Chiral (η^6-Arene)chromium Complexes in Organic Synthesis: Stereoselective Synthesis of Chiral (Arene)chromium Complexes Possessing Amine and Hydroxy Groups and Their Application to Asymmetric Reactions

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Received June 10, 1992

Optically active (1,2-disubstituted arene)chromium complexes with an amine and a hydroxy group in the two ortho benzylic positions were stereoselectively synthesized from a commercially available $\alpha(R)$-phenylethylamine. These chiral chromium complexes can be used as chiral ligands in a catalytic asymmetric ethylation of benzaldehyde with diethylzinc. Also, moderate enantioselectivity was observed in the 1,4-conjugated addition reaction of chalcone.

Introduction

The development of catalytic enantioselective reactions is now recognized as one of the most important and challenging problems in organic synthesis. Nucleophilic addition of organometallic reagents to carbonyl substrates constitutes one of the most fundamental operations. Modification of the organometallic compounds by chiral, nonracemic auxiliaries offers a general way to create optically active alcohols, and the catalytic version in particular provides maximum synthetic efficiency. The use of organozinc compounds allows catalytic enantioselective alkylation of aldehydes leading to a diverse array of secondary alcohols of high optical purity. Several groups have reported that the chiral amino alcohols not only accelerate the alkylation of aldehydes with dialkylzinc compounds but also direct the stereochemical outcome in an absolute sense.[1] Chiral β-amino alcohols have been most effective for the preparation of secondary alcohols with high optical purity, presumably owing to the formation of cyclic five-membered transition states by a coordination of the zinc metal with two heteroatoms. Also, an enantioselective conjugate addition of organometallic reagents to enones affords a useful synthetic approach to optically active β-substituted ketones.[2,3] Recently, chiral β-amino alcohols and related compounds have been used for the catalytic or stoichiometric enantioselective addition reactions to α,β-unsaturated enones in the presence of transition metals.[4]

In addition to the chiral center in the asymmetric ligands, planar chirality is also an important factor for the achievement of high enantioselectivity in the catalytic asymmetric reactions. (η^6-Arene)chromium complexes can exist in two enantiomeric forms, when the phenyl ring is substituted by two different substituents at ortho- or meta-positions. We report herein stereoselective synthesis of the chiral (1,2-disubstituted arene)chromium complexes having γ- or δ-amino alcohols and their effectiveness as chiral ligands.

Stereoselective Synthesis of Chiral (η^6-Arene)-chromium Complexes with Amine and Hydroxy Groups. Directed lithiation of the (arene)chromium complexes occurred easily at low temperature, and in some cases resulted in high regioselectivity.[5] Diastereoselective ortho lithiation of tricarbonyl(*N*,*N*-dimethyl-$\alpha(R)$-phenylethylamine)chromium (1) with *t*-BuLi in ether at −78 °C and followed by reaction with ketones gave exclusively one diastereomeric complex **3** (R = C_6H_5, Et) in good yield derived from the lithiated compound **2** at one proton (H^b) of two diastereomeric ortho positions according to literature methods.[6,7]

The stereochemistry at the newly created α'-benzylic position was examined by reactions of **2** with aldehydes

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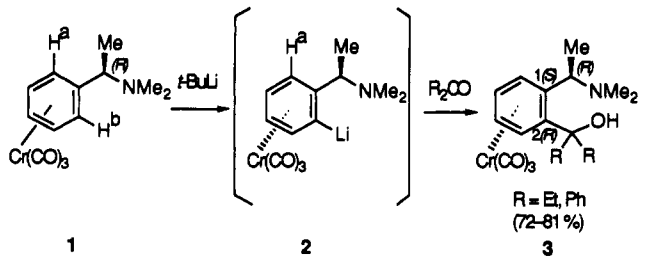
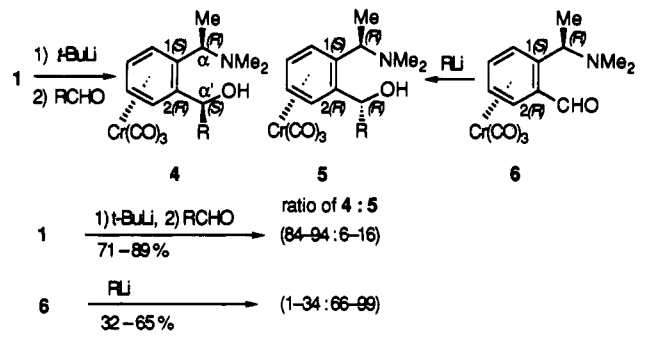
Scheme I



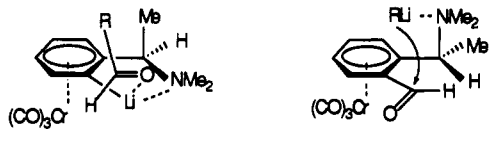
1 2 3

Scheme II. Diastereoselective Synthesis of Stereoisomeric Complexes



4 5 6

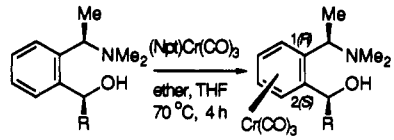
instead of ketones. Surprisingly, reaction[8] of the ortho-lithiated chromium complex **2** with aldehydes gave predominantly Ar(1*S*,2*R*), $\alpha(R)$,$\alpha'(S)$-chromium complex[9] **4** accompanied by $\alpha'(R)$-stereoisomeric complex **5** in a ratio of 88–92:12–8 (Scheme II). Stereochemistry of the major complex **4** (R = C_6H_5) was determined by X-ray crystallography, and the newly created stereogenic center at α'-position was found to possess the *S*-configuration (see X-ray **4** data). Thus, the *re*-face of the aldehydes was attacked in the proposed most stable transition state **7** with an exo-orientation of the R group of the aldehydes giving the α' (*S*)-complexes **4**. The alternative transition state with an endo-R group has a severe steric interaction between the R and $Cr(CO)_3$ groups.



7 8

On the other hand, the corresponding stereoisomeric complexes **5** with the *R*-configuration at the α'-benzylic position were easily prepared by reaction of the Ar(1*S*,2*R*)-tricarbonyl[(*o*-[$\alpha(R)$-(*N*,*N*-dimethylamino)ethyl]benzaldehyde]chromimum (**7**) with organolithiums. The selectivities in reaction with the sterically bulky organolithium compounds such as *i*-PrLi or *t*-BuLi were increased (ratio of **4:5**, 1–4:99–96). These two reactions provide versatile approaches for synthesis of the (arene)chromium complexes with two stereogenic centers at the both benzylic positions and are complementary with respect to stereochemistry at the newly created α'-position. The following

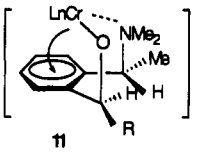
Scheme III. Preparation of Face-Inverted Chromium Complexes



9 10

transition state **8** would be proposed for the α' (*R*)-chromium complexes **5**. It is well known that a conformation of the benzylic carbonyl oxygen is preferred as an anti-form[10] to the ortho substituents due to a stereoelectronic effect in (ortho-substituted benzaldehyde or acetophenone)chromium complexes. The anti-conformation of these complexes is also supported even in a solution by the results of stereoselective nucleophilic additions[11,12] of alkyllithiums or hydrides to the benzylic carboxyl and a correlation[13] with the sign of optical rotation of the optically active arene chromium complexes. Therefore, the *o*-formyl complex **6** is proposed to exist in the conformation **8** with the formyl oxygen anti to the α-(dimethylamino)ethyl group, in which organolithiums react from the exo-side via a coordination of the lithium with the nitrogen atom.

The corresponding chromium complexes stereoisomers with respect to the aromatic face chirality were also prepared. Recomplexation of the air-oxidized compound **9** (R = Et) derived from **4** by a ligand-transfer reaction[14] with (naphthalene)$Cr(CO)_3$ produced exclusively the face-inverted chromium complex **10** (R = Et) in a ratio of 99:1 (Scheme III). The extremely high stereoselective chromium complexation resulted from an anchoring interaction between the chromium and two heteroatoms in a sterically most favored conformation **11**.



11

The corresponding chiral diamino alcohol chromium complex which contains an additionally potentially coordinating nitrogen atom on the side chain was prepared by a similar method (Scheme IV). Diastereoselective lithiation of the chromium complex **13** and subsequent reaction with diethyl ketone produced the corresponding 1,2-disubstituted arene complex **14**.

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(9) This nomenclature is based on the Cahn–Ingold–Prelog rule; see the following references: (a) Solladié-Cavallo, A. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1, pp 99–133. (b) Schlögl, K. *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Willey-Interscience: New York, 1967; Vol. 1. (c) Pairo, G.; Panuzi, A. *J. Am. Chem. Soc.* **1964**, *86*, 5148.

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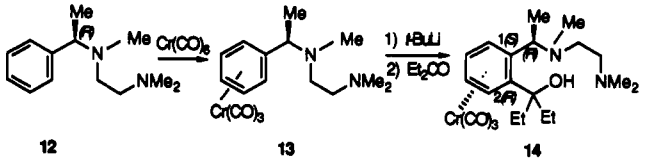
(13) The correlation between the sign of optical rotation and the absolute configuration can be easily explained by the reasonable model; see ref 9a.

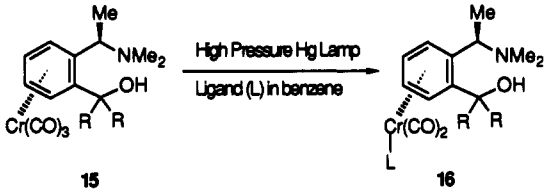
(14) (a) Uemura, M.; Minami, T.; Hayashi, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5277. Uemura, M.; Kobayashi, T.; Minami, T.; Hayashi, Y. *Tetrahedron Lett.* **1986**, *27*, 2479. Uemura, M.; Kobayashi, T.; Isobe, K.; Minami, T.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 2859. (b) Kündig, E. P.; Perret, C.; Spichinger, S.; Bernardienelli, G. *J. Organomet. Chem.* **1985**, *286*, 183. Kündig, E. P.; Desobry, V.; Grivet, C.; Rudolph, B.; Spichinger, S. *Organometallics*, **1987**, *6*, 4505.

Scheme IV



12 13 14

Table I. Ligand-Exchange Reaction by Irradiation



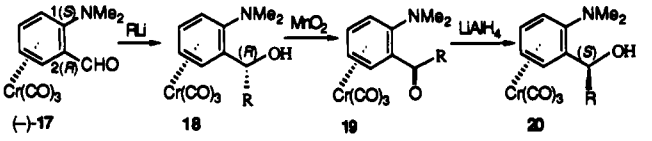
15 16

entry	complex 15	ligand (L)	yield (%)
1	R^1 = H, R^2 = Et	PPh_3	70
2	R^1 = H, R^2 = Et	$P(OPh)_3$	65
3	R^1 = R^2 = Et	PPh_3	66
4	R^1 = R^2 = Et	$P(OPh)_3$	60
5	R^1 = R^2 = C_6H_5	PPh_3	73

The properties of arenechromium complexes are significantly influenced by the ligands on the chromium metal, and, therefore, reactivities and selectivites in asymmetric reactions would be expected to be significantly influenced. One tricarbonyl ligand on the chromium atom of the (η^6-arene)chromium complexes could be easily exchanged with the other ligands. (η^6-Arene)chromium complexes with an electron-donating phosphine or phosphite ligand **16** were synthesized from the corresponding tricarbonyl ligand **15** by irradiation in benzene solution with a high-pressure mercury lamp[15] (Table I).

Since three types of the chiral (1,2-disubstituted arene)-chromium complexes with amine and hydroxy groups at both benzylic positions have been stereoselectively prepared in optically active forms, we next prepared optically active (arene)chromium complexes with the γ-amino alcohol as the chiral ligands. These chiral ligands would be formed by 6-membered transition states in the catalytic asymmetric ethylation of the aldehydes with diethylzinc. Racemic [*o*-(*N*,*N*-dimethylamino)benzaldehyde]$Cr(CO)_3$ was reacted with L-valinol to give the corresponding diastereomeric imine complexes, which were easily separated by column chromatography according to Davies' method.[16b] The resolved (1*S*,2*R*) (−)-chromium complex **17** was reacted with methyllithium at −78 °C in ether to afford predominantly one diastereomeric complex **18** (R = Me), accompanied by stereoisomeric complex **20** (R = Me) in a ratio of 92:8 in 86% yield (Table II). The absolute stereochemistry of the newly created benzylic position was determined as α (*R*) based on the analogous anti-transition state **8** (anti: C=O/NMe_2) as described previously. The corresponding stereoisomeric α (*S*)-complex **20** (R = Me) was stereoselectively prepared from **18** (R = Me) by oxidation[17] with active manganeses dioxide and subsequent reduction with $LiAlH_4$, although the yield in the oxidation step was very low.

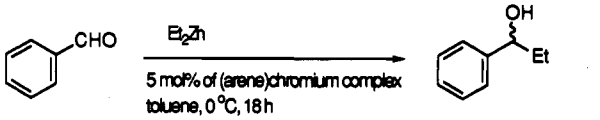
Table II. Preparation of (Ortho-substituted dimethylaniline)chromium Complexes 18 and 20



(−)-17 18 19 20

entry	complex	nucleophile	ratio 18:20	yield (%)
1	17	MeLi	92:8	86
2	17	C_6H_5Li	73:27	88
3	19 (R = Me)	$LiAlH_4$	1:99	63

Table III. Enanioselective Ethylation of Benzaldehyde with Diethylzinc Catalyzed by Chiral (Arene)chromium Complexes



entry	complex	yield (%)	% ee	absolute config
1	3 (R = H)	70	15	*S*
2	3 (R = Et)	89	95	*S*
3	3 (R = C_6H_5)	83	93	*S*
4	4 (R = Me)	83	63	*S*
5	4 (R = Et)	87	93	*S*
6	4 (R = *i*-Pr)	78	81	*S*
7	4 (R = C_6H_5)	82	83	*S*
8	4 (R = C_6F_5)	98	87	*S*
9	4 (R = *o*-MeC_6H_4)	95	81	*S*
10	4 (R = *o*-$CF_3C_6H_4$)	97	89	*S*
11	4 (R = *m*-$MeOC_6H_4$)	98	82	*S*
12	4 (R = *m*-$CF_3C_6H_4$)	96	89	*S*
13	4 (R = α-naphthyl)	96	78	*S*
14	5 (R = Et)	87	50	*S*
15	5 (R = *t*-Bu)	0		
16	9 (R = Et)	69	24	*S*
17	10 (R = Et)	82	29	*R*
18	14	43	1	*S*
19	16 (R^1 = R^2 = Et, L = PPh_3)	99	97	*S*
20	16 (R^1 = R^2 = C_6H_5, L = PPh_3)	99	94	*S*
21	16 (R^1 = R^2 = Et, L = $P(OPh)_3$)	96	97	*S*
22	16 (R^1 = H, R^2 = Et, L = PPh_3)	97	96	*S*
23	16 (R^1 = H, R^2 = Et, L = $P(OPh)_3$)	96	97	*S*
24	18 (R = Me)	49	6	*S*
25	18 (R = C_6H_5)	58	11	*S*
26	20 (R = Me)	56	12	*S*

Enantioselective Addition of Dialkylzinc to Aldehydes Catalyzed by Chiral (Arene)chromium Complexes. Among the various organometallic compounds, diorganozinc reagents act as ideal alkyl donors for catalytic asymmetric alkylation. In ordinary hydrocarbon or ethereal solvents, dialkylzinc compounds do not react with aldehydes. However, in the presence of catalytic amounts of sterically congested chiral β-dialkylamino alcohols, aldehydes can be alkylated with dialkylzinc to give secondary alcohol in high enantioselectivity.[1] Reaction of the diethylzinc with benzaldehyde was carried out in the presence of the chiral (1,2-disubstituted arene)-chromium complexes in order to examine the structural effect of the complexes upon enantioselectivity. Reaction was carried out in toluene at 0 °C for 18 h in the presence of 5 mol % of the chiral (arene)chromium complexes (Table III).

First, we examined catalytic and stereoselective activities of the chiral (arene)chromium complexes **3** without the chiral center at the α'-position bearing the hydroxy group. Complex **3** with an ethyl or phenyl group gave α(*S*)-phenylpropyl alcohol in good yield and high enantiose-

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(17) Jaouen, G.; Meyer, A. *J. Am. Chem. Soc.* **1975**, *97*, 4668.

lectivity (entries 2, 3).[18] These chiral ligands afforded high enantiomeric excess in the asymmetric ethylation of benzaldehyde with diethylzinc, regardless of the δ-amino alcohols. However, the unsubstituted complex **3** (R = H) at the α′-position exhibited very low selectivity (15.2% ee) (entry 1).

The effect of chirality at the benzylic alcohol moiety in the ligands was next examined in the enantioselective ethylation of benzaldehyde. It is known that the degree of enantioselectivity induced by β-amino alcohols as the chiral ligand depends on the bulk of substituents on the carbon bearing hydroxyl, and the absolute configuration of the products is related to the chirality of the alcohol moiety of the ligands.[1] Complexes **4** with the α′(*S*)-configuration gave a high degree of enantioselectivity in the catalytic ethylation of benzaldehyde giving the α(*S*)-phenylpropyl alcohol. Particularly, the (*S*)-ethyl substituent complex at the α′-position was most effective. The complexes with methyl or sterically bulky substituents, e.g., aromatics and isopropyl, at the α′-position resulted in lower enantioselectivities. The tridentate chiral ligand **14** with two nitrogen atoms gave no asymmetric induction and lower yields due to a steric hindrance (entry 18). The corresponding chromium-free chiral amino alcohol **9** (R = Et) resulted in less efficient 24% ee giving the (*S*)-product (entry 16). Thus, $Cr(CO)_3$ complexation of the ligands and a proper steric size of the substituents at the alcohol moiety have a large effect on the enantioselectivity.

On the other hand, stereoisomeric α′ (*R*)-chromium complexes **5** are less effective in producing the same (*S*)-alcohol (entry 14). Since both stereoisomeric chromium complexes **4** and **5** gave the same (*S*)-alcohol, the direction of the asymmetric induction is independent of the chirality of alcohol moiety in the chromium complexes. From these results, the chromium complexes with the (*S*)-configuration or disubstituents at the benzylic hydroxy position are significant for the achievement of high enantioselectivity in the catalytic ethylation. Similar results were also obtained with chiral ferrocenyl complexes of δ-amino alcohols which catalyzed ethylation of aldehydes in high enantioselectivity, regardless of the chirality of the position bearing the hydroxyl group.[19] In contrast to the Ar(1*S*,2*R*) complexes **4**, the face-inverted Ar(1*R*,2*S*)-chromium complex **10** gave the (*R*)-alcohol in 25% ee (entry 17). Thus, the face chirality of the (arene)chromium complexes determines the absolute configuration of the product.

The effect of electron-donating ligands on the chromium complexes was examined in the catalytic asymmetric ethylation. The enantioselectivities and yields of the catalytic asymmetric ethylation of benzaldehyde with diethylzinc with chromium complex **16** possessing triphenylphosphine or triphenyl phosphite increased (entries 19–23).

The three-dimensional structure of chromium complex **4** (R = C_6H_5) determined by X-ray crystallography[20] is shown in Figure 1. Both the benzylic hydroxy and amino

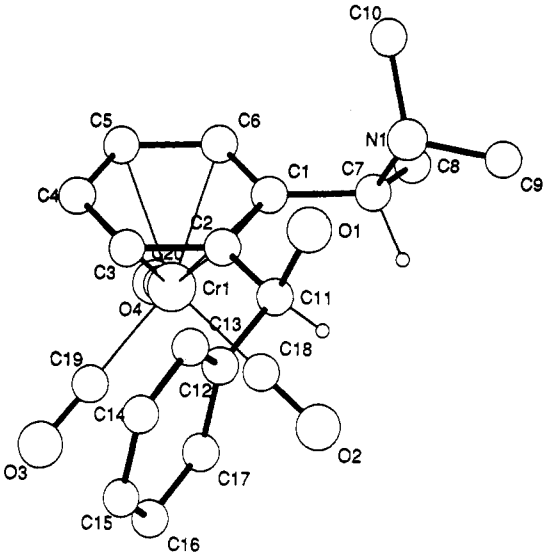
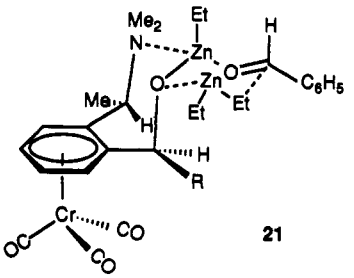


Figure 1. Molecular structure of **4** (R = C_6H_5).

groups are directed in the exo-orientation to the $Cr(CO)_3$ group due to an electronic effect. The N···O bond distance is 2.717 Å, and the zinc metal can easily coordinate with the nitrogen and hydroxyl groups. A proposed transition state **21** for the enantioselective addition of diethylzinc to an aldehyde with chromium complexes **4** is postulated as follows. The zinc alkoxide is formed as a seven-membered ring in the exo-configuration to avoid a severe steric interaction with the $Cr(CO)_3$ and α′-benzylic substituent groups. The ethylation can be interpreted in terms of a six-membered cyclic transition state with an equatorial orientation of the phenyl ring of the benzaldehyde, attacking the *si*-face of the aldehydes.



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We next examined the effectiveness of homologous γ-amino alcohol (arene)chromium complexes as chiral ligands, which would form 6-membered transition states. Unfortunately, both stereoisomeric chromium complexes **18** and **20** resulted in poor enantioselectivities. These results could be attributed to the unfavorable coordination ability of the zinc with two hetero atoms due to a smaller ring size. The asymmetric ethylation of aliphatic aldehydes catalyzed by the diphenyl complex **3** (R = Ph) resulted in lower enantioselectivities than those observed with benzaldehyde.[21]

In conclusion, the direction of $Cr(CO)_3$ complexation, the chirality of benzylic alcohol moiety, and the coordinating ring size of the chiral (1,2-disubstituted arene)-chromium complexes are important factors in the catalytic

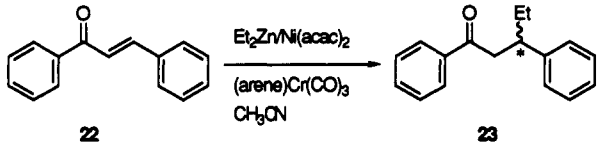
(18) A preliminary communication: Uemura, M.; Miyake, R.; Hayashi, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1696.

(19) Watanabe, M.; Araki, S.; Butsugan, Y.; Uemura, M. *J. Org. Chem.* **1991**, *56*, 2218.

(20) Crystal data for **4** (R = C_6H_5) (from ether/hexane): $C_{20}H_{21}NO_4Cr$; FW 391.40, orthorhobic, space group $P2_12_12_1$, a = 13.305 (2) Å, b = 14.450 (2) Å, c = 10.179 (1) Å, V = 1957.0 (5) Å^3, Z = 4, ρ (calcd) = 1.328 g·cm^{-3}, μ (Cu Kα) = 50.72 cm^{-1}, T = 298 K. Structure solved by the heavy-atom method, 1908 measured reflections, of which 1606 are considered as observed ($F_o > 3\sigma(F_o)$). Final residues: R = 0.057, R_w = 0.079.

(21) Reaction results of some aldehydes are as follows; (*E*)-C_6H_5-CH=CHCHO (95% yield, 73% ee, *S*), $C_6H_5(CH_2)_2CHO$ (89% yield, 54% ee, *S*), $CH_3(CH_2)_5CHO$ (86% yield, 42% ee, *S*).

Table IV. Enantioselective Conjugate Addition to Chalcone Catalyzed by Ni(II)/(arene)Cr(CO)$_3$ System



22 23

entry	(arene)Cr(CO)$_3$	mol % Ni(acac)$_2$	ratio of Ni(II):(arene)Cr(CO)$_3$	yield (%)	% ee (config)
1	**3** (R = Et)	5	1:10	92	1 (*R*)
2[a]	**3** (R = Et)	7	1:2.5	83	1 (*R*)
3	**3** (R = Et)	100	1:1	70	37 (*R*)
4	**3** (R = C_6H_5)	10	1:10	83	44 (*R*)
5	**3** (R = C_6H_5)	100	1:1	71	62 (*R*)
6	**4** (R = Et)	5	1:10	91	43 (*R*)
7	**4** (R = Et)	100	1:1	72	53 (*R*)
8	**4** (R = C_6H_5)	1	1:10	66	36 (*R*)
9	**4** (R = C_6H_5)	5	1:10	90	62 (*R*)
10	**4** (R = C_6H_5)	100	1:1	70	78 (*R*)
11	**5** (R = Et)	100	1:1	78	50 (*R*)

[a] Presence of 7 mol % of dipyridyl.

asymmetric ethylation of benzaldehyde.[22] The electron-donating phosphine and phosphite ligands on the chromium metal are significant for the achievement of high selectivity.

Enantioselective Conjugate Addition of Diethylzinc to α,β-Unsaturated Enones. Enantioselective conjugate additions of organometallic reagents to prochiral enones afford synthetically useful optically active β-substituted ketones. Rapid progress has been made recently in the field by modifying the organocopper reagents with nontransferable chiral ligands. In some cases, the enantioselective conjugate additions of organocopper reagents have been achieved by addition of chiral ligands.[3] However, most studies have employed stoichiometric conditions. A more attractive approach would effect enantioselective conjugate addition by use of catalytic amounts of the chiral ligands. It was recently reported[4,23] that the chiral β-amino alcohols and related compounds catalyze the conjugate addition of the dialkylzincs to enones in the presence of transition metals. We now report herein reactivities and enantioselectivities in the asymmetric conjugate addition of diethylzinc with the chiral (arene)-chromium complexes as the chiral ligands.

Conjugate addition reactions were carried out in acetonitrile at −30 °C with 2 equiv of diethylzinc in the presence of a chiral Ni(II) catalyst, generated in situ by mixing of Ni(acac)$_2$ and the chiral (arene)Cr(CO)$_3$ (Table IV). The diethyl-substituted complex **3** (R = Et), the most efficient ligand for the asymmetric ethylation of benzaldehyde, gave a racemic 1,3-diphenylpentan-1-one (**23**) under catalytic conditions with 5 mol % of Ni(acac)$_2$ and 50 mol % of the chromium complex (entry 1). Use of stoichiometric amounts of the Ni(II) and the complex **3** (R = Et) produced the (*R*)-conjugate addition product in 37% ee (entry 3). The asymmetric induction is highly dependent on the amount of the chiral catalyst. The corresponding diphenyl-substituted complex **3** (R = C_6H_5) resulted in higher selectivity. Among the (*S*)-configuration complexes, the phenyl-substituted complex **4** (R = C_6H_5) is an efficient chiral ligand for conjugate addition in both catalytic (62% ee) and stoichiometric (78% ee) reactions (entries 8–10).

Since it is possible to modify the chiral ligands, it seems that there is considerable opportunity for further improvement in this class of the chiral (arene)chromium complexes.

(22) Also, chromium complexation of norephedrine gave higher % ee in asymmetric ethylation to aldehyde than the corresponding chromium free ligand: Heaton, S. B.; Jones, G. B. *Tetrahedron Lett.* **1992**, *33*, 1693.

(23) Addition of diorganozinc to enones is known to be catalyzed by Ni(acac)$_2$ to give a racemic product: Green, A. E.; Lansard, J. P.; Luche, J. L.; Petrier, C. *J. Org. Chem.* **1984**, *49*, 931.

Experimental Section

All manipulations involving organometallics were carried out under an atmosphere of nitrogen or argon and using an inert gas/vaccum double-manifold techniques. Cr(CO)$_6$ was obtained from Strem Chemicals and used as received. Ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl immediately before use, and toluene was distilled from sodium metal. ^{1}H NMR spectra (δ) were measured at 90 or 400 MHz. *J* values are given in Hz. All melting points are uncorrected. Optical rotations were obtained on a JASCO DIP-370 automatic polarimeter at wavelength 589 nm (sodium D line) using a 1.0-dm cell with a total volume of 3 mL.

Tricarbonyl(*N*,*N*-dimethyl-α(*R*)-phenylethylamine)chromium (1). Optically active (*R*)-chromium complex **1** was prepared according to the previous method for the racemic form.[6,7] A mixture of *N*,*N*-dimethyl-α(*R*)-phenylethylamine (5.0 g, 33.5 mmol), Cr(CO)$_6$ (8.1 g, 36.9 mmol) in dibutyl ether (300 mL), heptane (30 mL), and THF (30 mL) was heated at 120–130 °C with stirring under nitrogen for 40 h. After being cooled to rt, the reaction mixture was evaporated under aspirator vacuum to remove solvents and the excess chromium hexacarbonyl. The yellow residue was dissolved in ether, and the precipitate was filtered off and washed with ether. The organic layer was evaporated in vacuo. The residue was chromatographed on silica gel with ether/hexane to give chromium complex **1** (3.34 g, 34%): mp 43 °C (recrystallization from ether/hexane); ^{1}H NMR ($CDCl_3$) 1.27 (3 H, d, *J* = 7), 2.19 (6 H, s), 3.40 (1 H, q, *J* = 7), 5.09–5.46 (5 H, m); IR ($CHCl_3$) 1960, 1880, 1460, 1260 cm^{-1}; $[\alpha]^{24}_D$ +14.4° (*c* = 0.78, $CHCl_3$). Anal. Calcd for $C_{13}H_{15}NO_3Cr$: C, 54.74; H, 5.30; N, 4.91. Found: C, 54.94; H, 5.32; N, 4.80.

Preparation of Chromium Complexes 3 and 4 via Ortho-Lithiation of 1. Ortho-lithiation of **1** was carried out under previously reported conditions.[6,7] A typical procedure is as follows. To a solution of **1** (200 mg, 0.70 mmol) in ether (10 mL) was added *t*-BuLi (0.50 mL, 1.7 M in pentane, 0.85 mmol) at −78 °C under argon. The mixture was warmed to −40 °C over 40 min with stirring. To the above reaction mixture was added a solution of 1–2 mmol of electrophile (ketones or aldehydes) in ether (1 mL) at the same temperature. The reaction mixture was warmed to −10 °C over 40 min, quenched with saturated aqueous NH_4Cl, and extracted with ether. The extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purifed by silica gel chromatography with ether/hexane to afford pure chromium complexes. The diastereomeric ratio of **4** and **5** obtained by reaction of the complex **1** with aldehydes was determined by the area of N*Me*$_2$ or MeC*H*NMe$_2$ in the 400-MHz ^{1}H NMR spectra of the crude products or the corresponding acetate complexes. Yields, ratio (**4**:**5**), and physical data of the complexes **3** and **4** are as follows.

3 (R = Et): mp 120 °C; ^{1}H NMR ($CDCl_3$) δ 0.73 (3 H, t, *J* = 7.3), 1.08 (3 H, t, *J* = 7.3), 1.21 (3 H, d, *J* = 6.7), 1.62 (1 H, dq, *J* = 14.0, 7.3), 1.72 (1 H, dq, *J* = 14.0, 7.3), 1.86 (1 H, dq, *J* = 14.0, 7.3), 1.99 (1 H, dq, *J* = 14.0, 7.3), 2.29 (6 H, s), 4.62 (1 H, q, *J* = 6.7), 5.03 (1 H, d, *J* = 6.1), 5.18 (1 H, t, *J* = 6.1), 5.35 (1 H, d, *J* = 6.7), 5.53 (1 H, t, *J* = 6.7), 8.28 (1 H, s); IR ($CHCl_3$) 3360, 1960, 1880, 1460, 1380 cm^{-1}; $[\alpha]^{25}_D$ +67.2° (*c* = 0.62, $CHCl_3$). Anal. Calcd for $C_{18}H_{27}NO_4Cr$: C, 58.21; H, 6.78; N, 3.77. Found: C, 58.09; H, 6.84; N, 3.74.

3 (R = C_6H_5): mp 73 °C; ^{1}H NMR ($CDCl_3$) δ 1.07 (3 H, d, *J* = 6.7), 2.03 (6 H, s), 3.76 (1 H, q, *J* = 6.7), 4.93 (1 H, t, *J* = 6.7), 4.98 (1 H, d, *J* = 6.7), 5.05 (1 H, d, *J* = 6.7), 5.67 (1 H, t, *J* = 6.2), 7.24–7.58 (10 H, m), 9.67 (1 H, brs); IR ($CHCl_3$) 3350, 1960, 1880, 1480, 1380, 1070 cm^{-1}; $[\alpha]^{25}_D$ +54.1° (*c* = 0.64, $CHCl_3$). Anal. Calcd for $C_{26}H_{27}NO_4Cr$: C, 66.80; H, 5.39; N, 3.00. Found: C, 66.42; H, 5.54; N, 2.91.

4 (R = Me): yield 75%; ratio of **4**:**5** (93:7); mp 119 °C; ^{1}H NMR ($CDCl_3$) δ 1.24 (3 H, d, *J* = 6.7), 1.45 (3 H, d, *J* = 6.1), 1.60 (1 H,

br), 2.28 (6 H, s), 4.22 (1 H, q, J = 6.7), 4.95 (1 H, q, J = 6.1), 5.03 (1 H, m), 5.40 (2 H, m), 5.47 (1 H, m); IR ($CHCl_3$) 3350, 1960, 1880, 1420 cm^{-1}; $[\alpha]^{19}_D$ +6.5° (c = 0.52, $CHCl_3$). Anal. Calcd for $C_{15}H_{19}NO_4Cr$: C, 54.71; H, 5.82; N, 4.25. Found: C, 54.52; H, 5.93; N, 4.16.

4 (R = Et): yield 80%; ratio of **4**:**5** (94:6); mp 62 °C; ^1H NMR ($CDCl_3$) δ 1.18 (3 H, t, J = 7.3), 1.23 (3 H, d, J = 6.1), 1.73 (2 H, m), 2.29 (6 H, s), 4.22 (1 H, q, J = 6.1), 4.52 (1 H, m), 5.25–5.33 (1 H, m), 5.34–5.48 (3 H, m), 7.60 (1 H, s); IR ($CHCl_3$) 3350, 2920, 1950, 1870, 1460, 1080 cm^{-1}; $[\alpha]^{20}_D$ +13.5° (c = 0.66, $CHCl_3$). Anal. Calcd for $C_{16}H_{21}NO_4Cr$: C, 55.97; H, 6.16; N, 4.08. Found: C, 56.05; H, 6.24; N, 4.03.

4 (R = $CHMe_2$): yield 73%; ratio of **4**:**5** (93:7); mp 100 °C; ^1H NMR ($CDCl_3$) δ 1.15 (3 H, d, J = 6.7), 1.17 (3 H, d, J = 6.7), 1.22 (3 H, d, J = 6.7), 2.02 (1 H, dq, J = 13.4, 6.7), 2.30 (6 H, s), 4.23 (1 H, q, J = 6.7), 4.35 (1 H, d, J = 6.7), 5.27 (1 H, d, J = 6.1), 5.38 (1 H, t, J = 6.1), 5.41 (1 H, d, J = 6.1), 5.46 (1 H, t, J = 6.1), 7.87 (1 H, s); IR ($CHCl_3$) 3360, 2950, 1960, 1880, 1460, 1070 cm^{-1}; $[\alpha]^{20}_D$ +61.5° (c = 1.01, $CHCl_3$). Anal. Calcd for $C_{17}H_{23}NO_4Cr$: C, 57.14; H, 6.49; N, 3.92. Found: C, 56.96; H, 6.43; N, 3.82.

4 (R = C_6H_5): yield 89%; ratio of **4**:**5** (92:8); mp 157 °C; ^1H NMR ($CDCl_3$) δ 1.29 (3 H, d, J = 6.7), 2.37 (6 H, s), 4.43 (1 H, q, J = 6.7), 4.59 (1 H, d, J = 6.5), 5.14 (1 H, t, J = 6.5), 5.21 (1 H, d, J = 6.5), 5.43 (1 H, t, J = 6.1), 7.35 (2 H, d, J = 7.3), 7.42 (2 H, t, J = 7.3), 7.55 (1 H, d, J = 7.3), 8.42 (1 H, brs); IR ($CHCl_3$) 3350, 1960, 1880, 1450, 1020 cm^{-1}; $[\alpha]^{25}_D$ −133.1° (c = 0.55, $CHCl_3$). Anal. Calcd for $C_{20}H_{21}NO_4Cr$: C, 61.38; H, 5.41; N, 3.58. Found: C, 61.27; H, 5.43; N, 3.56.

Ar(1*S*,2*R*)-Tricarbonyl[*N*,*N*-dimethyl-α(*R*)-(*o*-formylphenyl)ethylamine]chromium (6). The above-mentioned ortholithiated complex **2** (prepared from 1.4 mmol of the complex **1**) was treated with an excess of DMF (0.5 mL) under the same reaction conditions to afford complex **6** (459 mg, 99% yield) after purification by silica gel chromatography: mp 93 °C; ^1H NMR ($CDCl_3$) δ 1.24 (3 H, d, J = 6.7), 2.20 (6 H, s), 4.23 (1 H, q, J = 6.7), 5.14 (1 H, d, J = 6.7), 5.29 (1 H, t, J = 6.7), 5.69 (1 H, t, J = 6.1), 6.05 (1 H, d, J = 6.7), 9.74 (1 H, s); IR ($CHCl_3$) 2970, 1980, 1900, 1680, 1520, 1200 cm^{-1}; $[\alpha]^{18}_D$ −283° (c = 0.26, $CHCl_3$). Anal. Calcd for $C_{14}H_{15}NO_4Cr$: C, 53.68; H, 4.83; N, 4.47. Found: C, 53.40; H, 4.87, N, 4.40.

Ar(1*S*,2*R*)-Tricarbonyl[*N*,*N*-dimethyl-α(*R*)-[*o*-(hydroxymethyl)phenyl]ethylamine]chromium (4, R = H). To a mixture of $LiAlH_4$ (15 mg, 0.4 mmol) in THF (10 mL) was added a solution of the *o*-formyl chromium complex **6** (200 mg, 0.7 mmol) in THF (5 mL) at −78 °C under argon. The reaction mixture was warmed to 0 °C over 1 h with stirring and quenched with saturated aqueous Na_2SO_4. Filtration of the precipitate, evaporation in vacuo and purification with silica gel produced 172 mg (78%) of **4** (R = H): mp 114 °C; ^1H NMR ($CDCl_3$) δ 1.24 (3 H, d, J = 6.7), 2.28 (6 H, s), 3.87 (1 H, d, J = 12.2), 4.71 (1 H, d, J = 12.2), 4.13 (1 H, q, J = 6.7), 5.23–5.38 (4 H, m), 6.94 (1 H, brs); IR ($CHCl_3$) 3350, 1970, 1890, 1470, 1380, 1080, 1030, 950 cm^{-1}; $[\alpha]^{20}_D$ +36.9° (c = 0.63, $CHCl_3$). Anal. Calcd for $C_{14}H_{17}NO_4Cr$: C, 53.34; H, 5.43; N, 4.44. Found: C, 53.13; H, 5.42; N, 4.36.

Preparation of Chromium Complexes 5 by Reaction of Organolithiums with 6. A typical procedure for **5** (R = Me) is as follows: To a solution of **6** (200 mg, 0.64 mmol) in ether (10 mL) was added a solution of methyllithium (1.5 M in ether, 1.0 mL, 1.5 mmol) at −78 °C under argon. The reaction mixture was warmed to 0 °C over 2, quenched with saturated aqueous NH_4Cl, and extracted with ether (2 × 20 mL). The extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography (5 g) with ether/hexane (1/3) to give 131 mg (62%) of **5** (R = Me) as yellow oil, ratio of **5**:**4** (81:19): ^1H NMR ($CDCl_3$) δ 1.22 (3 H, d, J = 6.1), 1.60 (3 H, d, J = 6.1), 2.23 (6 H, s), 4.07 (1 H, q, J = 6.1), 4.30 (1 H, brs), 4.65 (1 H, q, J = 6.1), 5.22 (1 H, d, J = 6.0), 5.31 (1 H, t, J = 6.0), 5.45 (1 H, t, J = 6.0), 5.63 (1 H, d, J = 6.1); IR ($CHCl_3$) 3350, 1970, 1880, 1380, 1100 cm^{-1}; $[\alpha]^{21}_D$ +19.8° (c = 0.94, $CHCl_3$); MS m/e 329 (M^+), 273 (M^+ − 2CO), 245 (M^+ − 3CO), 184, 95; exact MS calcd for $C_{15}H_{19}NO_4Cr$ 329.0719, found 329.0709. Reactions of the complex **6** with other organolithiums were carried out under the same conditions. Yields, ratio (**5**:**4**), and the physical data of **5** were as follows.

5 (R = Et): yield 65%; ratio of **5**:**4** (83:13); mp 110 °C; ^1H NMR ($CDCl_3$) δ 1.10 (3 H, d, J = 7.3), 1.21 (3 H, d, J = 6.7), 1.67 (2 H, m), 1.96 (1 H, m), 2.22 (6 H, s), 4.01 (1 H, q, J = 6.7), 4.34 (1 H, d, J = 9.8), 5.23 (1 H, d, J = 6.7), 5.32 (1 H, t, J = 6.1), 5.44 (1 H, t, J = 6.1); IR ($CHCl_3$) 3350, 1960, 1880, 1460, 1370, 1100 cm^{-1}; $[\alpha]^{16}_D$ +20.7° (c = 0.83, $CHCl_3$). Anal. Calcd for $C_{16}H_{21}NO_4Cr$: C, 55.97; H, 6.16; N, 4.08. Found: C, 56.06; H, 6.25; N, 4.01.

5 (R = C_6H_5): yield 60%; ratio of **5**:**4** (66:34); mp 150 °C; ^1H NMR ($CDCl_3$) δ 1.12 (3 H, d, J = 6.1), 1.61 (1 H, brs), 2.14 (6 H, s), 3.81 (1 H, q, J = 6.1), 5.11 (1 H, d, J = 6.7), 5.25 (1 H, t, J = 6.1), 5.53 (1 H, t, J = 6.1), 5.55 (1 H, s), 5.78 (1 H, d, J = 6.1), 7.29 (1 H, d, J = 7.3), 7.37 (2 H, t, J = 7.3), 7.60 (2 H, d, J = 7.3); IR ($CHCl_3$) 3350, 1960, 1880, 1460, 1010 cm^{-1}; $[\alpha]^{18}_D$ −47.0° (c = 0.48, $CHCl_3$). Anal. Calcd for $C_{20}H_{21}NO_4Cr$: C, 61.38; H, 5.41; N, 3.58. Found: C, 61.30; H, 5.45; N, 3.57.

1-[α(*R*)-(*N*,*N*-Dimethylamino)ethyl]-2-(α′(*S*)-hydroxypropyl)benzene (9, R = Et). A solution of **4** (R = Et) (400 mg, 1.17 mmol) in ether (50 mL) was exposed to sunlight until the yellow color disappeared for 3 h. The precipitate was filtered off, and ether layer was evaporated in vacuo. Purification by silica gel chromatography gave 186 mg (90%) of **9** (R = Et), which was used for the next chromium complexation reaction without further purification: ^1H NMR δ 1.07 (3 H, t, J = 6.8), 1.37 (3 H, t, J = 6.8), 1.95 (2 H, q, J = 6.8), 2.09 (1 H, brs), 4.32 (1 H, q, J = 6.8), 4.78 (1 H, t, J = 6.8), 7.21–7.42 (4 H, m); IR (neat) 3370, 1460, 1370, 1190, 1040 cm^{-1}; MS m/e 207 (M^+), 192, 190, 178, 162, 133.

Ar(1*R*,2*S*)-Tricarbonyl[1-[α(*R*)-(*N*,*N*-dimethylamino)ethyl]-2-(α′(*S*)-hydroxypropyl)benzene]chromium (10, R = Et). (Naphthalene)$Cr(CO)_3$ (290 mg, 1.1 mmol) and **9** (R = Et) (200 mg, 1.0 mmol) were placed in a heavy-wall glass tube equipped with a valve and gas inlet. After addition of ether (10 mL) and THF (0.1 mL), the mixture was degassed by a freeze/pump/thaw cycle and then heated at 70 °C for 5 h in a closed system. Filtration, evaporation in vacuo, and silica gel chromatography with hexane/ether gave a face-inverted chromium complex **10** (R = Et) (268 mg, 78%): mp 93 °C; ^1H NMR ($CDCl_3$) δ 1.10 (3 H, t, J = 7.3), 1.34 (3 H, d, J = 7.3), 1.61 (2 H, dq, J = 14.3, 7.3), 1.78 (1 H, m), 2.37 (6 H, s), 3.32 (1 H, q, J = 7.3), 4.79 (1 H, dd, J = 8.9, 2.8), 5.16 (1 H, t, J = 6.7), 5.43 (1 H, d, J = 6.7), 5.51 (1 H, t, J = 6.1), 5.63 (1 H, d, J = 6.1); IR ($CDCl_3$) 3350, 1960, 1880, 1460, 1080 cm^{-1}; $[\alpha]^{21}_D$ +60.7° (c = 0.67, $CHCl_3$). Anal. Calcd for $C_{16}H_{21}NO_4Cr$: C, 55.97; H, 6.16; N, 4.08. Found: C, 55.86; H, 6.17; N, 3.97.

Tricarbonyl[*N*,*N*,*N*′-trimethyl-*N*′-(α(*R*)-phenylethyl)ethylenediamine]chromium (13). A mixture of *N*,*N*,*N*′-trimethyl-*N*′-(α(*R*)-phenylethyl)ethylenediamine (**12**) (3.0 g, 14.6 mmol) and $Cr(CO)_6$ (3.52 g, 16.0 mmol) in dibutyl ether (180 mL), heptane (18 mL), and THF (18 mL) was heated at 110 °C for 30 h under nitrogen. After being cooled to rt, the reaction mixture was distilled at 50 °C/20 mmHg to remove the solvents and excess of $Cr(CO)_6$. The residue was purified by silica gel chromatography with acetone to produce the corresponding chromium complex **13** (3.97 g, 80%): yellow oil; ^1H NMR ($CDCl_3$) δ 1.27 (3 H, d, J = 7.3), 2.22 (9 H, s), 2.38 (2 H, t, J = 6.7), 2.49–2.55 (2 H, m), 3.65 (1 H, q, J = 7.3), 5.29–5.34 (4 H, m), 5.55 (1 H, d, J = 6.0); IR ($CHCl_3$) 1960, 1880, 1450, 1250 cm^{-1}; $[\alpha]^{22}_D$ −36.3° (c = 1.29, $CHCl_3$); MS m/e 342 (M^+), 286 (M^+ − 2CO), 258 (M^+ − 3CO), 152.

Preparation of 14. To a solution of the complex **13** (400 mg, 1.17 mmol) in ether (25 mL) was added *t*-BuLi (1.7 M in pentane, 1.03 mL, 1.76 mmol) at −78 °C under argon. The reaction mixture was warmed to −40 °C over 45 min and stirred for further 30 min. After addition of THF (2 mL), a solution of diethyl ketone (201 mg, 2.34 mmol) in ether (3 mL) was added to the above reaction mixture at the same temperature, and the mixture was warmed to −10 °C over 45 min. The mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. The extract was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel chromatography with acetone to produce of 303 mg (61%) of **14** (R = Et): mp 122 °C; ^1H NMR ($CDCl_3$) δ 0.76 (3 H, t, J = 7.3), 1.06 (3 H, t, J = 7.3), 1.22 (3 H, d, J = 6.7), 1.61–1.76 (3 H, m), 1.88–1.94 (2 H, m), 2.22 (9 H, s), 2.38–2.45 (2 H, m), 2.50–2.70 (2 H, m), 4.75 (1 H, q, J = 6.7), 5.06 (1 H, d, J = 6.1), 5.17 (1 H, t, J = 6.1), 5.36 (1 H, d, J = 6.5), 5.52 (1 H, t, J = 6.1); IR ($CHCl_3$) 3150, 1960, 1880, 1460, 1040 cm^{-1}; $[\alpha]^{20}_D$ +4.5° (c = 1.0, $CHCl_3$). Anal. Calcd for $C_{21}H_{32}N_2O_4Cr$: C, 58.86; H, 7.53; N, 6.54. Found: C, 58.59; H, 7.54; N, 6.45.

Ligand-Exchange Reaction by Photoirradiation. A typical procedure of ligand-exchange reaction from tricarbonyl to the corresponding phosphine or phosphite is as follows: A solution of 15 ($R^1 = R^2 = Ph$) (200 mg, 0.4 mmol) and PPh_3 (224 mg, 0.8 mmol) in benzene (20 mL) was irradiated with a high-pressure mercury lamp for 30 min under nitrogen at rt. The precipitate was filtered off, and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel (5 g) chromatography with hexane/ether to produce 218 mg (73%) of 16 ($R^1 = R^2 = Ph$, L = PPh_3): mp 104 °C; ^1H NMR ($CDCl_3$) δ 1.01 (3 H, d, J = 6.7), 2.02 (6 H, s), 3.75 (1 H, q, J = 6.7), 4.13–4.15 (2 H, m), 4.59 (1 H, d, J = 6.1), 4.85 (1 H, d, J = 6.1), 7.25–7.69 (25 H, m), 9.73 (1 H, brs); IR ($CHCl_3$) 3350, 1960, 1880, 1480, 1440, 940 cm^{-1}; $[\alpha]^{25}_D$ +29.6° (c = 0.95, $CHCl_3$). Anal. Calcd for $C_{43}H_{40}NO_3PCr$: C, 73.60; H, 5.74; N, 2.00. Found: C, 73.34; H, 5.58; N, 2.37. Other ligand-exchange reactions were carried out under the same conditions.

16 (R^1 = H, R^2 = Et, L = PPh_3): yellow oil; ^1H NMR ($CDCl_3$) δ 0.91 (3 H, t, J = 7.3), 1.11 (3 H, d, J = 6.1), 1.45–1.71 (2 H, m), 2.23 (6 H, s), 4.20 (1 H, q, J = 6.1), 4.22 (1 H, t, J = 6.6), 4.53 (1 H, d, J = 6.6), 4.54 (1 H, dd, J = 5.7, 1.8), 4.60–4.78 (2 H, m), 7.20–7.58 (15 H, m), 7.70 (1 H, s); IR ($CHCl_3$) 3350, 1960, 1890, 1460, 1080, 920 cm^{-1}; $[\alpha]^{25}_D$ +5.6° (c = 0.86, $CHCl_3$); MS m/e 577 (M^+), 521 (M^+ – 2CO), 259 (M^+ – 2CO, PPh_3), 217.

16 (R^1 = H, R^2 = Et, L = $P(OPh)_3$): mp 43 °C; ^1H NMR ($CDCl_3$) δ 1.02 (3 H, t, J = 7.3), 1.08 (3 H, t, J = 6.1), 1.31–1.47 (2 H, m), 2.17 (6 H, s), 4.08 (1 H, q, J = 6.1), 4.39 (1 H, t, J = 6.1), 4.42 (1 H, d, J = 6.6), 4.57 (1 H, dd, J = 6.1, 2.0), 4.62–4.75 (2 H, m), 7.05–7.40 (15 H, m), 7.57 (1 H, s); IR ($CHCl_3$) 3350, 1900, 1850, 1590, 1490, 1200, 910 cm^{-1}; $[\alpha]^{26}_D$ +8.5° (c = 0.92, $CHCl_3$). Anal. Calcd for $C_{33}H_{36}NO_6PCr$: C, 63.36; H, 5.80; N, 2.24. Found: C, 63.14; H, 5.83, N, 2.19.

Resolution of (D,L)-Tricarbonyl[*o*-(*N*,*N*-dimethylamino)benzaldehyde]chromium. A mixture of racemic tricarbonyl[*o*-(*N*,*N*-dimethylamino)benzaldehyde]chromium (3.0 g, 10.5 mmol), (L)-valinol (3.25 g, 31.6 mmol), and molecular sieves 4A (1 g) in ether (20 mL) was stirred at rt under argon for 12 h. The mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was chromatographed on 70 g of silica gel by elution with hexane/ether/triethylamine (10/10/1) to separate two fractions. The first fraction was concentrated under reduced pressure, and the residue was dissolved in a mixture of THF (5 mL), water (1 mL), and five drops of concentrated HCl. The mixture was stirred for 1 h at rt under argon, was quenched with saturated aqueous $NaHCO_3$, and extracted with ether. The extract was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel chromatography with hexane/ether to give 1.08 g (36%) of (–)-chromium complex 17: mp 109 °C; $[\alpha]^{20}_D$ –903° (c = 0.99, $CHCl_3$). Similarly, the second fraction gave 980 mg of (+)-complex under the same conditions: mp 109 °C; $[\alpha]^{20}_D$ +902° (c = 1.03, $CHCl_3$). The optical purities (>99%) of the resolved chromium complexes were determined by HPLC with Daicel Chiralcel OJ eluted with 10% 2-propanol in hexane.

Tricarbonyl[α(*R*)-[*o*-(*N*,*N*-dimethylamino)phenyl]ethyl alcohol]chromium (18) (R = Me). To a solution of the resolved (–)-complex 17 (200 mg, 0.70 mmol) in ether (10 mL) was added MeLi (1.5 M in ether, 1 mL, 1.5 mmol) at –78 °C under argon. The reaction mixture was warmed to 0 °C over 90 min with stirring and quenched with saturated aqueous NH_4Cl and extracted with ether (20 mL × 2). The extract was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel chromatography with hexane/ether to produce 166 mg (79%) of 18 (R = Me) and 14 mg (7%) of 20 (R = Me). Physical data of 18 (R = Me) are follows: mp 75 °C; ^1H NMR ($CDCl_3$) δ 1.50 (3 H, d, J = 6.1), 2.70 (6 H, s), 3.33 (1 H, s), 5.05 (1 H, q, J = 6.1), 5.13 (1 H, t, J = 6.7), 5.15 (1 H, d, J = 6.7), 5.44 (1 H, t, J = 6.7), 5.63 (1 H, d, J = 6.7); IR ($CHCl_3$) 3350, 1970, 1890, 1070 cm^{-1}; $[\alpha]^{20}_D$ –3.3° (c = 1.19, $CHCl_3$). Anal. Calcd for $C_{13}H_{15}NO_4Cr$: C, 51.83; H, 5.02; N, 4.65. Found: C, 51.71; H, 5.01; N, 4.63.

Tricarbonyl[α(*S*)-[*o*-(*N*,*N*-dimethylamino)phenyl]ethyl alcohol]chromium (20) (R = Me). A mixture of the α (*R*)-complex 18 (R = Me) (200 mg, 0.7 mmol) and freshly prepared active manganese dioxide (1 g, 11.5 mmol) in ether (20 mL) was placed in Schlenk tube. The mixture was degassed by freeze/pump/thaw cycle and stirred at rt for 4 h. The precipitate was filtered and washed with ether. The organic layer was concentrated in vacuo and purified by silica gel (5 g) with ether/hexane to produce 80 mg (38%) of a ketone complex which was used for next step without further purification. To a suspended mixture of $LiAlH_4$ (10 mg, 0.27 mmol) in THF (5 mL) was added a solution of the above-prepared ketone complex (100 mg) in THF (0.5 mL) via a syringe at –78 °C under argon. The reaction mixture was warmed to 0 °C over 45 min and quenched with saturated aqueous Na_2SO_4. Usual workup and silica gel purification gave 52 mg of 20 (R = Me): mp 62 °C; ^1H NMR ($CDCl_3$) δ 1.55 (3 H, d, J = 6.1), 2.72 (6 H, s), 5.07 (1 H, q, J = 6.1), 5.26 (1 H, d, J = 6.1), 5.36 (1 H, t, J = 6.7), 5.41 (1 H, d, J = 6.1), 5.42 (1 H, t, J = 6.1), 7.27 (1 H, s); IR ($CHCl_3$) 3350, 1960, 1880, 1460, 1070, 940 cm^{-1}; $[\alpha]^{20}_D$ –6.7° (c = 1.02, $CHCl_3$). Anal. Calcd for $C_{13}H_{15}NO_4Cr$: C, 51.83, H, 5.02; N, 4.65. Found: C, 51.80; H, 5.00; N, 4.61.

General Procedure for Enantioselective Addition of Diethylzinc to Benzaldehyde Catalyzed by Chiral (Arene)chromium Complexes. Benzaldehyde (2.0 mmol), chiral (arene)chromium complex (0.1 mmol), and toluene (3 mL) were placed in a Schlenk tube with a valve and gas inlet. The mixture was degassed by three freeze/pump/thaw cycles. Diethylzinc (5.3 mL, 1.5 M in hexane, 8.0 mmol) was injected to the reaction mixture via syringe at 0 °C, and the reaction mixture was stirred for 18 h at the same temperature. Aqueous HCl (1 N, 5 mL) was added to quench the reaction. The resulting mixture was extracted with CH_2Cl_2 (30 mL × 2), and the extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ether) and then bulb to bulb distillation. The product was identified by comparing the ^1H NMR and IR spectra with those of an authentic sample, and the optical rotation was measured. Enantiomeric excess (% ee) was determined by HPLC analysis (Daicel Chiralcel OB, 10% 2-propanol in hexane).

General Procedure for Conjugate Addition to Chalcone Catalyzed by Ni(acac)$_2$/(Arene)chromium Complexes System. Nickel acetylacetonate (0.1 mmol), chiral (arene)$Cr(CO)_3$ (0.1 mmol), and acetonitrile (5 mL) were placed in Schlenk tube with a valve and gas inlet. The mixture was degassed by three cycles of freeze/pump/thaw and stirred for 1 h at rt under argon. A solution of chalcone (1 mmol) in acetonitrile (2 mL) was injected by syringe, and the mixture was cooled at –30 °C. After the mixture was stirred for 10 min, diethylzinc (1.4 mL, 1.5 M in hexane, 2 mmol) was added to the above mixture. The reaction mixture was stirred at –30 °C for 18 h, quenched with aqueous 1 M HCl (1 mL), and extracted with ether. The extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel to produce the conjugate addition product. Enantiomeric excess (% ee) was determined by HPLC analysis (Daicel Chiralcel OD, 0.25% 2-propanol in hexane). The absolute configuration was determined by a rotation value.

Acknowledgment. M.U. thanks a Grant-in-Aid for Special Scientific Research from Osaka City University.

Supplementary Material Available: Crystallographic data of 4 (R = C_6H_5) and physical data of the complexes 4 (R = C_6F_5, *o*-MeC_6H_4, *o*-$CF_3C_6H_4$, *m*-$CF_3C_6H_4$, *m*-$MeOC_6H_4$, α-$C_{10}H_7$), 5 (R = *i*-Pr, *n*-Bu, *t*-Bu), 16 ($R^1 = R^2$ = Et, L = PPh_3; $R^1 = R^2$ = Et, L = $P(OPh)_3$), and 18 (R = Ph) (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.