 Bull. Chem. Soc. Jpn., **74**, 2139–2150 (2001)

Highly Enantioselective Cyclopropanation of Styrenes and Diazoacetates Catalyzed by 3-Oxobutylideneaminatocobalt(II) Complexes, Part 1. Designs of Cobalt Complex Catalysts and the Effects of Donating Ligands

Taketo Ikeno, Mitsuo Sato, Hiroyuki Sekino, Asae Nishizuka, and Tohru Yamada*

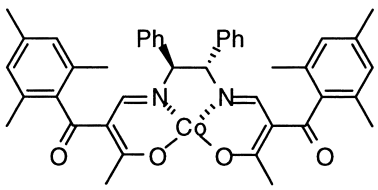
Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223-8522

(Received March 13, 2001)

Highly enantioselective cyclopropanation of styrene derivatives and diazoacetates was effectively catalyzed by reasonably designed 3-oxobutylideneaminatocobalt(II) complexes, whose ligands were prepared from 1,2-dimesitylethylenediamine and alkyl 3-oxobutanoates. The steric demand of the diamine unit of the complexes seriously influenced the enantioselectivity, and the ester groups on their side chains somewhat improved the *trans*-selectivity. Addition of a catalytic amount of *N*-methylimidazole significantly accelerated the reaction and enhanced the enantioselectivity due to its coordination to the center cobalt atom of the complex as an axial ligand. Alcoholic or aqueous alcoholic solvents were also effective particularly for the cyclopropanation of 1-substituted 1-phenylethylenes to achieve high enantioselectivity in aqueous methanol.

Since the catalytic enantioselective cyclopropanation of olefins with diazoacetates was first reported in 1966,[1] various transition metals and many varieties of optically active ligands have been subjected to this benchmark test reaction,[2] and some of them have been applied to the industrial synthesis of pyrethroids.[3] For example, chiral (dioximato)cobalt(II)[4] and chiral Schiff-base copper(II)[5] complex catalysts were originally proposed as the catalyst for enantioselective cyclopropanation. Recently, copper(I) complexes with semicorrin,[6] bis(oxazoline)[7] or bipyridine[8] ligands, ruthenium(II) complexes with bis(oxazolinyl)pyridine[9] ligands, and rhodium(III) complexes with proline derivative[10] ligands were developed as effective catalysts to provide an extremely high level of enantioselectivity. It was very recently reported that optically active (salen)cobalt(III) complexes[11] were efficient catalysts for the asymmetric cyclopropanation of styrene derivatives, and much effort has been devoted to developing more effective catalysts.[12]

The optically active 3-oxobutylideneamines derived from the corresponding 3-oxoalkanals and optically active 1,2-diaryl-1,2-ethylenediamines have been proposed to provide a new class of effective ligands for catalytic enantioselective reactions; manganese(III) complexes with optically active 3-oxoalkylideneaminato ligands have been employed as effective catalysts for the aerobic and enantioselective epoxidation of unfunctionalized olefins[13] and the asymmetric aerobic oxidation of sulfides to the corresponding optically active sulfoxides.[14] The corresponding cobalt(II) complexes, for example, MPAC (**1a**) (Chart 1), effectively catalyzed the enantioselective borohydride reduction of prochiral aryl ketones,[15] *N*-phosphinylimines,[16] and α,β-unsaturated carboxamides.[17] They also catalyzed an enantioselective hetero Diels–Alder reaction[18] as a Lewis Acid.



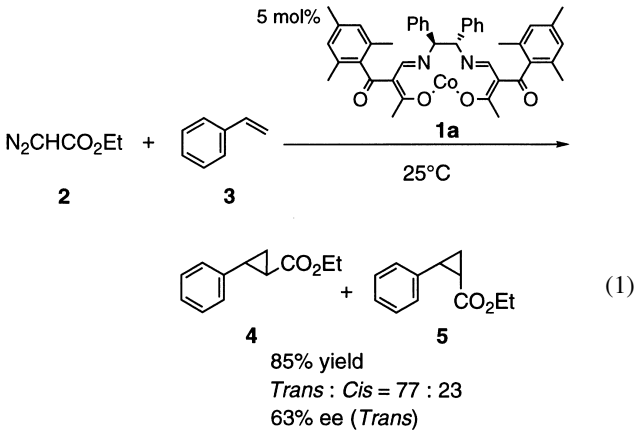
1a

Chart 1.

In the previous communications, we reported that the highly enantioselective cyclopropanation of styrenes with diazoacetates proceeded when catalyzed by rationally designed cobalt(II) complexes having 1,2-dimesitylethylenediamine in the diamine unit and ester moieties on the side chain and that addition of a catalytic amount of *N*-methylimidazole[19] or alcoholic solvent[20] caused a remarkable effect on the reaction. In this article, we would like to fully describe the details of the experiments and to discuss the effects of additives and/or solvents in the cobalt-complex-catalyzed cyclopropanation reaction.

Results and Discussion

Preliminary Experiments. Several experiments for enantioselective cyclopropanation were performed on the reaction of neat styrene with ethyl diazoacetate in the presence of 0.05 molar amount 3-oxobutylideneaminato cobalt complex **1a** at room temperature. The corresponding cyclopropanecarboxylate was obtained in 85% yield with moderate *trans*-selectivity (*trans*:*cis* = 77:23) and with moderate enantioselectivity (63% ee for *trans*-isomer, Eq. 1). This result encouraged us to improve the reaction system by the design of the cobalt-com-



(1)

plex catalysts and the optimization of the reaction conditions for achieving high diastereo- and enantioselectivity.

Solvents were first examined in the reaction of styrene with *t*-butyl diazoacetate in the presence of 0.05 molar amount of cobalt(II) complex **1a**. As shown in Table 1, the yields in 10 h depended on the solvents. In a nonpolar solvent such as toluene or CH_2Cl_2, yields of the product were below 40% (Entries 1–3), while the yield was increased up to 60% in THF (Entry 5). Rate enhancement of the reaction was observed in THF but not in Et_2O (Entry 4). It was noteworthy that the diastereo- and enantioselectivity of the product was also improved to some extent when THF was used as a solvent.

Effect of Axial Ligand. In most of the X-ray structures of 3-oxobutylideneaminato and salencobalt(II) and (III) complexes reported previously, donating ligands, such as alcohols, THF, or pyridine, were found in their axial positions.[21] It is noted that these axial ligands often exert considerable influence on the catalytic activities. The effects of the axial donor ligand were reported for manganese complex-catalyzed oxidations.[22] For example, pyridine *N*-oxide and 2-methylimidazole accelerated the reaction rate and improved the enantioselectivity in salenmanganese-catalyzed epoxidation using iodosylbenzene as a terminal oxidant,[22c] and reversal of the absolute configuration of the product was observed by addition of *N*-methylimidazole in salenmanganese-catalyzed aerobic oxidation.[22e] Based on this knowledge, we deduced that the THF coordinated to the cobalt atom as an axial ligand to accelerate the present cyclopropanation reaction. Several nitrogen-containing compounds were then screened to identify an appropriate additive to reveal that *N*-methylimidazole was the prominent accelerator of the reaction. Two molar amounts of the *N*-methylimidazole versus the cobalt complex greatly enhanced the reaction, and the yield of the product was remarkably improved. As shown in Fig. 1, in the absence of the *N*-methylimidazole, the reaction was not completed in 4 h; only 60% yield of the product was obtained. On the contrary, in the presence of *N*-methylimidazole, the reaction was completed in 4 h to afford the product in about 90% yield. Along with rate enhancement, the enantiomeric excess of the product was improved. In the absence of *N*-methylimidazole, enantiomeric excesses of the product ranged from 70% ee to 75% ee, whereas they were over 80% ee in the presence of *N*-methylimidazole.

Table 1. Solvent Effect on the Reaction of Styrene with *t*-Butyl Diazoacetate[a)]

Entry	Solvent	Yield/%[b)]	*trans*:*cis*[c)]	ee (*trans*)/%[d)]
1	—	26	71:29	62
2	Toluene	18	70:30	58
3	CH_2Cl_2	40	75:25	57
4	Et_2O	21	68:32	55
5	THF	60	76:24	75

a) Reaction conditions: Five hundredth molar amount of catalyst **1a** at 25 °C for 10 h (see the general procedure). b) Isolated yield based on *t*-butyl diazoacetate. c) Determined by GC. d) Determined by HPLC analysis after reduction of the isolated products into the corresponding alcohols (*Trans*: Daicel Chiralcel OD-H and/or OB-H, hexane/2-propanol).

Table 2. Amount of *N*-Methylimidazole[a)]

Entry	Molar amount[b)]	Yield/%	*trans*:*cis*	ee (*trans*)/%
1	0	62	76:24	75
2	1	97	76:24	84
3	2	94	76:24	84
4	4	91	76:24	82
5	8	98	79:21	84
6	16	88	76:24	82
7	32	94	76:24	85
8	solvent	quant	79:21	85

a) Reaction conditions: Five hundredth molar amount of catalyst **1a** and *N*-methylimidazole in THF at 25 °C for 2 h. b) Molar amount of *N*-methylimidazole vs Co(II) complex.

The loading amount of the *N*-methylimidazole versus the cobalt complex was next examined. As shown in Table 2, no effect on the diastereoselectivity was observed either in the presence or the absence of *N*-methylimidazole. Compared with the result of 2 molar amounts of *N*-methylimidazole (Entry 3), the yield and enantiomeric excess of the product were lower without *N*-methylimidazole (Entry 1), and it was revealed that an equimolar amount of *N*-methylimidazole was sufficient for acceleration (Entry 2). On the other hand, almost no additional improvement was observed when more than 2 molar amounts of *N*-methylimidazole were added (Entries 4–8). It was noteworthy that, when the reaction was performed in *N*-methylimidazole solvent, the reaction was smoothly completed in 2 h with the remaining enantio- and diastereoselectivity.

A variety of additives was scrutinized for the present cyclopropanation (Table 3). *N*-Phenyl and *N*-benzylimidazole showed an effect similar to that of *N*-methylimidazole both on the yield and the enantioselectivity (Entries 2 and 3). Pyridine and 5-methylimidazole increased the enantiomeric excess, while yields of the product were lower (Entries 4 and 5). The catalyst was deactivated, probably because these compounds coordinated the cobalt atom strongly enough to occupy both axial sides of the complex. Other nitrogen-containing aromatic compounds produced slightly worse results compared to that without additives (Entries 6–9). It seems that these heterocy-

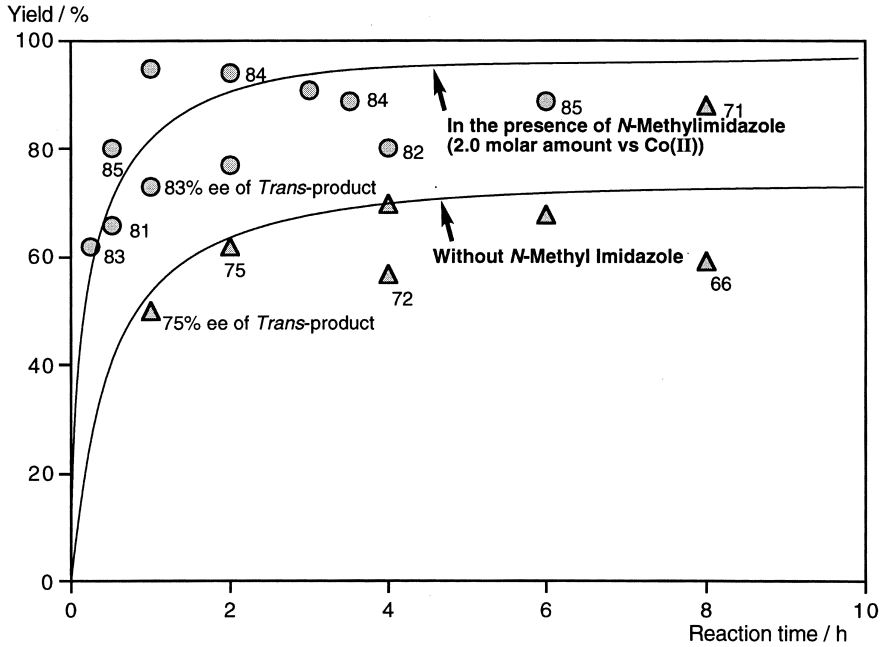


Fig. 1. Time-course of the cyclopropanation reaction in the presence and absence of *N*-methylimidazole.

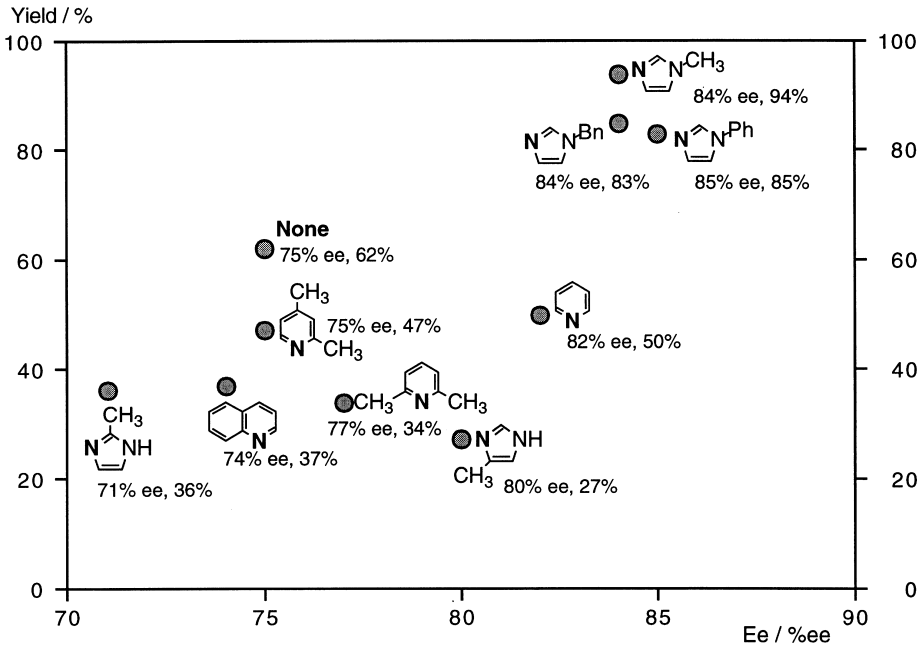


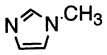
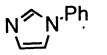
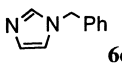
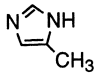
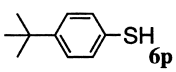
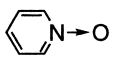
Fig. 2. Relation between yields and enantiomeric excesses for nitrogen-containing heteroaromatics.

cles could not coordinate the cobalt complex for steric reasons.[23] Aliphatic nitrogen compounds were not employed as effective additives (Entries 10–13). In the presence of a thiol derivative, the reaction soon stopped, and a small amount of di-*t*-butyl fumarate and di-*t*-butyl maleate were detected as by-products (Entry 16). This was in great contrast to the result where no dimeric products were obtained using nitrogen compounds as additives. Pyridine *N*-oxide (Entry 17) remarkably enhanced the *trans*-selectivity, but the enantiomeric excess was slightly lower than that in the presence of *N*-methylimidazole.

Figure 2 shows the relation between the yield and the enantiomeric excess using various nitrogen-containing heteroaromatics as additives. A tendency was observed in which the additives affording the product in a higher yield realized a higher enantiomeric excess. This figure clearly indicates that imidazole derivatives prominently enhanced both the yield and the enantiomeric excess.

Design of the Cobalt(II) Complex Catalyst. Based on the above-mentioned observation, standard reaction conditions were determined as follows: 5.0 mmol of styrene and 1.0 mmol of *t*-butyl diazoacetate in THF (1 mL) in the presence of 0.05 molar amount of cobalt(II) complex and 0.1 molar amount of *N*-methylimidazole. A variety of the cobalt complexes was examined under the standard conditions (Table 4).

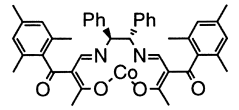
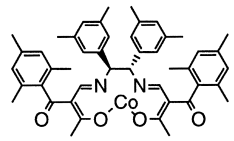
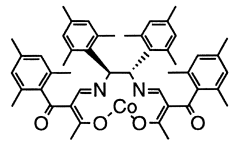
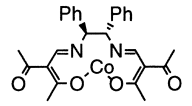
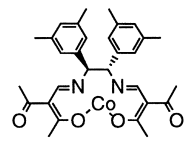
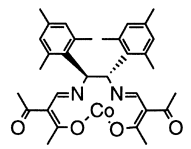
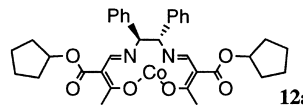
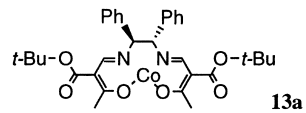
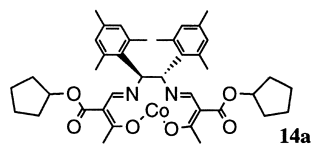
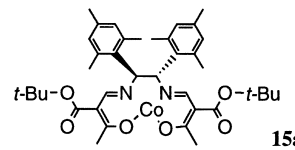
Table 3. Various Additives for Cyclopropanation[a)]

Entry	Additive[b)]	Yield/%	*trans*:*cis*	ee/%	
				trans	*cis*
1	 **6a**	94	76:24	84	85
2	 **6b**	85	77:23	84	82
3	 **6c**	83	75:25	85	83
4	 **6d**	27	73:27	80	81
5	 **6e**	43	74:26	77	78
6	 **6f**	36	73:27	71	82
7	 **6g**	47	74:26	75	82
8	 **6h**	34	72:28	77	75
9	 **6i**	37	73:27	74	84
10	Et_3N **6j**	72	72:28	52	62
11	 **6k**	62	78:22	76	78
12	*i*-Pr_2NEt **6l**	72	77:23	76	77
13	 **6m**	74	75:25	81	87
14	MeOH **6n**	62	75:25	76	80
15	EtOH **6o**	62	75:25	76	82
16	 **6p**	complex mixture			
17	 **6q**	quant	82:18	80	80
18	H_2O **6r**	57	76:24	76	79
19	None	62	76:24	75	84

a) Reaction conditions: Five hundredth molar amount of catalyst **1a** in THF at 25 °C for 2 h.
b) Two molar amount of additive vs catalyst were employed.

The cobalt(II) complexes **1a**, **7a**, and **8a** were prepared from the optically active 1,2-diphenylethylenediamine, 1,2-bis(3,5-dimethylphenyl)ethylenediamine, and 1,2-dimesitylethylenediamine, respectively. The cobalt(II) complexes **1a** and **7a** catalyzed the reaction to afford the resulting cyclopropanecarboxylates with 84–85% ee and 75–76% *trans*-selectivity, whereas complex **8a** improved the enantiomeric excess of the product to 90% ee but decreased the *trans*-selectivity (68:32) (Entries 1–3). The cobalt(II) complexes **9a**, **10a**, and **11a** with a smaller side chain (acetyl in **9a**–**11a** vs 2,4,6-trimethylbenzoyl in

Table 4. Various Cobalt(II) Complex Catalysts for Enantioselective Cyclopropanation[a)]

Entry	Catalyst	Temp/°C	Reaction time/h	Yield/%	*trans*:*cis*	ee (*trans*)/%
1	 **1a**	25	2	94	76:24	84
2	 **7a**	25	2	quant	75:25	85
3	 **8a**	50	20	89	68:32	90
4	 **9a**	25	2	quant	76:24	70
5	 **10a**	25	2	quant	78:22	61
6	 **11a**	40	10	80	83:17	96
7	 **12a**	25	2	quant	81:19	66
8	 **13a**	25	2	94	83:17	63
9	 **14a**	40	4.5	97	90:10	96
10	 **15a**	40	22.5	99	91:9	96

a) Reaction conditions: Five hundredth molar amount of catalyst and 0.1 molar amount (2.0 molar amount vs Co(II) complex) of *N*-methylimidazole in THF.

1a, **7a**, and **8a**) were then subjected to the cyclopropanation (Entries 4–6). When the complex catalyst **9a** or **10a** was employed, the enantiomeric excess of the product was lower than that using complex catalyst **1a** or **7a**. On the contrary, in the reaction catalyzed by complex **11a**, the enantiomeric excess of the product was remarkably improved to 96% ee and the *trans*-selectivity was also enhanced to 83%. These observations suggested that the sterically demanding diamine would be effective for improving the enantioselection. Various cobalt(II) complexes with ester moieties on the side chains were then synthesized and examined. When complexes **12a** and **13a** with the respective cyclopentyl and *t*-butyl esters were used as cata-

lysts, the enantiomeric excess was decreased, but the *trans*-selectivity was enhanced compared to that achieved by the complex catalyst **1a** (Entries 7 and 8). These results indicated that the ester side chain would be effective for improving *trans*-selectivity. Hence, we designed and synthesized cobalt(II) complexes **14a** and **15a** having ester side chains and an optically active 1,2-dimesitylethylenediamine unit. In the presence of these complexes, the cyclopropanation was smoothly completed and the products were obtained in 96% ee with 90% *trans*-selectivity (catalyst **14a**, Entry 9) and in 96% ee with 91% *trans*-selectivity (catalyst **15a**, Entry 10), respectively.

Examination of Reaction Conditions. Using rationally designed catalyst **14a**, the temperature dependence of the diastereo- and enantioselectivity was studied (Table 5). Whereas the reaction at 30 °C proceeded slowly (Entry 1), at 40 and 50 °C high diastereoselectivity and enantioselectivity were achieved, and the reaction time was substantially shortened (Entries 2 and 3). It was noteworthy that the high temperature, even the THF reflux temperature, induced high enantioselectivity in the cobalt(II) complex **14a**-catalyzed cyclopropanation (Entry 4).

The loading amount of styrene versus diazoacetate was then examined (Table 6). Compared to the result using 5 molar amounts of styrene, the reaction with 3 molar amounts of styrene produced similar results in yield, *trans*-selectivity, and enantiomeric excess (Entries 2 and 3). When an equimolar amount of styrene was used, the yield was decreased but the *trans*-selectivity and enantiomeric excess were maintained (Entry 1).

The catalytic amount of the cobalt complex was examined (Table 7). When 0.1 molar amount of the catalyst was used, the diastereo- and enantioselectivity were not improved (Entry 1). Although the diastereo- and enantioselectivity were preserved under the conditions of a 0.03 molar amount of catalyst load, its yield was slightly decreased (Entry 3). When 0.01 molar amount of catalyst was employed, the yield and *trans*-selectivity of the product were lowered but the ee of the *trans*-product was retained (Entry 4). Based on these experiments, it was noted that loading 0.05 molar amount of the catalyst was required for achieving a high yield.

Table 5. Temperature Effect on *Trans*- and Enantioselectivity[a)]

Entry	Temp. /°C	Time/h	Yield/%	*trans*:*cis*	ee (*trans*) /%
1	30	40	66	90:10	97
2	40	4.5	97	90:10	96
3	50	3.5	quant	89:11	96
4	reflux	4.5	90	85:15	89

a) Reaction conditions: Five hundredth molar amount of catalyst **14a** and 0.1 molar amount (2.0 molar amount vs Co(II) complex) of *N*-methylimidazole in THF.

Table 6. Amount of Styrene[a)]

Entry	Molar amount[b)]	Yield/%	*trans*:*cis*	ee (*trans*)/%
1	1	49	89:11	96
2	3	85	89:11	97
3	5	97	90:10	96

a) Reaction conditions: Five hundredth molar amount of catalyst **14a** and 0.1 molar amount (2.0 molar amount vs Co(II) complex) of *N*-methylimidazole in THF at 40 °C for 4.5–9 h. b) Against *t*-butyl diazoacetate.

Table 7. Loading Amount of the Cobalt(II) Complex Catalyst[a)]

Entry	Amount /mol%[b,c)]	Yield/%	*trans*:cis	ee (*trans*)/%
1	10	95	90:10	97
2	5.0	97	90:10	96
3	3.0	83	89:11	97
4	1.0	54	82:18	95

a) Reaction conditions: catalyst **14a** and 0.1 molar amount (2.0 molar amount vs Co(II) complex) of *N*-methylimidazole in THF at 40 °C for 3.5–38 h. b) Mol% means 10^{-2} molar amount against *t*-butyl diazoacetate.

Cyclopropanation of Various Diazoacetates and Alkenes. The cobalt(II) complex catalysts **14a** and **15a** were successfully applied to the enantioselective cyclopropanation of various diazoacetates with styrene. In the presence of 0.05 molar amount of cobalt(II) complex **14a** or **15a**, methyl, ethyl, cyclohexyl, and *t*-butyl diazoacetates (**16**, **2**, **17**, and **18**, Entries 1–4 in Table 8) were reacted with styrene to afford the corresponding cyclopropanecarboxylates in high yield with high diastereoselectivity (81–91%) and very high enantioselectivity (94–96% ee). It was reported that the high enantiomeric and diastereomeric excesses of the products were generally achieved using bulky alkyl diazoacetates, such as menthyl,[5,6] dicyclohexylmethyl,[7d] or 2,6-di-*t*-butyl-4-methylphenyl groups,[12,24] and that only a few complex catalysts realized highly enantioselective cyclopropanation with methyl or ethyl diazoacetate.[2] In the present cyclopropanation, the steric size of the alkyl groups of the diazoacetates had little influence on enantioselection. Even if methyl diazoacetate was used, 94% ee of the product was achieved by employing the cobalt complex **14a** as a catalyst.

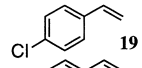
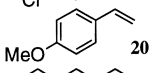
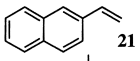
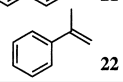
Thus, the procedure mentioned above was successfully applied to various styrene derivatives, such as 4-chloro- and 4-methoxystyrens, and 2-vinylnaphthalene, to afford the corresponding cyclopropanecarboxylates in high yields with 96%

Table 8. Cyclopropanation of Various Diazoacetates[a)]

Entry	Diazoacetate		Yield/%	*trans*:*cis*	ee (*trans*) /%
1	N_2CHCO_2Me	**16**	quant	83:17	94
2	N_2CHCO_2Et	**2**	96	81:19	95
3	N_2CHCO_2–⬡	**17**	94	86:14	94
4	N_2CHCO_2t-Bu	**18**	quant	91:9	96

a) Reaction conditions: Five hundredth molar amount of catalyst **14a** and 0.1 molar amount (2.0 molar amount vs Co(II) complex) of additive in THF at 50 °C for 2–17 h.

Table 9. Enantioselective Cyclopropanation of Various Alkenes[a)]

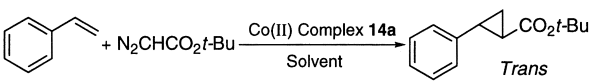
Entry	Alkene[b)]	Yield/%	*trans*:*cis*	ee (*trans*)/%
1	 **19**	93	90:10	96
2	 **20**	85	87:13	96
3	 **21**	95	87:13	96
4	 **22**	47	47:53	99 (93)[c)]

a) Reaction conditions: Five handredth molar amount of catalyst **14a** and 0.1 molar amount (2.0 molar amount vs Co(II) complex) of *N*-methylimidazole in THF at 40–50 °C for 4.5–30 h. b) Five molar amount vs *t*-butyl diazoacetate were employed. c) Ee of the *cis*-isomer is shown in parenthesis.

ee (Entries 1–3 in Table 9). 2-Phenylstyrene was also converted into the corresponding product with 99% ee (for the *trans*-product, Entry 4), while the yield and the diastereoselectivity were poor.

Cobalt(II) Complex-Catalyzed Cyclopropanation in Protic Solvents. Unexpectedly, an interesting solvent-effect was discovered by reexamination of the solvent in the cobalt(II) complex-**14a** catalyzed reactions (Table 10). It was pointed out that the reaction proceeded very slowly in a nonpolar solvent without *N*-methylimidazole, such as $CHCl_3$ or toluene, and that the reaction proceeded slightly faster in anhydrous THF (Table 1 and Table 10). As shown in Entry 8 of Table 3, a catalytic amount of water did not influence the reaction. Surprisingly, it was found that the reaction was significantly accelerated in aqueous THF solvent (5%(v/v) water) (Entry 4). It should be pointed out here that excess water did not inhibit the present cyclopropanation but remarkably enhanced the reaction rate to improve the diastereo- and enantioselectivity compared with that in a nonpolar solvent. Methanol was examined as the solvent instead of aqueous THF (Entry 5), and the reaction proceeded smoothly and was completed in 7 h. Besides,

Table 10. Various Solvents for Enantioselective Cyclopropanation[a)]



Entry	Solvent	Time /h	Yield /%	*trans*:*cis*	ee /%[b)]
1	$CHCl_3$	34	40	70:30	76
2	Toluene	34	31	72:28	76
3	THF	10	39	77:23	87
4	THF + H_2O[c)]	8	58	78:22	88
5	MeOH	7	88	83:17	93
6	MeOH + H_2O[c)]	7	89	83:17	92

a) Reaction conditions: Five hundredth molar amount of catalyst **14a** at 50 °C. b) Enantiomeric excesses of *trans*-products. c) Five %(v/v) water.

the diastereo- and enantioselectivities were considerably improved to 83% *trans*-selectivity and 93% ee. An aqueous alcoholic solvent was also effective (Entry 6). The cyclopropanation in aqueous methanol (5%(v/v) water) smoothly proceeded to afford the product in good *trans*-selectivity with high enantiomeric excess. It was recently reported that the addition of water remarkably decreased the enantiomeric excess of the product during the cyclopropanation catalyzed by dirhodium(II) tetrakis[(*S*)-1-(4-*t*-butylphenylsulfonyl)pyrrolidine-2-carboxylate] [Rh_2(TBSP)$_4$].[25] It was also reported that the use of a coordinating solvent, i.e., nitroethane, reduced the diastereo- and enantioselectivity in the Cu(OTf)$_2$-bisoxazoline-catalyzed cyclopropanation.[26] The opposite effect of water and alcohol was observed for the present 3-oxobutylideneaminatocobalt catalyzed cyclopropanation reaction.[27]

These observations were explained as follows: the tetradentate ligand of the 3-oxobutylideneaminatocobalt complex produced a rigid square planar structure around the cobalt atom,[28] and the structure of the complex was almost independent of solvent coordination. Therefore, the coordination of a donor solvent on a vacant axial position would directly lead to activating the carbene–carbon located at the other axial position.[29]

Among various alcoholic solvents and other polar solvents studied (Table 11), methanol was the most effective alcohol for achieving excellent yield and selectivity (Entry 1). In an alcohol with a longer alkyl chain, the reaction was slowed down (Entries 2–4). The enantioselectivities were affected by the alkyl size of the alcohol; i.e., the ee decreased in order, methanol (93% ee) > primary alcohol (88–90% ee) > secondary alcohol (85–86% ee) > tertiary alcohol (81% ee). As shown in Fig. 3, the plot of the dielectric constant of alcohols[30] vs enantioemeric excesses clearly indicated that the enantioemeric excess was related to the dielectric constant of the alcohols. Using an alcohol with a larger dielectric constant produced a higher enantiomeric excess of the product. These observations should also be ascribed to the stronger coordination of the alcohol to the cobalt atom and to increased electron density on the carbene carbon. During the [Rh_2(TBSP)$_4$]-catalyzed cyclopropanation in supercritical and liquid solvent, the enantioselectivity of the product was affected by the dielectric constant of the nonpolar solvent.[25] However, the present results clearly showed the opposite tendency.

Examination of other solvents indicated that the polarity of the solvents was not the only crucial factor for improving the present reaction.[31] Dimethylformamide was also a suitable solvent (Entry 11), while the product was obtained in low yield with low ee in AcOEt, acetone, and nitromethane (Entries 8, 9, and 12) or the reaction resulted in a complex mixture in acetonitrile (Entry 10). Precise study of the reaction mechanism will be required for clarifying the solvent effects.

The synthetic utilities of the alcoholic solvent for cobalt-catalyzed cyclopropanation were demonstrated. Various monosubstituted styrene derivatives were converted to the corresponding carboxylates in good-to-high yield with 90–96% ee (Entries 2–4 in Table 12). The superiority of methanol to the THF/*N*-methylimidazole system was observed for the cyclopropanation of 1,1-disubstituted ethylenes. Only a 47% yield of the product for 2-phenylpropene was obtained when the cyclopropanation was performed in THF in the presence of a cat-

Table 11. Various Alcoholic and Polar Solvents for Enantioselective Cyclopropanation[a)]

Entry	Solvent	ε[b)]	Time/h	Yield/%	*trans*:*cis*	ee/%[c)]
1	MeOH	32.6	7	88	83:17	93
2	EtOH	24.3	17	79	76:24	90
3	*n*-PrOH	20.1	26	60	79:21	88
4	*n*-BuOH	17.1	26	66	80:20	89
5	*i*-PrOH	18.3	26	66	73:27	86
6	*c*-HexOH	15.0	26	52	73:27	85
7	*t*-BuOH	10.9	26	62	74:26	81
8	CH_3COOEt	6.02	26	18	69:31	60
9	CH_3COCH_3	20.7	26	29	69:31	77
10	CH_3CN	36.2	32	complex mixture		
11	DMF	36.7	26	quant	82:18	94
12	CH_3NO_2	38.6	26	16	62:38	51

a) Reaction conditions: Five hundredth molar amount of catalyst **14a** at 50 °C.
b) Dielectric constant at 25 °C (see Ref. 30). c) Ee of *trans*-products.

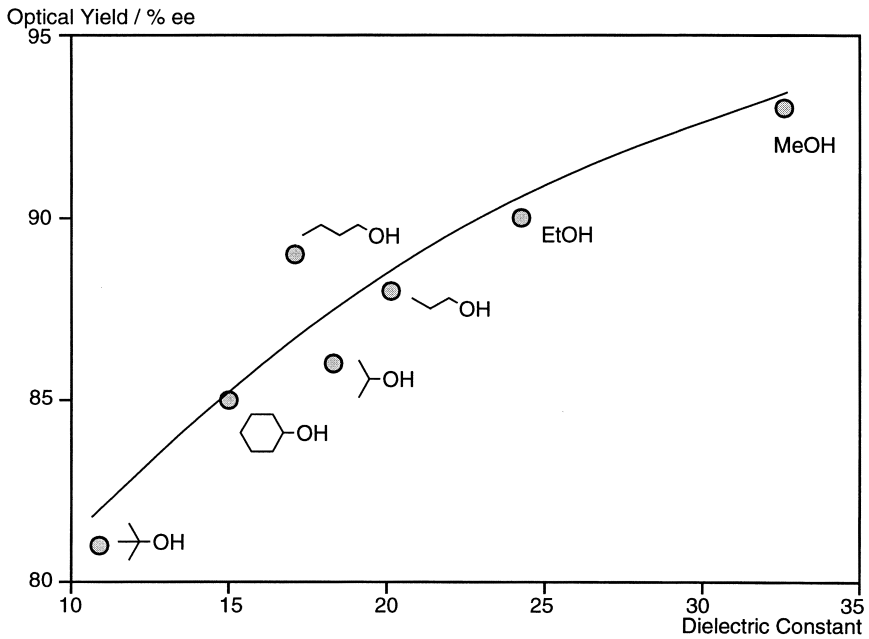


Fig. 3. The dependence of the optical yield of the product on the dielectric constant of the alcohols.

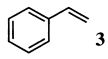
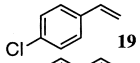
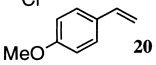
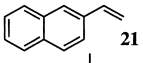
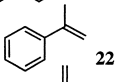
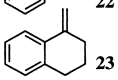
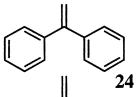
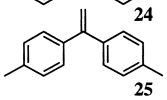
alytic amount of *N*-methylimidazole,[19] although the reaction smoothly proceeded in methanol and the enantiomeric excess of the products was very high (Entry 5). Other 1,1-disubstituted ethylenes, such as 3,4-dihydro-1(2*H*)methylenenaphthalene and the 1,1-diphenylethylenes, were also effectively converted to the products with high enantiomeric excesses (Entries 6–8).

The reaction mechanism involving diastereo- and enantioselections of the present cyclopropanation will be described using a computational method in a later paper.

Conclusion

Highly enantioselective cyclopropanation of styrenes was achieved in the presence of the rationally designed 3-oxobutylideneaminatocobalt(II) complex catalyst. Addition of *N*-methylimidazole had a significant effect on enhancing the reactivity and improving the enantiomeric excess. The steric size of the diamine unit of the complex remarkably influenced the enantioselectivity and its side chain influenced the diastereoselectivity. The cobalt(II) complexes composed of sterically demanding 1,2-dimesitylethylenediamine and ester side chains afforded the cyclopropanecarboxylates in excellent enantio- and high *trans*-selectivity (96% ee, *trans*:*cis* = 91:9) in the presence of a catalytic amount of *N*-methylimidazole. Diazoacetates with small alkyl groups such as methyl and ethyl esters were tolerable for obtaining the product with high enantiomeric excess (94% ee for methyl and 95% ee for ethyl). Although catalytic loading of water and alcohol had no effect on the reaction, the cyclopropanation was remarkably accelerated in aqueous or alcoholic solvents, even without *N*-methylimidazole, and the diastereo- and enantioselectivities were also improved. In aqueous methanol, 1,1-disubstituted ethylenes were smoothly cyclopropanated with high enantiomeric excesses.

Table 12. Enantioselective Cyclopropanation of Various Alkenes in Aqueous Methanol[a)]

Entry	Alkene	Yield/%	*trans*:*cis*	ee (*trans*)/%
1	 **3**	89	83:17	92
2	 **19**	83	84:16	96
3	 **20**	74	77:23	91
4	 **21**	67	86:14	90
5	 **22**	88	49:51	97 (51)[b)]
6	 **23**	85	28:72	96 (84)[b)]
7	 **24**	99	—	90
8	 **25**	95	—	89

a) Reaction conditions: Five handredth molar amount of catalyst **14a** in MeOH −5% H_2O at 50 °C for 7–26 h. b) Ee of *cis*-isomer is shown in parenthesis.

Experimental

General: The melting points were measured on an Electrothermal IA9100 apparatus or a Rigaku DSC-8230 apparatus (differential scanning calorimetry, DSC) and are uncorrected.

(a) Spectrometers: Infrared (IR) spectra were recorded on a JASCO Model FT/IR-410 infrared spectrometer on KBr pellets or liquid film on NaCl. ^{1}H NMR spectra and ^{13}C NMR spectra were measured on a JEOL Model GX-400 spectrometer using $CDCl_3$ as a solvent and with tetramethylsilane as an internal standard. High-resolution mass spectra were obtained with a HITACHI M-8013. FAB mass spectra were recorded with a JEOL MStation JMS-700 spectrometer using 3-nitrobenzyl alcohol (NBA) as a matrix agent.

(b) Chromatography: For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 F254, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel (silica gel 60N). High-performance liquid chromatography (HPLC) analyses were performed with a Shimadzu LC-6A chromatograph using an optically active column (Chiralcel OB-H, OD-H, and Chiralpak AD columns, Daicel Ltd., Co.); the peak areas were obtained with a Shimadzu Chromatopack CR-4A or a Varian Dynamax MacIntegrator.

(c) Optical Rotations: Optical rotations were measured with a JASCO DIP-370 digital polarimeter.

Styrenes: Styrene (**3**), *p*-chlorostyrene (**19**), *p*-methoxystyrene (**20**), 2-phenylpropene (**22**), and 1,1-diphenylethylene (**24**), were purchased from Tokyo Kasei Kogyo (TCI) Co., Ltd.. 2-Vinylnaphthalene (**21**) was purchased from Aldrich Co.. 3,4-Dihydro-1(2*H*)-methylenenaphthalene (**23**)[32] and 1,1-bis(4-methylphenyl)ethylene (**25**)[33] were each prepared by the reported method.

Diazoacetates: Methyl diazoacetate (**16**),[34] ethyl diazoacetate (**2**),[34] cyclohexyl diazoacetate (**17**)[24] and *t*-butyl diazoacetate (**18**)[24] were prepared according to the literature.

Preparation of Optically Active 3-Oxobutylideneaminato Ligands: The ligands **1b**, **7b**, and **8b** were prepared by the reported method[13] from 3-oxo-2-(2,4,6-trimethylbenzoyl)butanal and (1*S*,2*S*)-1,2-diarylethylenediamines.

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediamine (1b): ^{1}H NMR (400 MHz) δ 1.92 (6H, s), 1.98 (6H, s), 2.26 (6H, s), 2.63 (6H, brs), 4.41 (2H, d, J = 7.2 Hz), 6.72-6.74 (4H, m), 6.98–7.00 (6H, m), 7.24–7.26 (6H, m), 11.98 (2H, brs); ^{13}C NMR (100 MHz) δ 19.1, 21.1, 31.8, 69.4, 112.6, 126.5, 128.0, 128.2, 128.6, 128.9, 133.3, 133.4, 135.4, 137.4, 161.0, 196.2, 201.1; IR (KBr) 2971, 2917, 1615, 1454, 1405, 1353, 1299, 1252, 1200, 981, 849, 697 cm^{-1}. Found: C, 78.55; H, 6.91; N, 4.39%. Calcd for $C_{42}H_{44}N_2O_4$: C, 78.72; H, 6.92; N, 4.37%. Mp 210.4–211.2 °C. $[\alpha]_D^{28}$ +72.3° (*c* 0.507, $CHCl_3$).

(1*S*,2*S*)-1,2-Bis(3,5-dimethylphenyl)-*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]ethylenediamine (7b): ^{1}H NMR (400 MHz) δ 1.82 (6H, s), 1.99 (6H, s), 2.23–2.25 (18H, m), 2.66 (6H, brs), 4.34 (2H, d, J = 6.8 Hz), 6.63 (4H, s), 6.70 (4H, s), 6.83–6.95 (4H, m), 11.91 (2H, br); ^{13}C NMR (100 MHz) δ 19.0, 19.2, 21.1, 21.3, 31.8, 69.5, 112.5, 124.1, 128.0, 130.2, 133.3, 133.4, 135.4, 137.3, 138.6, 161.3, 196.2, 200.9; IR (KBr) 2921, 2860, 1620, 1407, 1352, 1307, 1257, 1200, 1169, 980, 849, 802 cm^{-1}. Calcd for $C_{46}H_{52}N_2O_4$: (M^+), 696.3927. Found: *m*/*z* 696.3914. Mp 211.3–213.3 °C. $[\alpha]_D^{22}$ +106.3° (*c* 1.006, $CHCl_3$).

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-dimesitylethylenediamine (8b): ^{1}H NMR(400 MHz) δ 1.42 (6H, s), 2.02 (6H, s), 2.10 (6H, s), 2.18 (6H, s), 2.23 (6H, brs), 2.28 (6H, s), 2.64 (6H, brs), 4.84 (2H, brs), 6.54 (2H, s), 6.73 (2H, s), 6.79 (4H, s), 7.07 (2H, brs), 11.52 (2H, brs); ^{13}C NMR (100 MHz) δ 19.01, 19.05, 19.9, 20.4, 20.8, 21.2, 31.6, 61.6, 112.7, 127.7, 128.1, 129.38, 129.44, 131.4, 133.0, 133.6, 134.8, 136.7, 137.5, 138.3, 140.7, 161.2, 196.3, 200.2; IR (KBr) 2921, 1624, 1404, 1350, 1305, 1257, 1200, 1171, 983, 849, 820 cm^{-1}. Found: C, 79.27; H, 7.70; N, 3.83. Calcd for $C_{48}H_{56}N_2O_4$: C, 79.52; H, 7.79; N, 3.86%. Mp 171.4–173.2 °C. $[\alpha]_D^{24}$ +27.5° (*c* 1.019, $CHCl_3$).

(1*S*,2*S*)-*N*,*N*′-Bis(2-acetyl-3-oxobutylidene)-1,2-diphenylethylenediamine (9b): ^{1}H NMR (400 MHz) δ 2.09 (6H, s), 2.50 (6H, s), 4.57–4.62 (2H, m), 7.11–7.14 (4H, m), 7.30–7.36 (6H, m), 7.55 (2H, d, J = 12.7 Hz), 11.97 (2H, br); ^{13}C NMR (100 MHz) δ 27.0, 31.9, 70.2, 112.1, 126.8, 128.8, 129.0, 135.4, 158.8, 194.0, 200.9; IR (KBr) 3445, 3029, 2925, 1613, 1398, 1250, 1194, 984, 694, 592 cm^{-1}. Found: C, 72.28; H, 6.52; N, 6.48%. Calcd for $C_{26}H_{28}N_2O_4$: C, 72.20; H, 6.53; N, 6.48%. Mp 209.3–210.3 °C. $[\alpha]_D^{27}$ +199.9° (*c* 1.036, $CHCl_3$).

(1*S*,2*S*)-*N*,*N*′-Bis(2-acetyl-3-oxobutylidene)-1,2-bis(3,5-dimethylphenyl)ethylenediamine (10b): ^{1}H NMR (400 MHz) δ 2.06 (6H, s), 2.27 (12H, s), 2.50 (6H, s), 4.49–4.54 (2H, m), 6.73 (4H, s), 6.95 (2H, s), 7.46 (2H, d, J = 12.2 Hz), 11.80 (2H, br); ^{13}C NMR (100 MHz) δ 21.3, 26.9, 31.9, 70.2, 111.9, 124.6, 130.3, 135.3, 138.7, 159.0, 194.0, 200.7; IR (KBr) 3448, 2921, 1632, 1397, 1313, 1245, 984, 851, 601 cm^{-1}. Found: C, 73.81; H, 7.38; N, 5.74%. Calcd for $C_{30}H_{36}N_2O_4$: C, 73.74; H, 7.43; N, 5.73%. Mp 217.5–219.3 °C. $[\alpha]_D^{27}$ +196.2° (*c* 1.041, $CHCl_3$).

(1*S*,2*S*)-*N*,*N*′-Bis(2-acetyl-3-oxobutylidene)-1,2-dimesitylethylenediamine (11b): ^{1}H NMR (400 MHz) δ 1.74 (6H, brs), 2.22 (12H, s), 2.46 (6H, s), 2.73 (6H, brs), 5.17–5.23 (2H, m), 6.66 (2H, brs), 6.91 (2H, brs), 7.66 (2H, d, J = 12.2 Hz), 11.89 (2H, br); ^{13}C NMR (100 MHz) δ 20.3, 20.8, 21.5, 27.1, 31.8, 62.9, 112.5, 129.4, 129.8, 131.4, 138.3, 158.5, 194.1, 200.5; IR (KBr) 3239, 2970, 1627, 1576, 1398, 1312, 1248, 1193, 799, 590 cm^{-1}.

Calcd for $C_{32}H_{41}N_2O_4$: $(M+H)^+$, 517.3066. Found: *m/z* 517.3090. Mp 165.8–167.3 °C. $[\alpha]_D^{25}$ +180.7° (*c* 1.003, $CHCl_3$).

(1*S*,2*S*)-*N*,*N*′-Bis(2-cyclopentyloxycarbonyl-3-oxobutylidene)-1,2-diphenylethylenediamine (12b): ^{1}H NMR (400 MHz) δ 1.55–1.72 (12H, m), 1.81–1.92 (4H, m), 2.48 (6H, s), 4.59–4.63 (2H, m), 5.17–5.21 (2H, m), 7.02–7.09 (4H, m), 7.25–7.33 (6H, m), 7.78 (2H, d, J = 12.7 Hz), 11.90 (2H, br); ^{13}C NMR (100 MHz) δ 23.8, 30.9, 32.7, 69.5, 76.2, 101.6, 126.9, 128.5, 128.7, 135.4, 158.8, 166.2, 199.5; IR (KBr) 3446, 2964, 1697, 1632, 1573, 1415, 1299, 1240, 1056, 699, 578 cm^{-1}. Calcd for $C_{34}H_{41}N_2O_6$: $(M+H)^+$, 573.2965. Found: *m/z* 573.2981. Mp 74.6–75.7 °C. $[\alpha]_D^{25}$ +77.64° (*c* 1.138, $CHCl_3$).

(1*S*,2*S*)-*N*,*N*′-Bis(2-*t*-butyloxycarbonyl-3-oxobutylidene)-1,2-diphenylethylenediamine (13b): ^{1}H NMR (400 MHz) δ 1.46 (18H, s), 2.47 (6H, s), 4.55–4.60 (2H, m), 7.04–7.06 (4H, m), 7.27–7.29 (6H, m), 7.77 (2H, d, J = 12.7 Hz), 11.85 (2H, br); ^{13}C NMR (100 MHz) δ 28.5, 31.2, 69.7, 79.8, 102.7, 127.0, 128.6, 128.8, 135.6, 158.9, 166.1, 199.7; IR (KBr) 3442, 3008, 2978, 1688, 1625, 1391, 1245, 1164, 1064, 802, 692 cm^{-1}. Calcd for $C_{32}H_{40}N_2O_6$: (M^+), 548.2886. Found: *m/z* 548.2902. Mp 143.4–144.4 °C. $[\alpha]_D^{24}$ +100.5° (*c* 1.009, $CHCl_3$).

(1*S*,2*S*)-*N*,*N*′-Bis(2-cyclopentyloxycarbonyl-3-oxobutylidene)-1,2-dimesitylethylenediamine (14b): ^{1}H NMR (400 MHz) δ 1.54–1.78 (16H, m), 1.81–1.90 (6H, m), 2.21 (6H, s), 2.43 (6H, s), 2.65 (6H, brs), 5.17–5.26 (4H, m), 6.63 (2H, brs), 6.88 (2H, brs), 7.89 (2H, d, J = 12.7 Hz), 11.79 (2H, br); ^{13}C NMR (100 MHz) δ 20.1, 20.7, 21.1, 23.7, 30.8, 32.8, 62.1, 76.3, 101.9, 129.5, 130.1, 131.3, 137.9, 158.7, 166.5, 198.8; IR (KBr) 3480, 2965, 2871, 1700, 1632, 1574, 1415, 1240, 1055, 794 cm^{-1}. Found: C, 73.05; H, 8.06; N, 4.12%. Calcd for $C_{40}H_{52}N_2O_6$: C, 73.14; H, 7.98; N, 4.26%. Mp 73.1–76.1 °C. $[\alpha]_D^{24}$ +48.51° (*c* 1.022, CH_2Cl_2).

(1*S*,2*S*)-*N*,*N*′-Bis(2-*t*-butoxycarbonyl-3-oxobutylidene)-1,2-dimesitylethylenediamine (15b): ^{1}H NMR (400 MHz) δ 1.50 (18H, s), 1.67 (6H, br), 2.20 (6H, s), 2.42 (6H, s), 2.67 (6H, brs), 5.17–5.19 (2H, m), 6.61 (2H, brs), 6.87 (2H, brs), 7.89 (2H, d, J = 12.7 Hz), 11.75 (2H, br); ^{13}C NMR (100 MHz) δ 20.1, 20.8, 21.2, 28.5, 31.2, 62.2, 79.8, 120.8, 129.5, 130.3, 131.3, 137.9, 159.0, 166.3, 198.9; IR (KBr) 3423, 2975, 2929, 1701, 1632, 1573, 1415, 1366, 1245, 1167, 1058, 792 cm^{-1}. Calcd for $C_{38}H_{53}N_2O_6$: $(M+H)^+$, 633.3904. Found: *m/z* 633.3945. Mp 74.2–75.4 °C. $[\alpha]_D^{27}$ +52.82° (*c* 1.059, $CHCl_3$).

Preparation of Optically Active 3-Oxobutylideneaminatocobalt(II) Complexes: Cobalt(II) complexes **1a**, **7a**, and **8a** were prepared by the reported method.[28]

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediaminatocobalt(II) (1a): MS (FAB^+) *m/z* 698 $(M+H)^+$. Mp 299.2 °C (DSC).

(1*S*,2*S*)-1,2-Bis(3,5-dimethylphenyl)-*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)]ethylenediaminato]cobalt(II) (7a): MS (FAB^+) *m/z* 754 $(M+H)^+$. Mp 334.1 °C (DSC).

(1*S*,2*S*)-*N*,*N*′-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-dimesitylethylenediaminatocobalt(II) (8a): MS (FAB^+) m/z 782 $(M+H)^+$. Mp 248.8 °C (DSC).

(1*S*,2*S*)-*N*,*N*′-Bis(2-acetyl-3-oxobutylidene)-1,2-diphenylethylenediaminatocobalt(II) (9a): MS (FAB^+) *m/z* 490 $(M+H)^+$. Mp 293.5 °C (DSC).

(1*S*,2*S*)-*N*,*N*′-Bis(2-acetyl-3-oxobutylidene)-1,2-bis(3,5-dimethylphenyl)ethylenediaminatocobalt(II) (10a): MS (FAB^+) *m/z* 546 $(M+H)^+$. Mp 268.6 °C (DSC).

(1*S*,2*S*)-*N*,*N*′-Bis(2-acetyl-3-oxobutylidene)-1,2-dimesitylethylenediaminatocobalt(II) (11a):[35] MS (FAB^+) *m/z* 574 $(M+H)^+$. Mp 286.7 °C (DSC).

(1*S*,2*S*)-*N*,*N*′-Bis(2-cyclopentyloxycarbonyl-3-oxobutylidene)-1,2-diphenylethylenediaminatocobalt(II) (12a): MS (FAB^+) *m/z* 630 $(M+H)^+$. Mp 262.2 °C (DSC).

(1*S*,2*S*)-*N*,*N*′-Bis(2-*t*-butoxycarbonyl-3-oxobutylidene)-1,2-diphenylethylenediaminatocobalt(II) (13a): MS (FAB^+) *m/z* 606 $(M+H)^+$. Mp 263.6 °C (DSC).

(1*S*,2*S*)-*N*,*N*′-Bis(2-cyclopentyloxycarbonyl-3-oxobutylidene)-1,2-dimesitylethylenediaminatocobalt(II) (14a): MS (FAB^+) *m/z* 714 $(M+H)^+$. Mp 249.3 °C (DSC).

(1*S*,2*S*)-*N*,*N*′-Bis(2-*t*-butoxycarbonyl-3-oxobutylidene)-1,2-dimesitylethylenediaminatocobalt(II) (15a): MS (FAB^+) *m/z* 690 $(M+H)^+$. Mp 227.6 °C (DSC).

General Procedure for the Enantioselective Cyclopropanation Reaction to *t*-butyl (1*R*,2*S*)-*cis*- and (1*S*,2*S*)-*trans*-2-phenylcyclopropane-1-carboxylate (26 and 27): To a solution of the cobalt complex **1a** (35.0 mg, 0.05 mmol) in THF (1.0 mL) was added styrene (0.57 mL, 5.0 mmol) and *t*-butyl diazoacetate (148 µL, 1.0 mmol) at 25 °C under a N_2 atmosphere, and then *N*-methylimidazole (8 µL, 0.1 mmol) was added to the solution. GC analysis after 2 h indicated that the diazoacetate was completely consumed and that the corresponding *t*-butyl 2-phenylcyclopropane-1-carboxylate was produced in a 76:24 ratio mixture of *trans* and *cis* isomers. The products, *t*-butyl *cis*- and *trans*-2-phenylcyclopropane-1-carboxylate (**26**[36] and **27**[11b]) and *cis*- and *trans*-2-phenylcyclopropylmethanol (**28** and **29**)[37] were identified with the corresponding materials reported previously. The reaction mixture was purified with silica-gel column chromatography to obtain the product in 98% yield. The mixture of *cis* and *trans* 2-phenylcyclopropane-1-carboxylate was treated with $LiAlH_4$ to afford the corresponding mixture of *cis*- and *trans*-2-phenylcyclopropylmethanol (**28** and **29**) and then HPLC analysis of the reduced mixture revealed that the *trans* isomer was 84% ee (Daicel Chiralcel OD-H, 5% 2-propanol in hexane, flow 1.0 mL/min, 12.9 min (major), 17.9 min (minor)) and that the *cis* isomer was 85% ee (Daicel Chiralcel OB-H, 5% 2-propanol in hexane, flow 1.0 mL/min, 7.2 min (minor), 8.0 min (major)).

2-Phenylcyclopropane-1-carboxylate derivatives: *t*-Butyl *cis*-2-(4-chlorophenyl)cyclopropane-1-carboxylate (**30**),[36] *t*-butyl *trans*-2-(4-chlorophenyl)cyclopropane-1-carboxylate (**31**),[11b] *t*-butyl *cis*-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (**32**),[36] *t*-butyl *trans*-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (**33**),[8] *t*-butyl *cis*-2-(2-naphthyl)cyclopropane-1-carboxylate (**34**),[38] *t*-butyl *trans*-2-(2-naphthyl)cyclopropane-1-carboxylate (**35**),[38] *t*-butyl (1*R**,2*S**)-*cis*-2-methyl-2-phenylcyclopropane-1-carboxylate (**36**),[36] *t*-butyl (1*R**,2*R**)-*trans*-2-methyl-2-phenylcyclopropane-1-carboxylate (**37**),[36] *t*-butyl 2,2-diphenylcyclopropane-1-carboxylate (**38**),[39] ethyl *cis*-2-phenylcyclopropane-1-carboxylate (**39**),[6b] ethyl *trans*-2-phenylcyclopropane-1-carboxylate (**40**),[6b] methyl *cis*-2-phenylcyclopropane-1-carboxylate (**41**),[40] and methyl *trans*-2-phenylcyclopropane-1-carboxylate (**42**)[40] were identified with the corresponding material reported previously.

***t*-Butyl (1*R**,2*R**)-spiro[cyclopropane-1,1′(2′*H*)-3′,4′-dihydronaphthalene]-2-carboxylate (43):** ^{1}H NMR (400 MHz) δ 1.45 (9H, s), 1.45–1.48 (1H, m), 1.52 (1H, dd, J = 5.1, 8.1 Hz), 1.70–1.80 (1H, m), 1.83–2.00 (4H, m), 2.87–2.90 (2H, m), 6.70–6.73 (1H, m), 7.08–7.13 (3H, m); ^{13}C NMR (100 MHz) δ 21.8, 22.3, 27.6, 28.3, 28.6, 30.6, 33.5, 80.3, 121.7, 125.5, 126.1, 128.9, 137.7, 139.8, 170.3; IR (neat) 2977, 2929, 1715, 1455, 1392, 1366, 1147, 841, 760, 742 cm^{-1}. Found: C, 79.05; H, 8.62%. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58%. $[\alpha]_D^{28}$ +226° (*c* 0.251, $CHCl_3$). Enantiomeric excess was determined by Chiralcel OB-H

(2% 2-propanol in hexane, flow 1.0 mL/min), 12.3 min (major), 13.5 min (minor), after the ester **43** was converted to the corresponding alcohol by $LiAlH_4$.

***t*-Butyl (1*R**,2*S**)-Spiro[cyclopropane-1,1′(2′*H*)-3′,4′-dihydronaphthalene]-2-carboxylate (44):** ^{1}H NMR (400 MHz) δ 1.08 (9H, s), 1.11–1.14 (1H, m), 1.20–1.22 (1H, m), 1.78 (1H, dd, J = 5.9, 7.6 Hz), 1.83–1.91 (1H, m), 2.00–2.03 (1H, m), 2.06–2.16 (2H, m), 2.80–2.96 (2H, m), 7.08 (4H, m); ^{13}C NMR (100 MHz) δ 16.1, 21.9, 27.8, 29.3, 31.0, 33.5, 35.1, 79.8, 124.6, 125.7, 126.1, 127.7, 135.2, 139.4, 169.2; IR (neat) 2976, 2931, 1725, 1456, 1391, 1366, 1232, 1148, 847, 789, 741 cm^{-1}. Calcd for $C_{17}H_{22}O_2$: (M^+), 258.1620. Found: *m/z* 258.1620. $[\alpha]_D^{28}$ +72.5° (*c* 0.306, $CHCl_3$). Enantiomeric excess was determined by Chiralcel OD-H (2% 2-propanol in hexane, flow 1.0 mL/min), 11.6 min (minor), 13.1 min (major), after the ester **44** was converted to the corresponding alcohol by $LiAlH_4$.

***t*-Butyl 2,2-bis(4-methylphenyl)cyclopropane-1-carboxylate (45):** ^{1}H NMR (400 MHz) δ 1.24 (9H, s), 1.47 (1H, dd, J = 4.9, 8.1 Hz), 2.04 (1H, dd, J = 4.9, 5.9 Hz), 2.27 (3H, s), 2.29 (3H, s), 2.40 (1H, dd, J = 5.9, 8.1 Hz), 7.03–7.07 (4H, m), 7.10–7.12 (2H, m), 7.21–7.23 (2H, m); ^{13}CNMR (100 MHz) δ 20.2, 21.0, 21.2, 27.9, 30.1, 38.9, 80.2, 127.2, 128.7, 128.9, 129.7, 135.7, 136.1, 137.3, 142.4, 169.7; IR (neat) 2977, 2925, 1729, 1515, 1366, 1150, 1090, 849, 811, 550 cm^{-1}. Found: C, 81.84; H, 8.02%. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13%. $[\alpha]_D^{25}$ +161° (*c* 0.622, $CHCl_3$). Enantiomeric excess was determined by Chiralcel OD-H (5% 2-propanol in hexane, flow 1.0 mL/min), 7.9 min (minor), 10.2 min (major), after the ester **45** was converted to the corresponding alcohol by $LiAlH_4$.

References

1 a) H. Nozaki, S. Moriuti, H. Takaya, and R. Noyori, *Tetrahedron Lett.*, **1966**, 5239. b) H. Nozaki, H. Takaya, S. Moriuti, and R. Noyori, *Tetrahedron*, **24**, 3655 (1968).

2 a) M. P. Doyle, M. A. McKervey, and T. Ye, "Modern Catalytic Methods for Organic Synthesis with Diazo Compounds," John Wiley & Sons, New York (1998). b) M. P. Doyle and M. N. Protopopova, *Tetrahedron*, **54**, 7919 (1998). c) M. P. Doyle and D. C. Forbes, *Chem. Rev.*, **98**, 911 (1998).

3 T. Aratani, *Pure Appl. Chem.*, **57**, 1839 (1985).

4 a) A. Nakamura, A. Konishi, Y. Tatsuno, and S. Otsuka, *J. Am. Chem. Soc.*, **100**, 3443, 6544 (1978). b) A. Nakamura, A. Konishi, R. Tsujitani, M. Kudo, and S. Otsuka, *J. Am. Chem. Soc.*, **100**, 3449 (1978). c) A. Nakamura, *Pure Appl. Chem.*, **50**, 37 (1978).

5 a) T. Aratani, Y. Yoneyoshi, and T. Nagase, *Tetrahedron Lett.*, **1975**, 1707. b) T. Aratani, Y. Yoneyoshi, and T. Nagase, *Tetrahedron Lett.*, **1977**, 2599. c) T. Aratani, Y. Yoneyoshi, and T. Nagase, *Tetrahedron Lett.*, **1982**, 685.

6 a) H. Fritschi, U. Leutenegger, and A. Pfaltz, *Angew. Chem., Int. Ed. Engl.*, **25**, 1005 (1986). b) H. Fritschi, U. Leutenegger, and A. Pfaltz, *Helv. Chim. Acta*, **71**, 1553 (1988). c) U. Leutenegger, G. Umbricht, C. Fahrni, and P. von Matt, and A. Pfaltz, *Tetrahedron*, **48**, 2143 (1992). d) A. Pfaltz, *Acc. Chem. Res.*, **26**, 339 (1993).

7 a) R. E. Lowenthal, A. Abiko, and S. Masamune, *Tetrahedron Lett.*, **31**, 6005 (1990). b) D. Müller, G. Umbricht, B. Weber, and A. Pfaltz, *Helv. Chim. Acta*, **74**, 232 (1991). c) D. A. Evans, K. A. Woerpel, M. M. Hinman, and M. M. Faul, *J. Am. Chem. Soc.*, **113**, 726 (1991). d) R. E. Lowenthal and S. Masamune, *Tetrahedron Lett.*, **32**, 7373 (1991). e) D. A. Evans, K. A. Woerpel, and M. Scott, *Angew. Chem., Int. Ed. Engl.*, **31**, 430 (1992).

8 K. Ito and T. Katsuki, *Tetrahedron Lett.*, **34**, 2661 (1993).

9 a) H. Nishiyama, Y. Itoh, H. Matsumoto, S.-B. Park, and K. Itoh, *J. Am. Chem. Soc.*, **116**, 2223 (1994). b) H. Nishiyama, Y. Itoh, Y. Sugawara, H. Matsumoto, K. Aoki, and K. Itoh, *Bull. Chem. Soc. Jpn.*, **68**, 1247 (1995).

10 a) M. P. Doyle, B. D. Brandes, A. P. Kazala, R. J. Poeters, M. B. Jarstfer, L. M. Watkins, and C. T. Eagle, *Tetrahedron Lett.*, **31**, 6613 (1990). b) M. P. Doyle, W. R. Winchester, J. A. A. Hoorn, V. Lynch, S. H. Simonsen, and R. Ghosh, *J. Am. Chem. Soc.*, **115**, 9968 (1993). c) H. M. L. Davies, P. R. Bruzinski, D. H. Lake, N. Kong, and M. J. Fall, *J. Am. Chem. Soc.*, **118**, 6897 (1996). d) H. M. L. Davies, D. G. Stafford, B. D. Doan, and J. H. Houser, *J. Am. Chem. Soc.*, **120**, 3326 (1998).

11 a) T. Fukuda and T. Katsuki, *Synlett*, **1995**, 825. b) T. Fukuda and T. Katsuki, *Tetrahedron*, **53**, 7201 (1997).

12 M. M.-C. Lo and G. C. Fu, *J. Am. Chem. Soc.*, **120**, 10270 (1998).

13 T. Nagata, K. Imagawa, T. Yamada, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **68**, 1455 (1995).

14 T. Nagata, K. Imagawa, T. Yamada, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **68**, 3241 (1995).

15 T. Nagata, K. Yorozu, T. Yamada, and T. Mukaiyama, *Angew. Chem., Int. Ed. Engl.*, **34**, 2145 (1995).

16 K. D. Sugi, T. Nagata, T. Yamada, and T. Mukaiyama, *Chem. Lett.*, **1997**, 493.

17 T. Yamada, Y. Ohtsuka, and T. Ikeno, *Chem. Lett.*, **1998**, 1129.

18 a) T. Yamada, S. Kezuka, T. Mita, and T. Ikeno, *Heterocycles*, **52**, 1041 (2000). b) S. Kezuka, T. Mita, N. Ohtsuki, T. Ikeno, and T. Yamada, *Chem. Lett.*, **2000**, 824. c) S. Kezuka, T. Mita, N. Ohtsuki, T. Ikeno, and T. Yamada, *Bull. Chem. Soc. Jpn.*, **74**, 1333 (2001).

19 a) T. Yamada, T. Ikeno, H. Sekino, and M. Sato, *Chem. Lett.*, **1999**, 719. b) T. Ikeno, M. Sato, and T. Yamada, *Chem. Lett.*, **1999**, 1345.

20 T. Ikeno, A. Nishizuka, M. Sato, and T. Yamada, *Synlett*, **2001**, 406.

21 For examples: a) M. Calligaris, G. Nardin, L. Randaccio, and G. Tauzher, *Inorg. Nucl. Chem. Lett.*, **9**, 419 (1973). b) M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Nucl. Chem. Lett.*, **8**, 477 (1972). c) M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc., A*, **1970**, 2411. d) R. S. Gall, J. F. Rogers, W. P. Schaefer, and G. G. Christoph, *J. Am. Chem. Soc.*, **98**, 5135 (1976). e) W. P. Schaefer, R. Waltzman, and B. T. Huie, *J. Am. Chem. Soc.*, **100**, 5062 (1978).

22 For examples: a) P. Battioni, J. P. Renaud, J. F. Bartoli, M. Reina-Artiles, and D. Mansuy, *J. Am. Chem. Soc.*, **110**, 8462 (1988). b) P. L. Anelli, S. Banfi, F. Montanari, and S. Quici, *J. Chem. Soc., Chem. Commun.*, **1989**, 779. c) R. Irie, Y. Ito, and T. Katsuki, *Synlett*, **1991**, 265. d) T. Schwenkreis and A. Berkessel, *Tetrahedron Lett.*, **34**, 4785 (1993). e) T. Yamada, K. Imagawa, T. Nagata, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **67**, 2248 (1994).

23 When *N*-methylimidazole was added to a solution of the cobalt(II) complex catalyst and diazoacetate, the color of the solution immediately turned brown. Whereas, when 2-methylimidazole was added to the solution, the color changed little.

24 M. P. Doyle, V. Bagheri, T. J. Wandless, N. K. Harn, D. A. Brinker, C. T. Eagle, and K.-L. Loh, *J. Am. Chem. Soc.*, **112**, 1906 (1990).

25 D. C. Wynne, M. M. Olmstead, and P. G. Jessop, *J. Am.*

Chem. Soc., **122**, 7638 (2000).

26 J. M. Fraile, J. I García, J. A.Mayora, and T. Tarnai, *J. Mol. Cat. A: Chem*., **144**, 85 (1999).

27 A similar effect of protic solvents was independently reported in Ru-pybox catalyzed cyclopropanation. S. Iwasa, F. Takezawa, Y. Tuchiya, and H. Nishiyama, *Chem. Commun*., **2001**, 59.

28 T. Yamada, T. Nagata, T. Ikeno, Y. Ohtsuka, A. Sagara, and T. Mukaiyama, *Inorg. Chim. Acta*, **296**, 86 (1999).

29 As an alternative possibility of the acceleration effect of the axial ligand, it should be considered that the transformation of the diazoacetate into the cobalt carbene complex could be accelerated by the coordination of *N*-methylimidazole to the cobalt(II) complex.

30 A. J. Gordon, and A. F. Ford, "The Chemist's Companion A Handbook of Practical Data, Techniques, and References," John Wiley & Sons, New York (1972).

31 Not only the polarity of the solvents, but the other factors, such as the donating and accepting nature of the solvent depended on its heteroatom and/or functional group of coordination, the environment around the complex influenced by the solvent, and the side reactions between the solvent and the diazoester or between the solvent and the cobalt carbene complex, would play important roles for the enhancement of the reaction rate and the improvement of the stereoselectivities. Therefore, it is reasonable that the correlation between the dielectric constant and stereoselectivities could not be observed among different types of solvents. On the contrary, these factors should be similar or have a relation with the dielectric constant in a series of alcohols. Therefore, the correlation between the dielectric constant and enantioselectivity could be observed.

32 M. M. Campbell, N. Abbas, and M. Sainsbury, *Tetrahedron*, **41**, 5637 (1985).

33 C. F. H. Allen and S. Converse, *Org. Synth*., Coll. Vol. **1**, 226 (1941).

34 E. B. Womack and A. B. Nelson, *Org. Synth*., Coll. Vol. **3**, 392 (1955).

35 S. Ohba, T. Nagata, and T. Yamada, *Acta Crystallogr., Sect. E*, **E57**, m124 (2001).

36 T. Uchida, R. Irie, and T. Katsuki, *Tetrahedron*, **56**, 3501 (2000).

37 B. Scholl and H.-J. Hansen, *Helv. Chim. Acta*, **69**, 1936 (1986).

38 P. Müller, C. Baud, D. Ené, S. Motallebi, M. P. Doyle, B. D. Brandes, A. B. Dyatkin, and M. M. See, *Helv. Chim. Acta*, **78**, 459 (1995).

39 A. V. Bedekar, E. B. Koroleva, and P. G. Andersson, *J. Org. Chem*., **62**, 2518 (1997).

40 P. E. Krieger and J. A. Landgrebe, *J. Org. Chem*., **43**, 4447 (1978).