the corresponding (*R*)-3,3′-bis(diphenylphosphanyl)-BINOL [(*R*)-**6**] in moderate yield was realized by refluxing with trichlorosilane (10 equivs.) and *N*,*N*-dimethylaniline (40 equivs.) in toluene. Sulfidation[16] of (*R*)-**6** by elemental sulfur (2.2 equivs.) in refluxing benzene gave (*R*)-**4** in good yield.

First, 10 mol % of (*R*)-**3** bearing a P=O moiety with a BINOL skeleton was used to catalyze the addition of diethylzinc (3 equivs.) to aldehydes in THF-toluene (1:1) at room temperature without Ti(O-*i*-Pr)$_4$. These results



Scheme 1. Preparation of (*R*)-**3** and (*R*)-**4**.

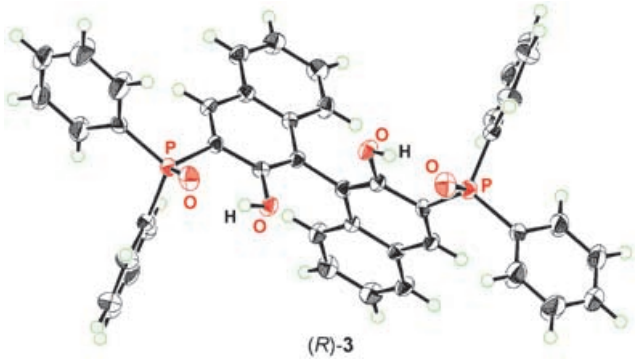
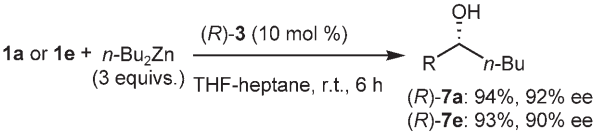


Figure 1. ORTEP drawing of (*R*)-**3**.

are summarized in Table 1. (*R*)-**3** was shown to be highly effective for not only aromatic but also aliphatic aldehydes, and gave the corresponding ethyl adducts with high enantioselectivities in good to quantitative yields within 24 h. Particularly, aromatic aldehydes with electron-donating or -withdrawing groups showed excellent enantioselectivities (up to 97% ee) in almost quantitative yields (entries 1–11). The reactions also proceeded smoothly for α,β-unsaturated aldehyde (entry 12). For aliphatic aldehydes, in which competitive reduction often occurs along with ethylation, the corresponding secondary aliphatic alcohols were obtained with high enantioselectivities (up to 94% ee) in good yields (entries 13–17). (*R*)-**3** could also be used for heterocycles to give the desired ethyl adducts with 81–92% ee within 3 h, although low conversion was observed with 3-pyridinecarboxaldehyde, and the starting material was recovered without side reactions (entries 18–20).

Interestingly, a dramatic increase in the catalytic activity of (*R*)-**3** was observed at 50 °C without a serious loss of enantioselectivity (Table 2). The heat conditions in catalytic asymmetric diethylzinc addition have been limited[17] because the reaction is usually performed at room temperature or lower to establish and/or maintain high enantioselectivities. In sharp contrast, our catalyst showed great performance even at 50 °C probably due to the rigid chelation of the P=O moiety to the Zn(II) center (*vide infra*), and the catalyst loading could be decreased to 5 mol %. Along with a dramatic decrease in the reaction time, aromatic aldehydes with electron-withdrawing or -donating groups gave successful results; for instance, 88% ee and 84% yield within 2 h for **1a**, 88% ee and 96% yield within 3 h for **1c**, 90% ee and 92% yield within 0.5 h for **1e**, 90% ee and 98% yield within 1 h for **1f**, 90% ee and 98% yield within 0.1 h for **1h**, and 93% ee and 92% yield within 1.5 h for **1k**.

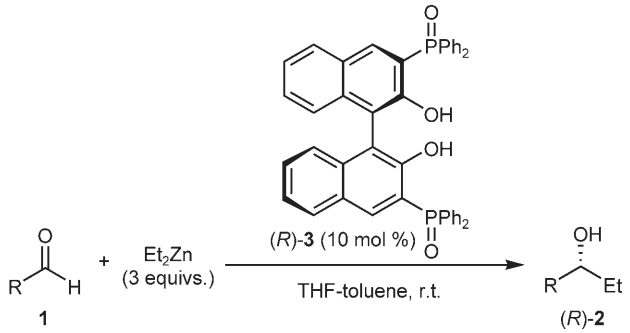
Encouraged by the high performance of (*R*)-**3**, we examined catalytic asymmetric addition to aldehydes with other organozinc reagents such as *n*-Bu_2Zn and Ph_2Zn. Butylation with aryl aldehydes **1a** and **1e** was carried out with 10 mol % of (*R*)-**3** and 3 equivs. of *n*-Bu_2Zn in THF-heptane at room temperature to give the desired butyl adducts **7a** and **7e**; 92% ee and 94% yield for **7a** and 90% ee and 93% yield for **7e**, respectively [Eq. (1)]. Enantioselective phenylation to **1** with 1 equiv. of Ph_2Zn was also established in the presence of 10 mol % of Et_2Zn,[18] and gave the desired phenyl adducts (*R*)-**8** with 81–88% ee in excellent yields (Table 3).



(1)

(*R*)-**4** bearing a P=S moiety was examined in the diethylzinc addition without Ti(IV) complexes (Table 4).

Table 1. Enantioselective ethylation of aldehydes with (*R*)-**3** at room temperature.



Entry	Aldehyde (**1**)	Time [h]	Yield [%]	ee [%][a]
1	PhCHO (**1a**)	3 (12)[b]	95 (98)[b]	95 (96)[b]
2	*p*-$MeOC_6H_4CHO$ (**1b**)	18	89	89
3	*p*-MeC_6H_4CHO (**1c**)	8	>99	93
4	*p*-PhC_6H_4CHO (**1d**)	4	>99	93[d]
5	*p*-ClC_6H_4CHO (**1e**)	1 (24)[c]	98 (>99)[c]	94 (96)[c]
6	*p*-FC_6H_4CHO (**1f**)	3	94	94
7	*o*-FC_6H_4CHO (**1g**)	9	89	86
8	*p*-$CF_3C_6H_4CHO$ (**1h**)	0.5 (4)[c]	>99 (91)[c]	94 (97)[c]
9	3,4-$(OCH_2O)C_6H_3CHO$ (**1i**)	4	95	95
10	α-NaphCHO (**1j**)	6	82	80
11	β-NaphCHO (**1k**)	4	95	95[d]
12	PhC≡CCHO (**1l**)	1	86	86[e]
13	$PhCH_2CH_2CHO$ (**1m**)	6	73	82[d]
14	*c*-$C_6H_{11}CHO$ (**1n**)	12	55	91
15	*n*-$C_5H_{11}CHO$ (**1o**)	12	71	94
16	*n*-$C_9H_{19}CHO$ (**1p**)	12	72	90
17	*n*-$C_{11}H_{23}CHO$ (**1q**)	6	66	93
18	2-FurylCHO (**1r**)	3	90	84
19	3-ThienylCHO (**1s**)	2	94	92
20	3-PyridylCHO (**1t**)	0.5	30	81

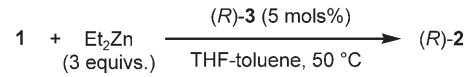
[a] Absolute configuration of **2** is *R*. The ee values were determined by chiral GC analysis unless otherwise noted.
[b] Temperature was 0 °C.
[c] Temperature was −20 °C.
[d] HPLC analysis on OD-H.
[e] HPLC analysis on OJ-H.

High enantioselectivities (83–85% ee) were observed for aromatic aldehydes **1a**, **1b** and **1e**, although the catalytic activity was lower than that of (*R*)-**3** bearing a P=O moiety to give corresponding (*R*)-**2**.

The presence of P=O in the BINOL structure is critical (Fig. 2). The lack of P=O moieties at the 3,3′-positions in the C_2-symmetrical BINOL backbone resulted in failure: lower enantioselectivities and reactivities were observed with the use of (*R*)-**6** and (*R*)-**9**, which have bulky substituents at the 3,3′-positions but lack the key P=O units. These results mean that mere bulkiness at the 3,3′-positions is insufficient to improve the enantioselectivities. Furthermore, two C_2-symmetrical P=O moieties at the 3,3′-positions in the BINOL skeleton are necessary to achieve high catalytic activity, since (*R*)-**10**, which has a diphenylphosphine oxide on only one side was ineffective for this catalysis. The low performance of (*R*)-**10** with respect to (*R*)-**3** is probably not only due to the rigidity of chelation network, but also to the fact that the missing second diphenylphosphinoyl moiety induces a competing chelation mode. (*R*)-BINOL, (*R*)-BINAP, and (*R*)-BINAPO were ineffective under our reaction conditions even though they have the same C_2-symmetrical binaphthyl structures.

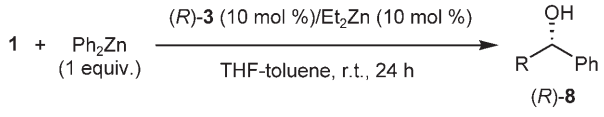
We should address the association between the characteristics of the active Zn(II) catalyst and mechanistic aspects. The key to solving these problems should be to clarify whether coordination of P=O (or P=S) to the Zn(II) center is present or not (*vide supra*), and if so to isolate the active catalyst or its precursor. Fortunately, a single crystal for X-ray analysis was obtained from a mixture of (*R*)-**3** and Et_2Zn (1 equiv. each) in CH_2Cl_2-hexane at room temperature for 24 h. The ORTEP drawings are shown in Fig. 3. The structure of the ob-

Table 2. Enantioselective ethylation of aldehydes with (*R*)-**3** under heat conditions (50 °C).



Entry	**1**	Time [h]	Yield [%]	ee [%]
1	**1a**	2	84	88
2	**1b**	7	95	85
3	**1c**	3	96	88
4	**1d**	2	98	85
5	**1e**	0.5	92	90
6	**1f**	1	98	90
7	**1h**	0.1	98	90
8	**1i**	1	93	89
9	**1k**	1.5	92	93
10	**1m**	4	50	86
11	**1r**	1.5	93	80
12	**1s**	1.5	95	83

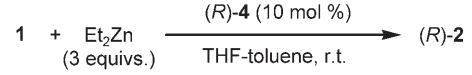
Table 3. Enantioselective phenylation of aldehydes with (*R*)-**3**.



Entry	**1**	Yield [%]	ee [%][a]
1	**1c**	86	85
2	**1d**	93	82
3	**1e**	96	88[b]
4	**1f**	>99	86[b]
5	**1h**	93	88[b]
6	**1k**	95	81

[a] Absolute configuration of **8** is *R*. The ee values were determined by HPLC analysis (OD-H) unless otherwise noted.
[b] HPLC analysis on OB-H.

Table 4. Enantioselective ethylation of aldehydes with (*R*)-**4** at room temperature.



Entry	**1**	Time [h]	Yield [%]	ee [%]
1	**1a**	8	85	83
2	**1b**	24	61	85
3	**1e**	6	48	85

tained Zn(II) cluster $[Zn_4\{(R)\text{-}3,3'\text{-bis(diphenyphosphinoyl)-BINOLate}\}_3(\mu_4\text{-}O)]\cdot(CH_2Cl_2)_3$ (**11**) was self-assembled from four Zn(II) metals and three units of (*R*)-**3**. At the center of this cluster, μ_4-*O*, which might be derived from adventitious water during recrystallization, coordinates to four Zn(II) centers. The Zn(II) center in the top position coordinates to μ_4-*O* (1.930 Å) and three P=*O* (1.926–1.955 Å) in three different (*R*)-**3** units. Each of the other three Zn(II) centers in bottom positions coordinates to μ_4-*O* (1.949–1.966 Å), Naph–*O* (1.874–1.887 Å), and *O*=P–C=C–*O* (1.986–2.011 Å and 1.941–1.956 Å, respectively) through chelation. However, the essential BINOLate(κ^2*O*,*O*′) chelation to the Zn(II) center did not exist in **11**, while we obtained solid evidence of the coordination of P=*O* to the Zn(II) center. As expected, this Zn(II) cluster (**11**) was not an active species; ethylation of **1a** proceeded with 3.3 mol % of isolated crystal **11** under the same reaction conditions at room temperature for 24 h to give (*R*)-**2a** in 38% yield and 20% ee. In fact, in a ^{31}P NMR study in CD_2Cl_2 under anhydrous conditions, the addition of 1 equiv. of Et_2Zn to (*R*)-**3** led to a new complex (**12**) with a singlet peak at 45.84 ppm (major, >98%) along with **11** as a minor product at 38.75 and 39.40 ppm (<2%) (Fig. 4). Complex **12** was found to be highly moisture sensitive, and gave the inactive catalyst **11** almost quantitatively with the partial release of **3** for 24 h under open-air conditions. This major complex **12** in the NMR study implied a symmetrical structure with two P=O units coordinating to Zn(II) centers, due to the downfield shift from 38.82 ppm of the free ligand (*R*)-**3**. By analogy to the structure of **11**, **12** is assumed to be an oligomeric species without BINOLate(κ^2*O*,*O*′) chelation to the Zn(II) center (Fig. 4).[19]

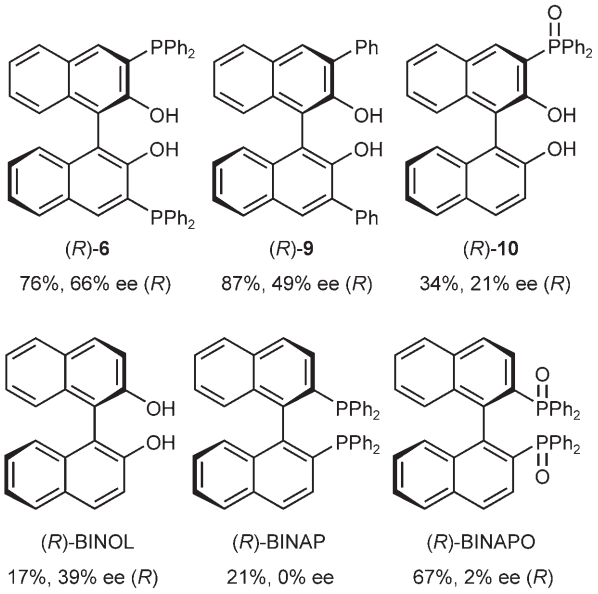


Figure 2. Results of ethylation to **1a** by chiral binaphthyl ligands (10 mol %) at room temperature for 24 h.

Finally, we turned our attention to the mechanistic aspects of the transition states. Based on the lack of a nonlinear relationship between the ee of (*R*)-**3** (10 mol %) and the ee of (*R*)-**2a** under room temperature conditions, the structure of the Zn(II) complex in our catalysis

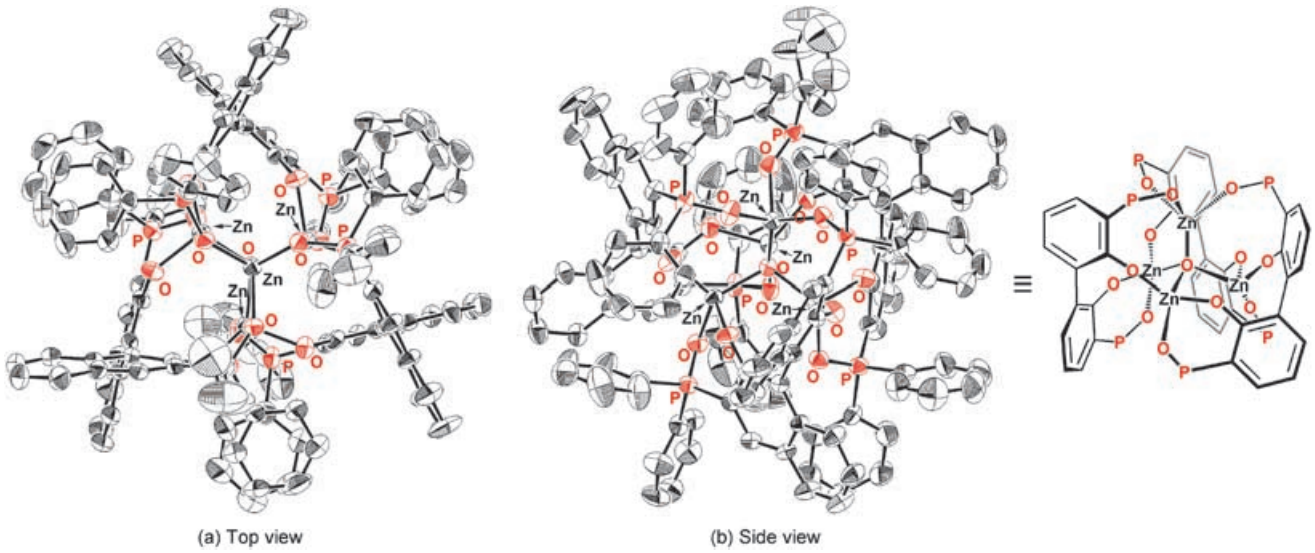


Figure 3. ORTEP drawings of self-assembled Zn(II) cluster **11** (hydrogen atoms are omitted for clarity).

is likely to be a monomeric or homochiral oligomeric species. Although further investigation is necessary to achieve a full understanding, a catalytic cycle that includes the transition states is proposed in Fig. 4.[20] Particularly with our ligand **3**, oligomeric complex **12** should dissociate to monomeric species **A** with two independent *O*=P–C=C–*O* chelations before forming BINOLate(κ^2*O*,*O*′) chelation, taking advantage of the postulated *non*-BINOLate(κ^2*O*,*O*′)-Zn(II) structure by Pu.[21] Eventually, active species **B** with a C_2-symmet-

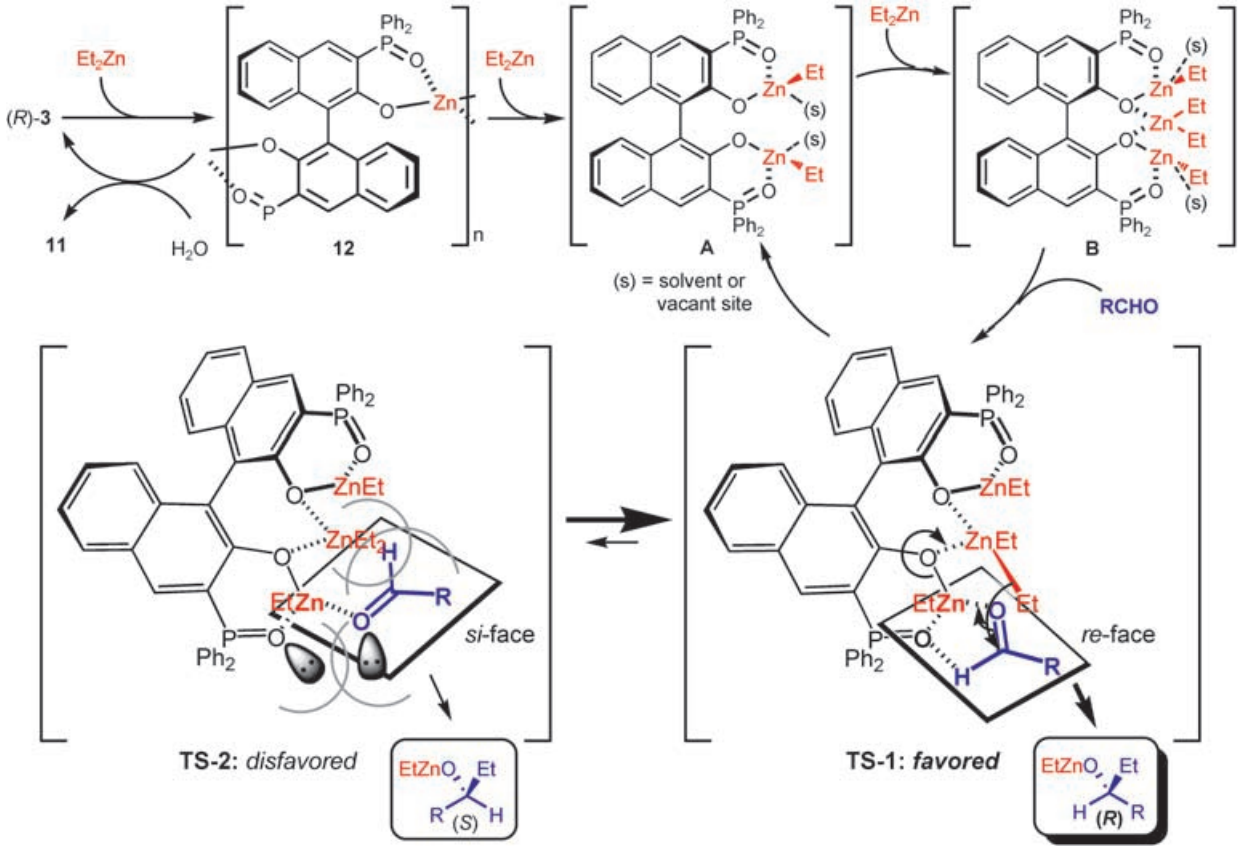


Figure 4. Proposed catalytic cycle and transition states for enantioselective diethylzinc addition to aldehydes with (*R*)-**3**.

rical structure should be formed by Et_2Zn with coordination to BINOLate(κ^2O,O').[22] Coordination of the aldehyde to **B** leads to two possible transition states: **TS-1** *via re*-face attack and **TS-2** *via si*-face attack. In these transition states, Et_2Zn at the center position [BINOLate(κ^2O,O')-Zn(II)] acts as a reagent in ethylation and EtZn at both side positions (*O*=P−C=C−*O*) is coordinated to an aldehyde in a vacant site and acts as a Lewis-acid.[11d,11e,11g,22] Transition state **TS-1** is much preferable to **TS-2** for two important reasons, and eventually leads to (*R*)-**2**: 1) it avoids not only steric hindrance between the aldehyde and Et_2Zn but also the electrical repulsion of lone pairs between P=O: and C=O: in the same direction, and 2) it covers the hydrogen bonding between formic proton and P=O to form a five-membered ring.[23] Transition state **TS-1** can explain the ligand effect on enantioselectivity and/or reactivity (**3** > **4** > > **10**) due to these rigid chelations and the strength of the Lewis acidity of the Zn(II) center in side positions. After carbon-carbon bond-formation, intermediate **A** is regenerated.

In summary, we have developed a highly enantioselective addition of organozinc reagents to aromatic or aliphatic aldehydes catalyzed by (*R*)-3,3′-bis(diphenylphosphinoyl)-BINOL, which could be prepared quantitatively in two steps from commercially available (*R*)-BINOL. The coordination to the Zn(II) center with phosphine oxide (P=*O*) in our ligand could promote carbon-carbon bond-formation without $Ti(O\text{-}i\text{-}Pr)_4$ at room temperature, or at an unprecedented higher temperature (50 °C) with a dramatic increase in catalytic activity. Studies are now underway to establish the asymmetric alkynylation and enantioselective addition to ketones and imines.

Experimental Section

General Remarks

All experiments were carried out under an atmosphere of dry nitrogen. In experiments that required dry solvents, hexane (dehydrate), benzene (dehydrate), toluene (dehydrate), dichloromethane (dehydrate), and tetrahydrofuran (dehydrate) were purchased from Kanto Chemical Co., Inc. Et_2Zn (1.10 M in toluene, Aldrich); $n\text{-}Bu_2Zn$ (1.0 M in heptane, Fluka); Ph_2Zn (Strem). NMR (^1H, ^{31}P) spectra were measured on a Varian Mercury 300 spectrometer. Chemical shifts of ^{31}P NMR are expressed in parts per million downfield from 85% H_3PO_4 as an external standard ($\delta = 0$). High performance liquid chromatography (HPLC) analysis was conducted using a Shimadzu LC-10 AD coupled diode array-detector SPD-MA-10A-VP and a chiral column of Daicel CHIRALCEL, CHIRALPAK; OD-H, OJ-H, OB-H. GC analysis was performed with Shimadzu 17A instruments using CP-cyclodextrin-β-2,3,6-M-19 (i.d. 0.25 mm × 25 m; CHROMPACK; GL Science Inc.).

Characterization data for compounds **2**–**8** can be found in the Supporting Information.

(*R*)-1,1′-Binaphthalene-2,2′-bis(diphenylphosphinate) (5)

A solution of (*R*)-BINOL (2.86 g, 10 mmol) and NaH (*ca.* 60% w/w oil suspension) (0.880 g, 22 mmol) in THF (50 mL) was stirred for 15 min at 0 °C under a nitrogen atmosphere. To this solution was slowly added diphenylphosphinic chloride (4.19 mL, 22 mmol) at 0 °C. The mixture was stirred for 15 min at 0 °C, then warmed to room temperature, and stirred for 3 h. The resulting mixture was cooled in an ice bath, diluted with ether (100 mL) and then water (100 mL). The product was extracted with ether (30 mL × 2) and washed by brine (20 mL). The combined extracts were dried over $MgSO_4$. The organic phase was concentrated under reduced pressure to give the crude product [(*R*)-**5**] in quantitative yield (6.86 g). This crude was used to next rearrangement without further purification.

(*R*)-3,3′-Bis(diphenylphosphinoyl)-BINOL (3)

To a solution of $i\text{-}Pr_2NH$ (19.2 mL, 137 mmol) in THF (50 mL) was added *n*-BuLi (86.7 mL of 1.58 M solution in hexane) at −78 °C under a nitrogen atmosphere. After 30 min at −78 °C, to this solution was slowly added the THF solution (100 mL) of (*R*)-**5** (13.6 mmol, 9.33 g) *via* cannula. The mixture was stirred for 3 h at −78 °C. The resulting mixture was diluted with ether (50 mL), with brine (50 mL), and with 1 M HCl to acidify it to *ca.* pH 1. The product was extracted with ether (30 mL × 2) and washed by brine (20 mL). The combined extracts were dried over $MgSO_4$. The organic phase was concentrated under reduced pressure to give the crude product. Recrystallization from toluene/hexane (1/5) gave (*R*)-**3** as colorless crystals in quantitative yield (9.33 g).

General Procedure for the Enantioselective Diethylzinc Addition to Aldehydes (Tables 1 and 2)

A solution of (*R*)-**3** (0.1 mmol) in THF (3 mL) was stirred in a pyrex Schlenk tube at room temperature for 5 min under a nitrogen atmosphere. To the solution was added Et_2Zn (2.7 mL of 1.10 M solution in toluene) at −78 °C. This solution was stirred for 30 min, and aldehyde (**1**) (1 mmol) was added. The resulting mixture was then gradually warmed to room temperature or 50 °C, and stirred for 0.1–24 h. After hydrolysis with 10 mL of saturated NH_4Cl aqueous solution, the product was extracted with ether (10 mL × 3) and washed by brine (10 mL). The combined extracts were dried over $MgSO_4$. The organic phase was concentrated under reduced pressure and the crude product was purified by neutral silica gel column chromatography (eluent: hexane/EtOAc or pentane/ether), to give the desired products **2**. The enantiomeric purity was determined by GC or HPLC on chiral column.

X-Ray Crystallographic Study

The single crystal was grown from a dichloromethane-hexane mixed solution at room temperature. The X-ray crystallographic analysis was performed with a Bruker SMART APEX diffractometer (graphite monochromator, MoKα radiation, λ = 0.71073 Å). The structure was solved by direct methods and expanded using Fourier techniques.

Crystal data for (*R*)-3,3′-bis(diphenylphosphinoyl)-BINOL [(*R*)-3]: formula $C_{264}H_{192}O_{24}P_{12}$, colorless, crystal dimensions $0.20 \times 0.20 \times 0.10$ mm^3, monoclinic, space group *C*2 (#5), $a = 10.709(5)$ Å, $b = 18.515(5)$ Å, $c = 53.426(5)$ Å, $\beta = 90.282(5)^\circ$, $V = 10593(6)$ Å^3, $Z = 2$, $\rho_{calc} = 1.292$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 0.167$ mm^{-1}, $T = 173$ K. 25528 reflections were independent and unique, and 21519 with $I > 2\sigma(I)$ ($2\theta_{max} = 29.31^\circ$) were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. $R = 0.0555$ and $Rw = 0.1320$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-262636. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336–033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal data for $[Zn_4\{(R)\text{-3,3′-bis}(Ph_2P{=}O)\text{-BINOLate}\}_3(\mu_4\text{-O})]\cdot(CH_2Cl_2)_3$ (11): formula $C_{132}H_{90}O_{13}P_6Zn_4\cdot C_3H_6Cl_6$, yellow, crystal dimensions $0.25 \times 0.20 \times 0.15$ mm^3, monoclinic, space group $P2_1$ (#4), $a = 15.803(3)$ Å, $b = 22.033(4)$ Å, $c = 19.949(3)$ Å, $\beta = 103.148(4)^\circ$, $V = 6763.9(19)$ Å^3, $Z = 2$, $\rho_{calc} = 1.270$ g cm^{-3}, $\mu(\text{MoK}\alpha) = 0.946$ mm^{-1}, $T = 223$ K. 33967 reflections were independent and unique, and 22259 with $I > 2\sigma(I)$ ($2\theta_{max} = 29.21^\circ$) were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. $R = 0.0709$ and $Rw = 0.1812$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-261552. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336–033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

Financial support for this project was provided by the JSPS. KAKENHI (15205021) and the 21st Century COE Program "Nature-Guided Materials Processing" of MEXT.

References and Notes

[1] R. Noyori, M. Kitamura, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 40–69.

[2] For reviews, see: a) K. Soai, S. Niwa, *Chem. Rev.* **1992**, *92*, 833–856; b) L. Pu, H.-B. Yu, *Chem. Rev.* **2001**, *101*, 757–824; c) L. Pu, *Tetrahedron* **2003**, *59*, 9873–9886.

[3] a) B. Schmidt, D. Seebach, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 99–101; b) B. Schmidt, D. Seebach, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1321–1323; c) D. Seebach, A. K. Beck, B. Schmidt, Y. M. Wang, *Tetrahedron* **1994**, *50*, 4363–4384; d) B. Weber, D. Seebach, *Tetrahedron* **1994**, *50*, 7473–7484; e) D. Seebach, A. Pichota, A. K. Beck, A. B. Pinkerton, T. Litz, J. Karjalainen, V. Gramlich, *Org. Lett.* **1999**, *1*, 55–58.

[4] P. J. Walsh, *Acc. Chem. Res.* **2003**, *36*, 739–749.

[5] M. Mori, T. Nakai, *Tetrahedron Lett.* **1997**, *38*, 6233–6236.

[6] a) F.-Y. Zhang, C.-W. Yip, R. Cao, A. S. C. Chan, *Tetrahedron: Asymmetry* **1997**, *8*, 585–589; b) F.-Y. Zhang, A. S. C. Chan, *Tetrahedron: Asymmetry* **1997**, *8*, 3651–3655.

[7] a) K. Ding, A. Ishii, K. Mikami, *Angew. Chem. Int. Ed.* **1999**, *38*, 497–501; b) K. Mikami, M. Terada, T. Korenaga, Y. Matsumoto, M. Ueki, R. Angeland, *Angew. Chem. Int. Ed.* **2000**, *39*, 3532–3556; c) K. Mikami, R. Angeland, K. Ding, A. Ishii, A. Tanaka, N. Sawada, K. Kudo, M. Senda, *Chem. Eur. J.* **2001**, *7*, 730–737; d) A. M. Costa, C. Jimeno, J. Gavenonis, P. J. Carroll, P. J. Walsh, *J. Am. Chem. Soc.* **2002**, *124*, 6929–6941; e) K. Ding, H. Du, Y. Yuan, J. Long, *Chem. Eur. J.* **2004**, *10*, 2872–2884.

[8] a) K. Maruoka, N. Murase, H. Yamamoto, *J. Org. Chem.* **1993**, *58*, 2938–2939; b) K. Ishihara, H. Yamamoto, *J. Am. Chem. Soc.* **1994**, *116*, 1561–1562.

[9] a) H. Kitajima, K. Ito, T. Katsuki, *Chem. Lett.* **1996**, 343–344; b) H. Kitajima, K. Ito, T. Katsuki, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 207–217; c) W.-S. Huang, Q.-S. Hu, L. Pu, *J. Org. Chem.* **1998**, *63*, 1364–1365; d) H. Kodama, J. Ito, A. Nagaki, T. Ohta, I. Furukawa, *Appl. Organometal. Chem.* **2000**, *14*, 709–714; e) Z.-B. Li, L. Pu, *Org. Lett.* **2004**, *6*, 1065–1068.

[10] a) Y. Hamasima, D. Sawada, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **1999**, *121*, 2641–2642; b) M. Kanai, Y. Hamashima, M. Takamura, M. Shibasaki, *J. Synth. Org. Chem. Jpn.* **2001**, *59*, 766–778.

[11] Precedent examples have been limited to phosphoramide [$R_nN_{3-n}P(=O)$] or thiophosphoramide [$R_nN_{3-n}P(=S)$]; a) K. Soai, Y. Hirose, Y. Ohno, *Tetrahedron: Asymmetry* **1993**, *4*, 1473–1474; b) R. Hulst, H. Heres, K. Fitzpatrick, N. C. M. W. Peter, R. M. Kellogg, *Tetrahedron: Asymmetry* **1996**, *7*, 2755–2760; c) T. Shibata, H. Tabira, K. Soai, *J. Chem. Soc. Perkin Trans. 1* **1998**, 177–178; d) J.-M. Brunel, T. Constantieux, O, Legrand, G. Buono, *Tetrahedron Lett.* **1998**, *39*, 2961–2964; e) O. Legrand, J.-M. Brunel, G. Buono, *Tetrahedron Lett.* **1998**, *39*, 9419–9422; f) M. Shi, W.-S. Sui, *Tetrahedron: Asymmetry* **1999**, *10*, 3319–3325; g) O. Legrand, J.-M. Brunel, G. Buono, *Tetrahedron Lett.* **2000**, *41*, 2105–2109; h) M. Shi, W.-S. Sui, *Chirality* **2000**, *12*, 574–580.

[12] Compound **3** was synthesized *via* asymmetric oxidative biaryl coupling with chiral Cu catalyst in 29% and 96% ee: X. Li, J. Hewgley, C. A. Mulrooney, J. Yang, M. C. Konzlowski, *J. Org. Chem.* **2003**, *68*, 5500–5511.

[13] T.-L. Au-Yeung, K.-Y. Chan, R. K. Haynes, I. D. Williams, L. L. Yeung, *Tetrahedron Lett.* **2001**, *42*, 453–456.

[14] T.-L. Au-Yeung, K.-Y. Chan, R. K. Haynes, I. D. Williams, L. L. Yeung, *Tetrahedron Lett.* **2001**, *42*, 457–460.

[15] H. Takaya, K. Mashima, K. Koyano, M. Yagi, H. Kumobayashi, T. Taketomi, S. Akutagawa, R. Noyori, *J. Org. Chem.* **1986**, *51*, 629–635.

[16] a) D. P. Young, W. E. McEwen, D. C. Velez, J. W. Johnson, C. A. VanderWerf, *Tetrahedron Lett.* **1964**, *5*, 359–364; b) C. J. Chapman, C. G. Frost, M. P. Gill-Carey, G. Kociok-Köhn, M. F. Mahon, A. S. Weller, M. C. Willis, *Tetrahedron: Asymmetry* **2003**, *14*, 705–710.

[17] a) H. Wally, M. Widhalm, W. Weissensteiner, K. Schlögl, *Tetrahedron: Asymmetry* **1993**, *4*, 285–288; b) W.-S. Huang, L. Pu, *J. Org. Chem.* **1999**, *64*, 4222–4223.
[18] Pioneering work of diphenylzinc transfer: a) C. Bolm, N. Hermanns, J. P. Hildebrand, K. Muñiz, *Angew. Chem. Int. Ed.* **2000**, *39*, 3465–3467; b) C. Bolm, M. Kesselgruber, N. Hermanns, J. P. Hildebrand, G. Raabe, *Angew. Chem. Int. Ed.* **2001**, *40*, 1488–1490; c) C. Bolm, J. P. Hildebrand, K. Muñiz, N. Hermanns, *Angew. Chem. Int. Ed.* **2001**, *40*, 3284–3308; d) J. Rudolph, T. Rasmussen, C. Bolm, P.-O. Norrby, *Angew. Chem. Int. Ed.* **2003**, *42*, 3002–3005.
[19] For **12**, a 3:3 Zn(II):(*R*)-**3** complex similar to the structure reported by Katsuki cannot be ruled out completely. See ref.[9b]
[20] We cannot explain the stereoselectivities by the similar mechanism with *N,N,N′,N′*-tetraalkyl-BINOL-3,3′-dicarboxamides postulated by Katsuki, because the steric repulsions between aldehyde and phenyl group in the diphenylphosphinoyl moiety are not clear in any transition states with our ligand **3**. See ref.[9b]
[21] W.-S. Huang, Q.-S. Hu, L. Pu, *J. Org. Chem.* **1999**, *64*, 7940–7956.
[22] W.-S. Huang, L. Pu, *Tetrahedron Lett.* **2000**, *41*, 145–149.
[23] E. J. Corey, T. W. Lee, *Chem. Commun.* **2001**, 1321–1329.

