Preparation of Optically Active [1-(Methoxycarbonyl)ethyl]cobaloximes Coordinated with Various Axial Ligands and Their Photoracemization. Remarkable Steric Effect of Axial Ligand on the Co-C Bond Homolysis[1)]

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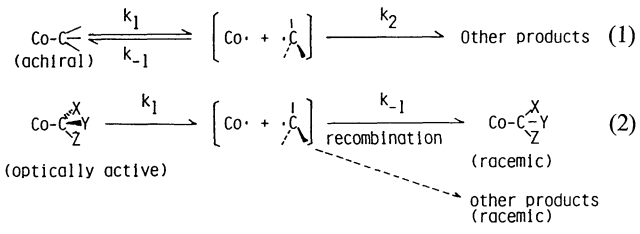
(Received November 28, 1990)

Optically active [1-(methoxycarbonyl)ethyl]cobaloximes coordinated with various axial bases were prepared and their photoracemization rates were measured in a solution state. It was found that although the electronic effect of the axial ligand was negligible on the rate of photochemical Co–C bond homolysis, the steric bulkines accelerated the rate remarkably. These results had a similar tendency to those observed in a previously reported reaction wtih 1-cyanoethyl cobaloximes, though the degree of rate enhancement due to the steric bulkiness of the axial ligand was extremely enlarged. The reason is also discussed.

Extensive investigations concerning the reactions of alkyl cobalt complexes have been carried out by spectrophotometric methods using achiral complexes. However, these methods include inherent possibilities for underestimating the rate of Co–C bond homolysis (k_1) (Eq. 1), when accompanied by a rapid backward reaction (recombination of alkyl radical and Co(II) species).



On the other hand, a chiroptical measurement using optically active alkylmetal complexes provides a more simple and precise evaluation of the forward rate (k_1). Since the alkyl radicals formed by bond homolysis are either planar or a rapidly inverting pyramid, the recombination of these species with Co(II) and other subsequent reactions (such as radical coupling and beta-elimination) should give substantially racemic or achiral products (Eq. 2). Thus, the Co–C bond homolysis rate constant of alkyl cobalt complexes (k_1) can be directly evaluated from the optical rotational change. We have shown that optically active alkylcobalt complexes are useful for the elucidation of both solution-state[2-4)] and solid-state[5-13)] reactions involving cobalt–carbon bond formation and cleavage, especially for the case of a system accompanied by an extremely rapid backward reaction.

In a previous paper[2a)] we reported on the photoracemization of 1-cyanoethyl cobaloxime complexes. Here, we wish to describe the preparation of new optically active [1-(methoxycarbonyl)ethyl]bis(dimethylglyoximato)cobalt(III) complexes which have chirality at the carbon bound directly to the cobalt atom; we also describe the effect of the axial ligand on the rate of photochemical Co–C bond homolysis.

Results and Discussion

Preparation of Optically Active [1-(Methoxycarbonyl)ethyl]cobaloxime Complexes. Bis(dimethylglyoximato)[(*S*)-1-(methoxycarbonyl)ethyl][(*S*)-1-phenylethylamine]cobalt(III), (***S,S***)-1, was prepared according to almost the same procedure as that described in a previous paper in which the preparation of the enantiomer, (***R,R***)-**1**, was reported.[2b)] Five recrystallizations gave a constant optical rotation ($[\alpha]_{589}$ −205.6, $[\alpha]_{578}$ −226.7, $[\alpha]_{546}$ −253.3(*c* 0.180, chloroform)). 4-Substituted pyridine complexes of bis(dimethylglyoximato)[(*S*)-1-(methoxycarbonyl)ethyl]cobalt(III) were easily prepared by a ligand exchange of (*S*)-1-phenylethylamine [(*S*)-1-PEA] with the corresponding pyridine derivatives in methanol in the presence of dilute hydrochloric acid. Tributylphosphine, ethyldiphenylphosphine, and diethylphenylphosphine complexes of bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III) were also prepared by an axial ligand exchange of (***R,R***)-**1** with the corresponding phosphines in methanol in the presence of dilute hydrochloric acid. The newly prepared complexes were characterized by IR, NMR, and elemental analyses (see experimental part); the structures are shown in Fig. 1. Triphenylphosphine and tricyclohexylphosphine-coordinated complexes can not be isolated in their pure form, probably due to partial ligand dissociation. These complexes were, accordingly, prepared in situ by an addition of the corresponding axial ligand to a solution of aqua complex:

$$(CH_3CHCOOCH_3)Co(Hdmg)_2(H_2O)+B \longrightarrow (CH_3CHCOOCH_3)Co(Hdmg)_2B+H_2O.$$

The addition of 50-fold free phosphine was found to be sufficient to complete the ligand-exchange reaction, even in the case of the most bulky tricyclohexylphosphine (Fig. 2). The (*RS*)-1-phenylethylamine-coordinated complex was also prepared in situ by the addition of

(*RS*)-1-phenylethylamine to a solution of the aqua complex. The structures of the substrates prepared in situ are also shown (bracketed) in Fig. 1.

Photoracemization. The optical rotation of a chloroform solution of optically active 1-(methoxycarbonyl)ethyl cobaloxime complexes which were coordinated with various axial ligands(shown in Fig. 1) gradually decreased due to Co–C bond homolysis upon visible-light irradiation. Kinetic studies were performed by measuring the decrease in the optical rotation of a 3.79×10^{-3} mol dm^{-3} chloroform solution of each complex (containing a 100-fold excess of a corresponding ligand, which is sufficient to prevent ligand dissociation) under either a nitrogen or argon atmosphere at room temperature (23±2 °C). The first-order rate plots ($\ln\alpha$ vs. time) exhibited excellent linearity and yielded the photoracemization rate constants (summarized in Table 1). In the cases of triphenylphosphine and tricyclohexylphosphine-coordinated complexes, racemization occurred even in the dark. The rates were therefore corrected for the corresponding thermal racemization under the same conditions. The reaction rate of a series of amine-coordinated complexes remained almost unaltered, in spite of the rather wide range of pK_a change. On the other hand, the rate in a series of phosphine-coordinated complexes (Entry 6—10) changed remarkably, and although the order was independent of the pK_a value of the axial ligand, the rates increased with increasing cone angle.[14a,b] A similar tendency was previously observed in the photoracemization of a series of 1-cyanoethyl cobaloximes; this tendency was remarkably enlarged in the present series (Fig. 3). The acute dihedral angle (θ) between the planes of the two dimethylglyoximato groups, the displacement (d) of the Co atom toward the axial ligand from the mean plane (composed of four nitrogen atoms in the equatorial ligand), and the Co–P bond length of a series of 1-cyanoethyl cobaloximes[2a,10,11] have been shown to increase with an increase in the cone angle of the phosphine ligand, in order to avoid repulsion due to the short contacts between the substituent of phosphine ligand and dimethylglyoxime

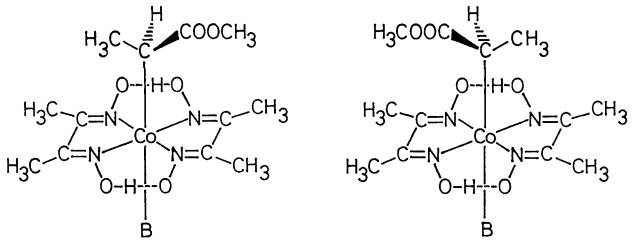


Fig. 1. Structures of Chiral Alkyl Cobaloximes

(*S*,*S*)-**1**	B=(*S*)-1-PEA	[(*R*)-**1**	B=(*RS*)-1-PEA]
(*S*)-**2**	B=pyridine	(*R*)-**5**	B=aqua
(*S*)-**3**	B=4-CN-pyridine	(*R*)-**6**	B=Bu_3P
(*S*)-**4**	B=4-Me-pyridine	(*R*)-**7**	B=Et_2PhP
		(*R*)-**8**	B=$EtPh_2P$
		[(*R*)-**9**	B=Ph_3P]
		[(*R*)-**10**	B=(*c*-$C_6H_{11})_3P$]

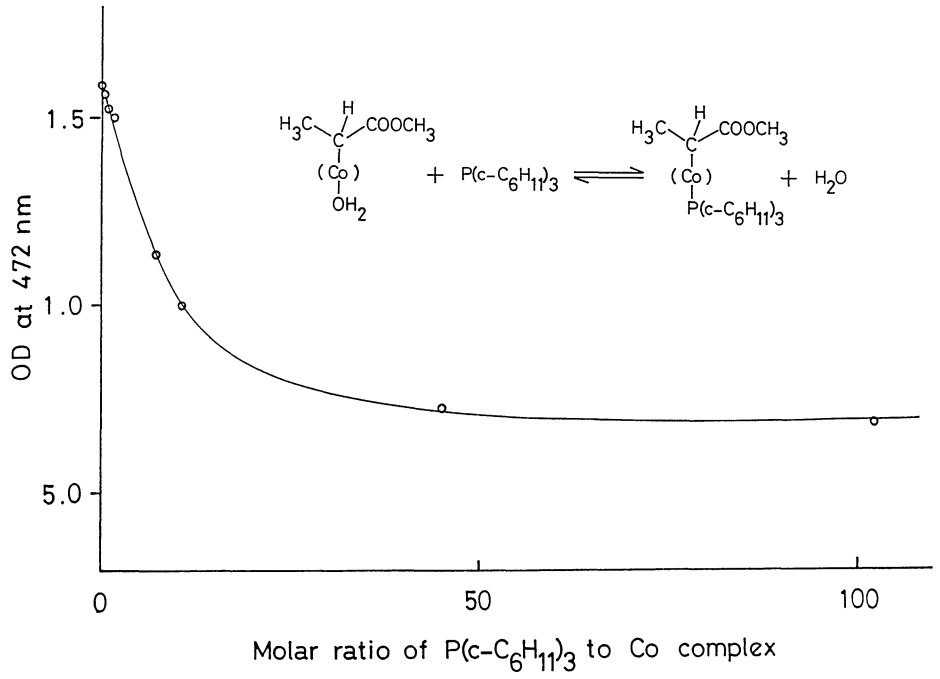


Fig. 2. Absorbance change at 472 nm with added tricyclohexylphosphine to aqua[(*R*)-1-(methoxycarbonyl)ethyl]cobaloxime in cyclohexanone.

Table 1. Photoracemization Rate Constants of Optically Active 1-(Methoxycarbonyl)ethyl Cobaloximes in a Chloroform Solution

Entry	Complex	Rate constant (κ) 10^{-5} s^{-1}	Axial base (B)	pK_a[e]	Cone angle deg
1	(*S*)-**3**	8.9	4-CN-py	1.86	
2	(*S*)-**2**	9.2	Pyridine	5.19 5.25	
3	(*S*)-**4**	8.7	4-Me-py	6.03	
4	(*R*)-**1**	9.9	1-PEA[a]	a)	
5	(*R*)-**5**	8.1	Aqua		
6	(*R*)-**6**	6.4	Bu_3P	8.43	127[b]
7	(*R*)-**7**	7.3	Et_2PhP	6.25	136[c]
8	(*R*)-**8**	8.9	$EtPh_2P$	4.91	140[b]
9	(*R*)-**9**	14.4(15.5)[d]	Ph_3P	2.73	159[b]
10	(*R*)-**10**	38(62)[d]	$(c\text{-}C_6H_{11})_3P$	9.70	173[b]

a) 1-PEA: 1-Phenylethylamine; the pK_a of 1-phenylethylamine was not reported, but is expected to be about 9—10 from those of $PhCH_2NH_2$ (9.35) and $PhC(Me)_2NH_2$ (10.27). b) Experimental cone angle (see Ref. 14b). c) Tolman's cone angle (see Ref. 14a). d) The rate constants are corrected for the thermal racemization at 23°C under the same conditions: the rate constants in parenthesis are net observed values in which the contribution from the thermal racemization is involved. e) See Ref. 19 for those of pyridine derivative, and Ref. 20 for phosphines.

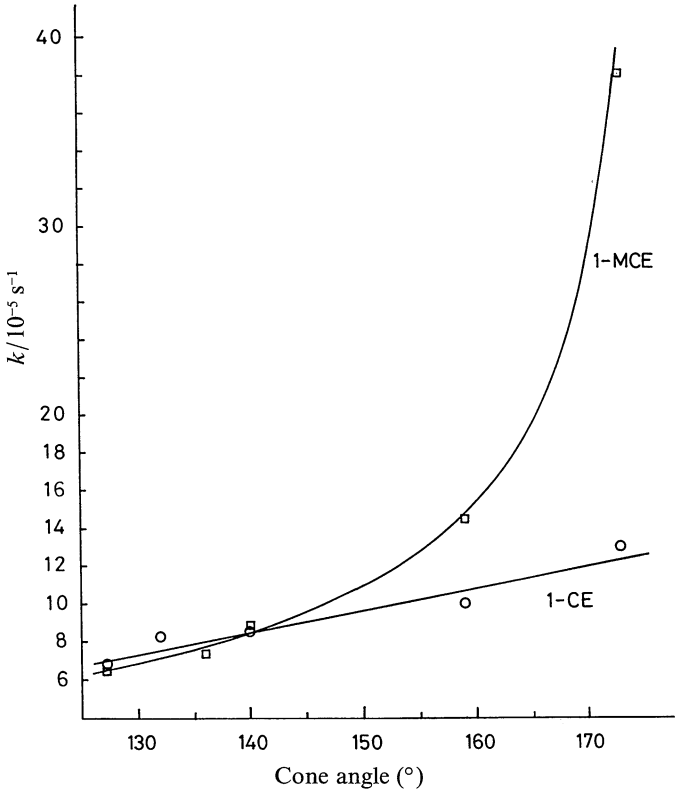


Fig. 3. The correlation between racemization rates of 1-(methoxycarbonyl)ethyl cobaloximes (1-MCE) and the cone angles of the coordinated phosphines, in comparison with that of 1-cyanoethyl cobaloximes (1-CE).

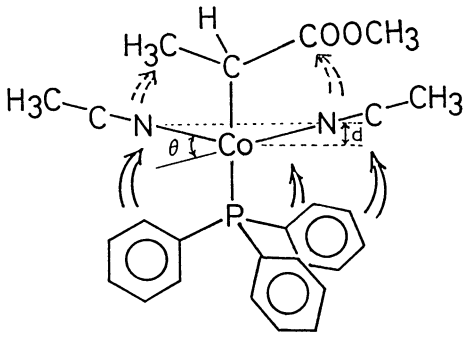


Fig. 4. Repulsive interaction in the phosphine-coordinated cobaloximes.

moiety. Although we do not have X-ray crystallographic data for a series of 1-(methoxycarbonyl)ethyl cobaloximes, a similar situation may be expected to occur for the series as well (Fig. 4). Since the Co–C bond lengths in 1-(methoxycarbonyl)ethyl cobaloximes[12,13,17] are not so much lengthened, compared with those in 1-cyanoethyl derivatives,[2a,7,15,16] and the bond lengths are almost unaltered with a change in the axial phosphine ligand,[2a,10,11] a steric repulsion between the larger alkyl (1-(methoxycarbonyl)ethyl) and the in-plane dimethylglyoximato ligand are much more serious than that between 1-cyanoethyl group and the in-plane ligands. Consequently, the Co–C bonds in 1-(methoxycarbonyl)ethyl cobaloximes are more highly strained than those in 1-cyanoethyl cobaloximes with increasing bulkiness of the axial ligand, being more susceptible to photochemical Co–C bond homolysis. In conclusion, it follows that the electronic effect of the axial ligand is negligible and that the steric effect is overwhelmingly dominant in determining the rate of photochemical Co–C bond homolysis in the solution state: the steric bulkiness of both the axial base and the axial alkyl group accelerates the rate (k_1) both remarkably and cooperatively.

Experimental

The IR spectra were recorded on a JASCO A-3 spectrometer. The NMR spectra were obtained on a JEOL FX-200 spectrometer, using TMS as the internal standard. The optical rotations were measured on a Perkin–Elmer 241 polarimeter.

Photoracemization. All of the operations, except for photoreactions, were carried out in the dark. Each sample (3.79 mmol dm^{-3}) and 100-fold excess of the corresponding axial ligand were dissolved in degassed chloroform under an Ar atmosphere. In the cases of Entries 5, 9 and 10, 3.79 mmol dm^{-3} of (*R*)-aqua[1-(methoxycarbonyl)ethyl]cobaloxime and 100 fold of (*RS*)-1-phenylethylamine, triphenylphosphine or tricyclohexylphosphine were dissolved in degassed chloroform under an Ar atmosphere. Each solution was transferred to a glass (Pyrex) cell in order to measure the optical rotation. The cell was placed at a distance of ca.3.0 m from the light source [four 40 W fluorecent lamps "white" (Matsushita Electric Ind. Co.)], at that distance, the flux density was 0.009 mW cm^{-2}. The optical rotation, which gradually decreased upon irradiation, was measured at regular time intervals.

Materials. Bis(dimethylglyoximato)[(*S*)-1-(methoxycarbonyl)ethyl][(*S*)-1-phenylethylamine]cobalt(III) [(*S,S*)-1] was prepared by almost the same procedure as the enantiomer, except for using (*S*)-1-phenylethylamine (Aldrich, $[\alpha]_D$ −39) as the axial ligand. Five recrystallizations from methanol–water gave a constant optical rotation: $[\alpha]_{589}$ −205.6, $[\alpha]_{578}$ −226.7, $[\alpha]_{546}$ −253.3 (*c* 0.180, chloroform). Found: C, 48.40; H, 6.46; N, 13.93%. Calcd for $C_{20}H_{32}N_5O_6Co$: C, 48.29; H, 6.48; N, 14.08%.

Bis(dimethylglyoximato)[(*S*)-1-(methoxycarbonyl)ethyl](pyridine)cobalt(III). To a methanol (10 cm^3) solution of 1 g of **(*S,S*)-1** was added 2 cm^3 of 2 mol dm^{-3} hydrochloric acid and 0.32 cm^3 of pyridine with stirring. After standing for 15—20 min at room temperature, the reaction mixture was extracted with dichloromethane and washed with water. The dichloromethane layer was dried over anhydrous sodium sulfate, and concentrated in vacuo to give 0.72 g of a crude product (79%). The crude product (0.4 g) was recrystallized from methanol (4.5 cm^3) and water (5.5 cm^3) to give leaflets (0.32 g), $[\alpha]_{589}$ −172.2, $[\alpha]_{578}$ −189.3, $[\alpha]_{546}$ −227.8 (*c* 0.170, chloroform). The IR and NMR spectra were identical with those of the (*R*)-isomer.

(4-Cyanopyridine)bis(dimethylglyoximato)[(*S*)-1-(methoxycarbonyl)ethyl]cobalt(III). To a methanol (10 cm^3) solution of 1 g of **(*S,S*)-1** was added 2 cm^3 of 2 mol dm^{-3} hydrochloric acid and 0.48 g of 4-cyanopyridine with stirring. After 5 min small amounts of crystals were deposited. After 20 min the reaction mixture was extracted with dichloromethane and washed with water. The dichloromethane layer was dried over anhydrous sodium sulfate and concentrated in vacuo to give 0.76 g (79%). The crude product (0.4 g) was recrystallized from methanol (7 cm^3) and water (9 cm^3) to give dark-red crystals (0.31 g). ^1H NMR ($CDCl_3$) δ=0.375 (d, 3H, $C\underline{H}_3CH(Co)COOCH_3$), 2.199 and 2.216 ($CH_3$ of dmgH, in the same region the signal of $CH_3C\underline{H}(Co)COOCH_3$ is overlapped), 3.487 (s, 3H, $COOCH_3$), 7.54 (d, 2H, cyanopyridine), 8.76 (d, 2H, cyanopyridine). $[\alpha]_{589}$ −150.6, $[\alpha]_{578}$ −165.9, $[\alpha]_{546}$ −194.5 (*c* 0.132, chloroform). Found: C, 45.08; H, 5.22; N, 17.46%. Calcd for $C_{18}H_{25}N_6O_6Co$: C, 45.01; H, 5.25; N, 17.50%.

Bis(dimethylglyoximato)[(*S*)-1-(methoxycarbonyl)ethyl](4-methylpyridine)cobalt(III). To a methanol (10 cm^3) solution of 1 g of **(*S,S*)-1** was added 2 cm^3 of 2 mol dm^{-3} hydrochloric acid and 0.36 cm^3 of 4-methylpyridine with stirring. After 7 min the crystals began to deposit (0.2 g). After standing for about 20 min at room temperature the reaction mixture was extracted with dichloromethane and washed with water. The dichloromethane layer was dried over anhydrous sodium sulfate, and concentrated in vacuo to give 0.7 g of a crude product. The combined yield was 0.9 g (95%). The crude product (0.4 g) was recrystallized from methanol (18 cm^3) and water (22 cm^3) to give plates (0.28 g). ^1H NMR ($CDCl_3$) δ=0.404 (d, 3H, $C\underline{H}_3CH(Co)COOCH_3$), 2.190 and 2.207 ($CH_3$ of dmgH, and in the same region the signal of $CH_3C\underline{H}(Co)COOCH_3$ is overlapped), 2.317 (s, 3H, CH_3 of 4-methylpyridine), 3.484 (s, 3H, $COOCH_3$), 7.06 (d, 2H, arom-H of 4-methylpyridine), 8.32 (d, 2H, arom-H of 4-methylpyridine). $[\alpha]_{589}$ −152.9, $[\alpha]_{578}$ −171.2, $[\alpha]_{546}$ −211.8 (*c* 0.170, chloroform). Found: C, 45.58; H, 5.93; N, 14.63%. Calcd for $C_{18}H_{28}N_5O_6Co$: C, 46.06; H, 6.01; N, 14.92%.

(Tributylphosphine)bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III). To a methanol (13 cm^3) solution of 1 g of **(*R,R*)-1** ($[\alpha]_{578}$ +223.0, *c* 0.145, chloroform) was added 1.5 cm^3 of 2 mol dm^{-3} hydrochloric acid and 0.5 cm^3 of tributylphosphine with stirring. The reaction was monitored by TLC. After completion of a ligand exchange, 9 cm^3 of water was added to the reaction mixture. The solution was left standing overnight in a refrigerator. Crude crystals (0.43 g) were deposited. Another crop of crystals (0.11 g) was obtained from the filtrate. The combined yield was 0.54 g (46%). The crude product was recrystallized twice from methanol–water (2/1) to give light-yellow crystals. ^1H NMR ($CDCl_3$) δ=0.560 (t, 3H, $C\underline{H}_3CH(Co)COOCH_3$), 0.884 (t, 9H, 3×$CH_3$ of Bu_3P), 1.1—1.4 (m, 18H, methylene of Bu_3P), 1.649 (s, 2H, 2×OH of dmgH). $[\alpha]_{589}$ +143.1, $[\alpha]_{578}$ +156.6, $[\alpha]_{546}$ +207.1 (*c* 0.139, chloroform). Found: C, 49.62; H, 8.75; N, 9.66%. Calcd for $C_{24}H_{48}N_4O_6PCo$: C, 49.82; H, 8.36; N, 9.68%.

(Ethyldiphenylphosphine)bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III). To a methanol (19 cm^3) solution of 2 g of **(*R,R*)-1** ($[\alpha]_{578}$ +212.6, *c* 0.180, chloroform) was added 3 cm^3 of 2 mol dm^{-3} hydrochloric acid and 0.9 cm^3 of ethyldiphenylphosphine with stirring. The reaction was monitored by TLC. After completion of a ligand exchange, water (14.5 cm^3) was added to the reaction mixture. The solution was left standing overnight in a refrigerator. Crude crystals (1.92 g, 81% yield) deposited, which was recrystallized twice from methanol–water (10/8—10/9) to give dark-red crystals. ^1H NMR ($CDCl_3$) δ=0.502 (t, 3H, $C\underline{H}_3CH(Co)COOCH_3$), 0.805 (quint, methyl of $EtPh_2P$), 1.947, 1.962, 1.972, 1.986 (12H, methyl of dmgH), 2.094 (quint, 1H, $CH_3C\underline{H}(Co)COOCH_3$), 2.31 (m, 2H, methylene of $EtPh_2P$), 3.405 (s, 3H, $COOCH_3$), 7.38 (m, 10H, Ph). $[\alpha]_{589}$ +153.4, $[\alpha]_{578}$ +167.5, $[\alpha]_{546}$ +218.9 (*c* 0.121, chloroform). Found: C, 52.84; H, 6.32; N, 9.49%. Calcd for $C_{26}H_{36}N_4O_6PCo$: C, 52.89; H, 6.15; N, 9.49%.

(Diethylphenylphosphine)bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III). To a methanol (15 cm^3) solution of 1.6 g of **(*R,R*)-1** ($[\alpha]_{578}$ +212.6, *c* 0.180, chloroform) was added 3 cm^3 of 2 mol dm^{-3} hydrochloric acid and 0.701 cm^3 of diethylphenylphosphine with stirring. The reaction was monitored by TLC. After completion of a ligand exchange, water (4 cm^3) was added to the reaction mixture. The solution

was left standing overnight in a refrigerator. Crystals (0.48 g) deposited. ^{1}H NMR ($CDCl_3$) δ=0.556 (t, 3H, $C\underline{H}_3CH(Co)COOCH_3$), 0.935 (quint, 6H, $(C\underline{H}_3CH_2)_2P$), 1.947, 1.962, 1.972, 1.986 (12H, CH_3 of dmgH), 1.9—2.2 (m, signals of $(CH_3C\underline{H}_2)_2PhP$ and $CH_3C\underline{H}(Co)COOCH_3$ were overlapped in this region), 3.418 (s, 3H, $COOCH_3$), 7.04 (m, 2H, arom), 7.36 (m, 3H, arom). $[\alpha]_{589}$ +168.0, $[\alpha]_{578}$ +184.1, $[\alpha]_{546}$ +247.3 (*c* 0.260, chloroform). Found: C, 48.52; H, 6.95; N, 10.31%. Calcd for $C_{22}H_{36}N_4O_6PCo$: C, 48.71; H, 6.69; N, 10.33%. Another crop of crystals (0.63 g) was obtained from the filtrate. The combined yield was 1.11 g (64%).

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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