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Reactions in Solid and Constrained State. IV.[1a—c] Preparation and Solid-State Photoracemization of Optically Active Alkyl Cobaloxime Complexes

Yoshifusa Arai and Yoshiaki Ohgo*

Niigata College of Pharmacy, Kamishin'ei-cho, Niigata 950-2081

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Various optically active 1-substituted and 1,2-disubstituted ethyl cobaloxime [bis(dimethylglyoximato)cobalt(III)] complexes including deuterium-labeled complexes were prepared. Their photoracemization was found to occur upon irradiation of visible light in the solid-state. The reaction rate was much greater than that of solid-state racemization by irradiation of X-rays. The rates were not controlled by the electronic character of axial base and alkyl group but by the crystal lattice: the volume and shape of the reaction cavity, flexibility of the cavity, and intermolecular interaction such as hydrogen bonding. The experiments using deuterium-labeled complexes revealed the main reaction path in which the racemization proceeds mainly through out-of-plane rotation of the alkyl radical.

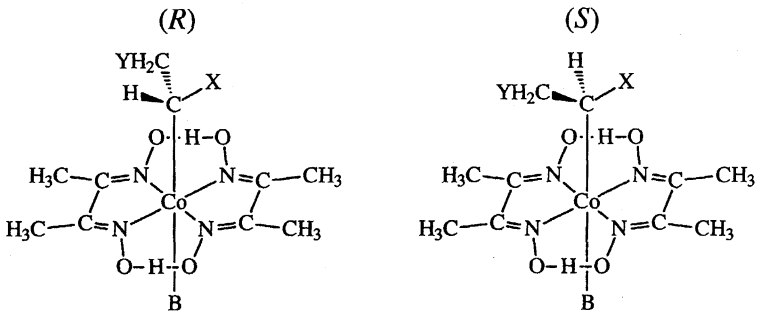
Since reactive molecules or groups are surrounded and constrained by other molecules in the solid-state, the reaction, if possible, proceeds with high selectivity, or a unique reaction can occur which is unable to proceed in a solution state. As such we previously reported the solid-state specific and unidirectional ($\beta-\alpha$)photoisomerization.[1a,1c,2]

We also found that optically active 1-cyanoethyl cobaloximes [bis(dimethylglyoximato)cobalt(III)] coordinated with various axial ligands racemize upon X-ray exposure without degradation of crystallinity in the solid-state.[3a—3h] However, X-ray-induced racemization was not observed at room temperature in the series of complexes coordinated with 1-(methoxycarbonyl)ethyl[4a—4c] and 1,2-bis(methoxycarbonyl)ethyl. Occurrence of photoracemization in a solution[5,6] suggested a possibility of those in the solid and crystalline-state. If racemization proceeds upon visible light irradiation in the solid-state, the rate can be controlled by light intensity. Then, we can investigate the reaction over a wide range of reaction rates. This, in combination with development of an X-ray diffractometer for rapid data collection,[7] may allow us to obtain structural information concerning an unstable intermediate which is impossible to capture in a solution. Thus, we have found that all the optically active 1-cyanoethyl, 1-(methoxycarbonyl)ethyl, 1,2-bis(methoxycarbonyl)ethyl, 1,2-bis(ethoxycarbonyl)ethyl, and 1,2-bis(allyloxycarbonyl)ethyl (base)bis(dimethylglyoximato)cobalt(III) complexes examined racemize upon visible light irradiation in the solid-state. Solid-state specific and abnormal phenomena have been observed in several cases of each series shown above except for 1-cyanoethyl complexes. The results have, in part, been communicated previously.[1b,8] The purpose of this paper is to describe more detailed results, the mechanism bringing about the solid-state specific phenomenon, the major reaction paths, and factors controlling the reaction rate of the solid-state racemization.

Results and Discussion

Substrates. Optically active substrates with various axial ligands were prepared by direct ligand displacement of optically active diastereomers: (*R*)-**1m**, (*S*)-**1m**, (*R*)-**2l**, (*R*)-**3m**, (*R*)-**4m**, and (*S*)-**5m** with the corresponding axial ligand or by ligand displacement of them with the corresponding axial ligand via aqua complexes [(*R*)-**1v**, (*S*)-**1v**, (*R*)-**2v**, (*R*)-**3v**, (*R*)-**4v**, or (*S*)-**5v**] which were easily prepared by treating diastereomeric complexes with water in the presence of ion-exchange resins (Dowex 50w-X2). Diastereomeric complexes, (*R*)-**1m**, (*S*)-**1m**, and (*R*)-**2l** have already been reported in previous papers.[9] Preparation of (*R*)-**3m** will be published later. Preparations of (*R*)-**4m** and (*S*)-**5m** are newly described in this paper. Details for preparation of newly prepared complexes will be described in the Experimental section. The structures of the substrates are shown in Fig. 1.

Solid-State Photoracemization. Powdered crystals of optically active alkyl complexes, suspended in an insoluble liquid such as a liquid paraffin, were irradiated by a solar simulator (Flux density: 100 mW cm^{-2}) at room temperature. In every case, TLC of the irradiated sample showed almost a single spot. In spite of an aerobic condition, alkyldioxy complexes were not formed. This is in striking contrast to solution state reactions which give alkyldioxy complexes exclusively, and implies that molecular oxygen can not intrude into the crystal lattice. Optical rotations of the irradiated samples were measured after column-chromatographic purification, which decreased gradually with irradiation time. Racemization occurred in every substrate examined here. The optical rotational change of the early stage fits the first-order rate expression (a typical example is shown in Fig. 2), from which the rate constants were obtained in every case.



1 X=CN, Y=H
2 X=$COOCH_3$, Y=H
3 X=$COOCH_3$, Y=$COOCH_3$
4 X=$COOC_2H_5$, Y=$COOC_2H_5$
5 X=$COOCH_2CH=CH_2$, Y=$COOCH_2CH=CH_2$

a B=4-Cyanopyridine
b B=4-Chloropyridine
c B=3-Aminopyridine
d B=Pyridine
e B=4-Methylpyridine
f B=Imidazole
f' B=1-Methylimidazole
g B=Tributylphosphine
h B=Methyldiphenylphosphine
i B=Dimethylphenylphosphine
j B=Ethyldiphenylphosphine
k B=Tris(2-cyanoethyl)phosphine
l B=(*R*)-1-Phenylethylamine
m B=(*S*)-1-Phenylethylamine
n B=Butylamine
o B=Propylamine
p B=Methylamine
q B=Allylamine
r B=Benzylamine
s B=Cyclohexanemethylamine
t B=Cyclohexylamine
u B=Pyrrolidine
v B=Water

Fig. 1. Structure of optically active alkyl(base)bis(dimethylglyoximato)cobalt(III).

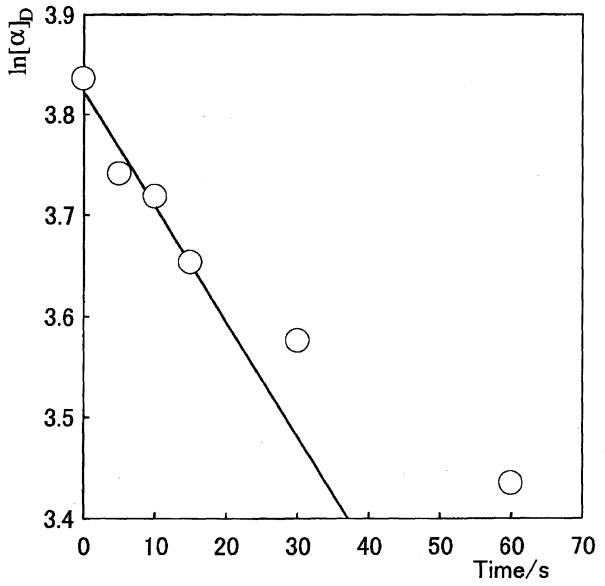


Fig. 2. Time course of solid-state photoracemization for (*R*)-**1g**.

The plots deviate gradually from the line of the expression. It can be considered that the deviation is caused by gradual darkening of crystals, as the reaction proceeds, because it becomes harder for light to reach the inner part of the crystals on darkening of the crystals. The rate constants of each series of 1-cyanoethyl-, 1-(methoxycarbonyl)ethyl-, 1,2-bis(methoxycarbonyl)ethyl-, 1,2-bis(ethoxycarbonyl)ethyl, and 1,2-bis(allyloxycarbonyl)ethyl complexes are given with the reaction cavities[10] in Tables 1, 2, 3, 4, and 5, respectively. A part of these data has been communicated previously.[1b,8]

Reaction Rates and the Controlling Factors. The reaction rates of a series of 1-cyanoethyl complexes were rather rapid (Table 1). The rate constants lay in a rather narrow range (10^{-2}—10^{-3}) and are roughly proportional to the volume of the cavity for the reactive group (Fig. 3), but not to the electronic character of the axial ligand: There is no relation between the pK_a of axial ligand and the rate constant of racemization.

In the series of 1-(methoxycarbonyl)ethyl, 1,2-bis(methoxycarbonyl)ethyl, 1,2-bis(ethoxycarbonyl)ethyl, and 1,2-bis(allyloxycarbonyl)ethyl complexes, the rates of complexes coordinated with pyridines, imidazoles, and phosphines as the axial ligand are also dependent on the volume of the cavity for the reactive group, but those of complexes coordinated with alkylamines are not dependent on the volume of the cavity for the reactive group, and the rate constants for (*R*)-**2l**, (*R*)-**3m**, and (*S*)-**5m** are extremely small (10^{-5}—10^{-6} s^{-1}). The differences in the rates are extremely large: The ratio of the greater-to-smaller rate constants reached almost 10000 (compare the rates of (*R*)-**2k** and (*R*)-**2l** in Table 2). Since these differences were not observed in the solution-state reaction,[5,6] the phenomenon is defined to be solid-state specific.

In order to reveal the solid-state specificity, crystal structures were inspected. The inspection revealed that the rates are lowered when the complexes have reactive groups constrained by intermolecular interaction such as a hydrogen

Table 1. Photoracemization Rates of Optically Active (Base)(1-cyanoethyl)bis(dimethylglyoximato)cobalt(III) Complexes in the Solid-State

Complex	Axial ligand B (pK_a[a])	Rate constant s^{-1}	Volumes of the cavity Å^3
(*R*)-**1a**	4-Cyanopyridine (1.86)	7.50×10^{-3}	(A) 7.97, (B) 10.37[b,c]
(*R*)-**1c**	3-Aminopyridine	7.11×10^{-2}	
(*R*)-**1d**	Pyridine (5.19/5.25)	1.63×10^{-2}	(A) 8.89, (B) 11.34[b,d,e]
(*R*)-**1f'**	1-Methylimidazole	8.93×10^{-3}	7.95[f]
(*R*)-**1g**	Tributylphosphine (8.43)	1.19×10^{-2}	10.64[g]
(*R*)-**1h**	Methyldiphenylphosphine (4.65)	6.09×10^{-2}	(A) 17.08, (B) 18.01[b,h]
(*S*)-**1i**	Dimethylphenylphosphine	2.74×10^{-2}	17.97[e]
(*R*)-**1j**	Ethyldiphenylphosphine (4.91)	5.23×10^{-3}	10.18[i]
(*R*)-**1m**	(*S*)-1-Phenylethylamine[j]	1.14×10^{-2}	14.53[k]
(*R*)-**1q**	Allylamine	3.72×10^{-2}	
(*S*)-**1u**	Pyrrolidine	2.58×10^{-2}	

a) See Ref. 17. b) Two crystallographically independent molecules, (A) and (B) are involved in the unit cell, and each volume of the cavity is given. c) See Ref. 3c. d) See Ref. 3b. e) This is the volume of the cavity of the enantiomer, (*S*)-**1d**. f) See Ref. 17. g) See Ref. 3d. h) See Ref. 3g. i) See Ref. 3e. j) The pK_a of (*S*)-phenylethylamine is not reported, but is expected to be about 9—10 from those of $PhCH_2NH_2$ (9.35) and $PhC(CH_3)_2NH_2$ (10.27). k) See Ref. 3a.

Table 2. Photoracemization Rates of Optically Active (Base)[1-(methoxycarbonyl)ethyl]bis(dimethylglyoximato)cobalt(III) in the Solid-State

Complex	Axial ligand B	Rate constant s^{-1}	Volumes of the cavity Å^3
(*R*)-**2a**	4-Cyanopyridine	1.58×10^{-4}	18.84[a,b]
(*R*)-**2b**	4-Chloropyridine	1.03×10^{-3}	(A) 19.01, (B) 20.22[c,d]
(*R*)-**2c**	3-Aminopyridine	4.04×10^{-3}	
(*R*)-**2d**	Pyridine	6.49×10^{-3}	(A) 14.56, (B) 14.67[b,c,e]
(*R*)-**2e**	4-Methylpyridine	6.97×10^{-4}	
(*R*)-**2f**	Imidazole	3.57×10^{-3}	20.79[f]
(*R*)-**2g**	Tributylphosphine	5.23×10^{-3}	
(*R*)-**2i**	Dimethylphenylphosphine	3.54×10^{-3}	22.24[f]
(*R*)-**2k**	Tris(2-cyanoethyl)phosphine	1.52×10^{-2}	27.80[f]
(*R*)-**2l**	(*R*)-1-Phenylethylamine	2.31×10^{-6}	23.83[g]
(*R*)-**2m**	(*S*)-1-Phenylethylamine	9.21×10^{-5}	24.51(T), 21.49(M)[b,h,i]
(*R*)-**2n**	Butylamine	9.70×10^{-5}	
(*R*)-**2o**	Propylamine	9.87×10^{-4}	
(*R*)-**2p**	Methylamine	1.18×10^{-2}	
(*R*)-**2r**	Benzylamine	2.91×10^{-3}	
(*R*)-**2s**	Cyclohexanemethylamine	7.69×10^{-3}	(A) 20.42, (B) 23.86[c,f]
(*R*)-**2t**	Cyclohexylamine	4.15×10^{-3}	(A) 18.49, (B) 19.24[c,f]
(*R*)-**2v**	H_2O	3.03×10^{-3}	

a) See Refs. 4b and 19. b) This is the volume of the cavity for the enantiomer. c) Two crystallographically independent molecules, (A) and (B) are involved in the unit cell, and each volume of the cavity is given. d) See Refs. 4a and 4b. e) See Ref. 4c. f) See Ref. 15. g) See Refs. 4b and 11. h) See Ref. 4b. i) There are two forms of crystals, triclinic (T) and monoclinic (M), in a batch, although they are indistinguishable in appearance.

bond. The crystal structures of (*R*)-**2l**,[11] (*R*)-**2m**,[4b] and (*R*)-**3m**[12] clearly indicate that each reactive group in these complexes is constrained by a hydrogen bond. The reason for the extremely slow rates of these complexes can be understood based on this fact.

In the case of (*S*)-**5m**, the reactive group is not directly concerned with the hydrogen bond, but the motion of the group is constrained by the phenyl group of the axial ligand on a neighboring molecule whose motion is restricted by the hydrogen bond between the amino hydrogen of the axial ligand and an oxygen of the glyoxime ligand of another neighboring molecule (Fig. 4),[13] which also explains the very low racemization rate.

(*R*)-**3o** has a moderate rate constant, in spite of having hydrogen bonds in the crystal structure. This can be explained as follows. Both hydrogen atoms of the amino group of the axial ligand are bound with hydrogen bonding: One with carbonyl oxygen of 1-methoxycarbonyl group on the neigh-

Table 3. Photoracemization Rates of Optically Active (Base)[1,2-bis(methoxycarbonyl)ethyl]bis(dimethylglyoximato)cobalt(III) in the Solid-State

Complex	Axial ligand B	Rate constant s^{-1}	Volumes of the cavity Å^3
(*R*)-**3d**	Pyridine	1.18×10^{-3}	(A) 37.6, (B) 45.0[a,b]
(*R*)-**3f'**	1-Methylimidazole	3.30×10^{-3}	
(*R*)-**3h**	Methyldiphenylphosphine	2.54×10^{-2}	(A) 42.1, (B) 56.8[a,b]
(*R*)-**3l**	(*R*)-1-Phenylethylamine	1.89×10^{-4}	37.6[b]
(*R*)-**3m**	(*S*)-1-Phenylethylamine	4.07×10^{-6}	45.7[b]
(*R*)-**3o**	Propylamine	1.92×10^{-4}	35.7[b]
(*R*)-**3v**	H_2O	3.97×10^{-3}	

a) Two crystallographically independent molecules, (A) and (B) are involved in the unit cell, and each volume of the cavity is given. g) See Ref. 20.

Table 4. Photoracemization Rates of Optically Active (Base)[1,2-bis(ethoxycarbonyl)ethyl]-bis(dimethylglyoximato)cobalt(III) in the Solid-State

Complex	Axial ligand B	Rate constant s^{-1}	Volumes of the cavity Å^3
(*R*)-**4d**	Pyridine	2.48×10^{-3}	76.5[a]
(*R*)-**4h**	Methyldiphenylphosphine	2.18×10^{-5}	
(*R*)-**4i**	Dimethylphenylphosphine	6.51×10^{-3}	
(*R*)-**4m**	(*S*)-1-Phenylethylamine	1.48×10^{-4}	
(*R*)-**4o**	Propylamine	1.13×10^{-3}	58.7[a]

a) See Ref. 15.

Table 5. Photoracemization Rates of Optically Active (Base)[1,2-bis(allyloxycarbonyl)ethyl]bis(dimethylglyoximato)cobalt(III) in the Solid-State

Complex	Axial ligand B	Rate constant s^{-1}
(*S*)-**5e**	4-Methylpyridime	1.10×10^{-3}
(*S*)-**5m**	(*S*)-1-Phenylethylamine	4.60×10^{-6}

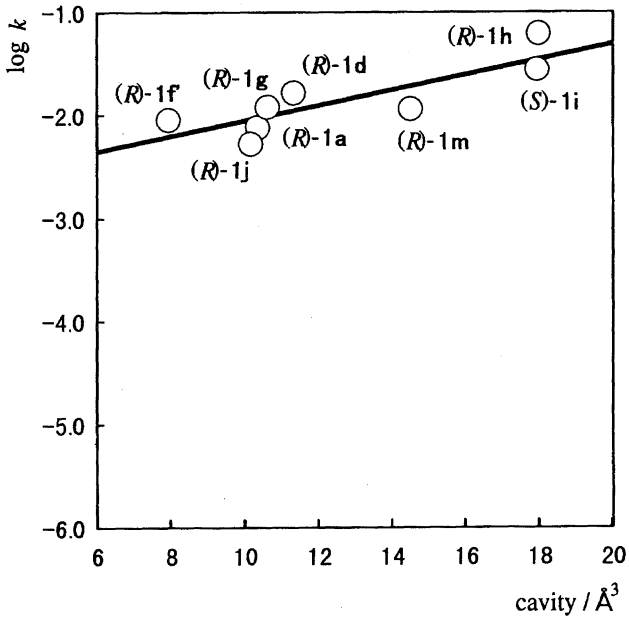


Fig. 3. Dependence of solid-state photoracemization rate constants of 1-cyanoethyl complexes on the volume of the cavity.

boring molecule through the methanol which is incorporated, and the other with the 2-methoxycarbonyl group on another molecule (Fig. 5).[14] We therefore consider that the average bond energy per one hydrogen bond is rather small and that weakening of one bonding by stretching vibration or motion on Co–C(1) bond homolysis will strengthen the other bond in compensation. Thus, the NH–O(MeOH) bond is considered to be easily cleaved. Once the bond is cleaved, solvate MeOH has such large freedom of motion that it furnishes the alkyl group with large flexibility. This, in turn, makes it easy for the alkyl radical to rotate with inversion. C(1)–C(2)–C=O lay almost in a plane and the hydrogen bonding between C=O on C(2) and NH on the neighboring molecule is directed upward and almost parallel to the C(2)–$COOCH_3$ bond (Fig. 6). Therefore, hydrogen and methoxycarbonyl group on C(1) can easily rotate around the C(1)–C(2) axis without a substantial constraint, when the Co–C(1) bond is cleaved.

On the other hand, there is no intermolecular interaction or the reactive group is not constrained by hydrogen bonding in crystals of (*R*)-**2a**, (*R*)-**2b**, (*R*)-**2d**, (*R*)-**2f**, (*R*)-**2i**, (*R*)-**2s**, and (*R*)-**2t** whose reaction rates are relatively fast (although hydrogen bond exists in the crystals of (*R*)-**2s**, the reactive group is not involved in the hydrogen bonding). Of those, the reaction rates of (*R*)-**2d** and (*R*)-**2t** are especially fast, despite the fact that the volumes of the reaction cavities are

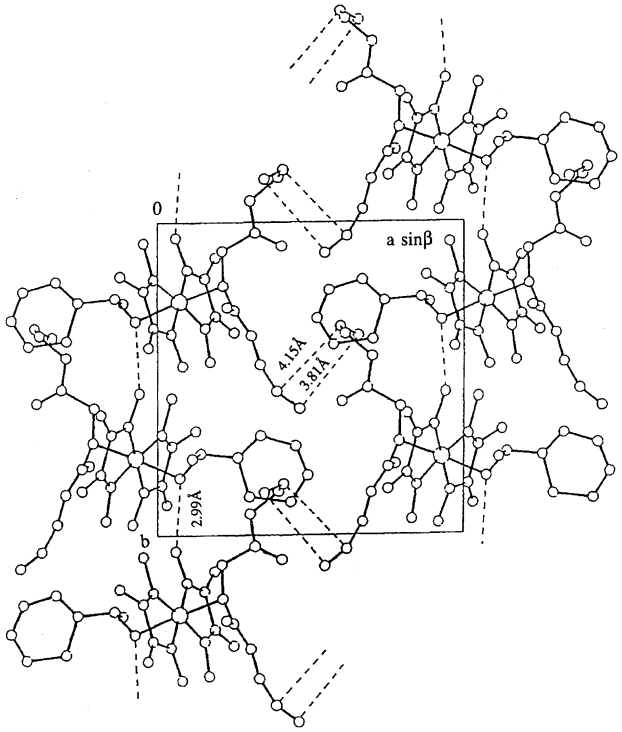


Fig. 4. Crystal structure of (*S*)-**5m** viewed along the *c* axis.[13]

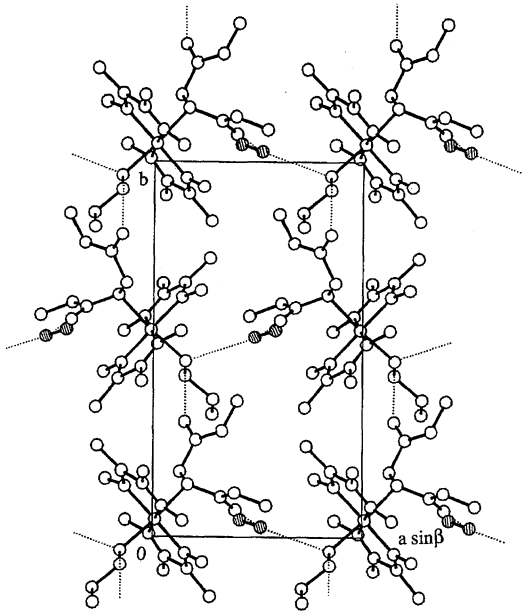


Fig. 5. Crystal structure of (*R*)-**3o** viewed along the *c* axis.[14] Intermolecular hydrogen bonds are indicated by dotted line and methanol molecules are marked by slant line.

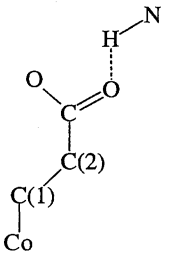


Fig. 6. Hydrogen bond of reactive group of (*R*)-**3o**.

rather small. Since a few molecules of solvent methanol and benzene molecule occupy the space around the reactive group in crystals of (*R*)-**2d** and (*R*)-**2t**, respectively, and these molecules are in disorder, the surroundings of the reactive group must have some flexibility. This situation can explain why the reaction rates of (*R*)-**2d** and (*R*)-**2t** are somewhat faster than those of complexes ((*R*)-**2a** and (*R*)-**2b**) which have a comparable volume of cavity.

It was, thus, found that the rate of the reaction was controlled by the additional factors: constraint of the reactive group by intermolecular hydrogen bonds and flexibility around the reactive group, as well as by the factors due to the volume of the cavity.

In order to scrutinize the correlation between the reaction rates and the factors controlling them in detail, log *k* (rate constant) values of 1-(methoxycarbonyl)ethyl and 1,2-bis-(methoxycarbonyl)ethyl complexes are plotted against the volume of the cavity, and the plots are marked separately with or without additional factors, constraint of the reactive group by hydrogen bonding and/or flexibility of the reaction cavity brought about by mobile solvent molecules (Figs. 7 and 8).

In both figures, the complexes are marked by a skew square and a square including hydrogen bond and solvent molecules in the crystal lattice, respectively. But the complexes marked by a circle do not include any hydrogen bond and solvent molecule in the crystal lattice.

The circles fall on or near lines shown in Figs. 7 and 8, indicating that rate constants of the solid-state racemization depend roughly on the volume of the cavity for the reactive group in cases of having neither hydrogen bond nor solvent

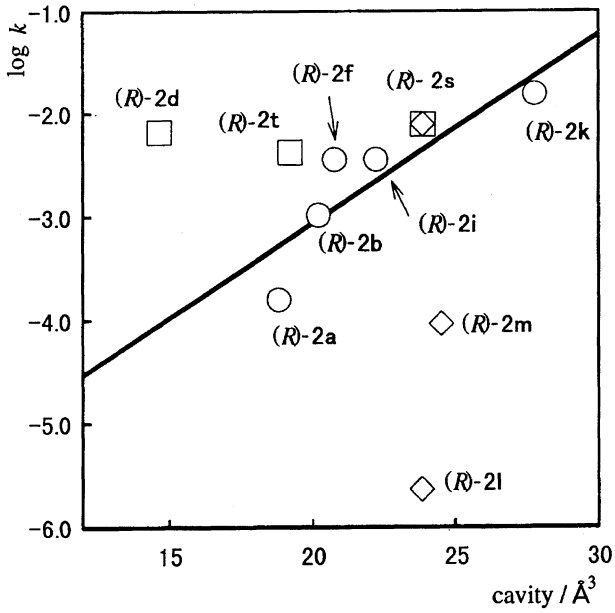


Fig. 7. Dependence of solid-state photoracemization rate constants of 1-(methoxycarbonyl)ethyl complexes on the volume of the cavity; □ solvent molecules are included in the crystal lattice, ◇ hydrogen bonds are included in the crystal lattice, ○ solvent molecules and hydrogen bonds are not included in the crystal lattice.

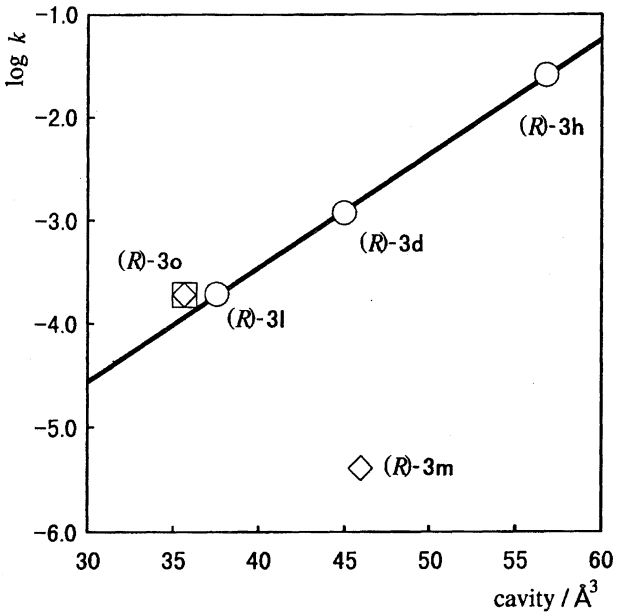


Fig. 8. Dependence of solid-state photoracemization rate constants of 1,2-bis(methoxycarbonyl)ethyl complexes on the volume of the cavity; □ solvent molecules are included in the crystal lattice, ◇ hydrogen bonds are included in the crystal lattice, ○ solvent molecules and hydrogen bonds are not included in the crystal lattice.

molecule in the crystal lattice. The skew squares fall far beneath the line, indicating that the constraint of a reactive group by hydrogen bonding decreases the racemization rates remarkably. On the other hand, all of the squares fall above the line, indicating that flexibility around a reactive group causes an increase in reaction rate to some extent.

Reaction Mechanism. Three possible pathways (A), (B), and (C) are considered for the racemization reaction (Fig. 9): (1) path (A) proceeds via 180° out-of-plane rotation of the radical produced by photohomolysis of Co–C(1) bond, followed by the recombination; (2) path (B) involves 180° out-of-plane rotation of the olefin formed by H-atom abstraction from the initially formed alkyl radical species; and (3) path (C) is possible for symmetrically 1,2-disubstituted ethyl complexes. Abstraction of hydrogen on the carbon (2) adjacent to the free radical by Co(II) species gives (*E*)- and (*Z*)-olefins, and an incidental attack of H-atom of hydride complex to either carbon (1) or (2) of the (*Z*)-olefin can afford racemate without a 180° out-of-plane rotation of the radical or olefin.

In order to clarify which pathway the racemization of each substrate proceeds through, first we attempted to detect olefins by NMR measurements. Finely powdered samples were irradiated by a solar simulator for a definite time, then dissolved in $CDCl_3$ immediately, and the ^1H NMR spectrum was measured. The irradiation time $T_{1/3}$ was defined as the time required for about 1/3 racemization, in order to normalize the condition. The results are shown in Table 6. Typical spectra are shown in Fig. 10.

Signals due to acrylonitrile were not detected in the NMR spectra of the irradiated samples of any of the 1-cyanoethyl complexes examined. This implies that the racemization of 1-cyanoethyl complexes proceeds mainly through path (A). On the other hand, signals due to olefins were observed in the NMR spectra of the irradiated samples of 1-(methoxycarbonyl)ethyl, 1,2-bis(methoxycarbonyl)ethyl, 1,2-bis(ethoxycarbonyl)ethyl, and 1,2-bis(allyloxycarbonyl)ethyl complexes. However, there is not necessarily a correlation between the

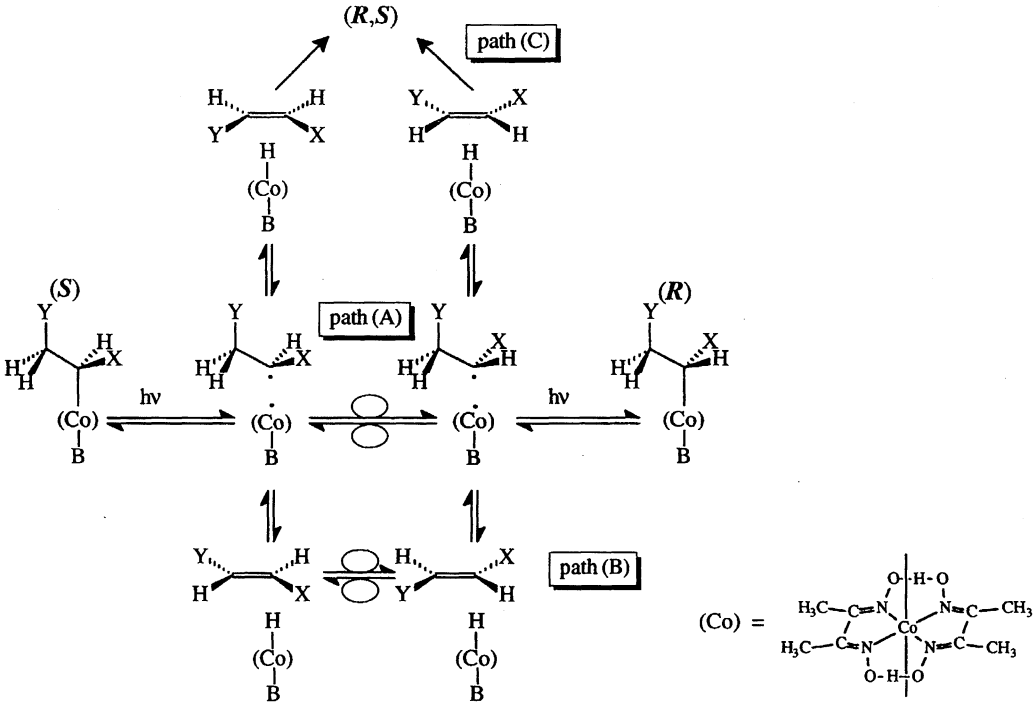


Fig. 9. Three possible pathways for solid-state photoracemization.

Table 6. Olefinic Proton Detected by ^{1}H NMR

Complex	Axial ligand	Irradiation time[a]		
	B	$T_{1/3}\times 3$	$T_{1/3}\times 12$	$T_{1/3}\times 36$
(*R*)-**1c**	3-Aminopyridine	n.d.[b]	—	n.d.
(*R*)-**1d**	Pyridine	n.d.	n.d.	n.d.
(*R*)-**1m**	(*S*)-1-Phenylethylamine	n.d.	—	n.d.
(*R*)-**2c**	3-Aminopyridine	n.d.	—	Detected
(*R*)-**2d**	Pyridine	n.d.	Detected	—
(*R*)-**2h**	Tributylphosphine	—	Detected	—
(*R*)-**2s**	Cyclohexanemethylamine	Detected	—	—
(*R*)-**3d**	Pyridine	Detected	—	Detected
(*R*)-**3h**	Methyldiphenylphosphine	n.d.	—	Detected
(*R*)-**3l**	(*R*)-1-Phenylethylamine	Detected	Detected	—
(*R*)-**4d**	Pyridine	Detected	Detected	Detected
(*S*)-**5e**	4-Methylpyridine	Detected	—	Detected

a) $T_{1/3}$ is time required for about 35% racemization in each reaction system. b) n.d. = not detected.

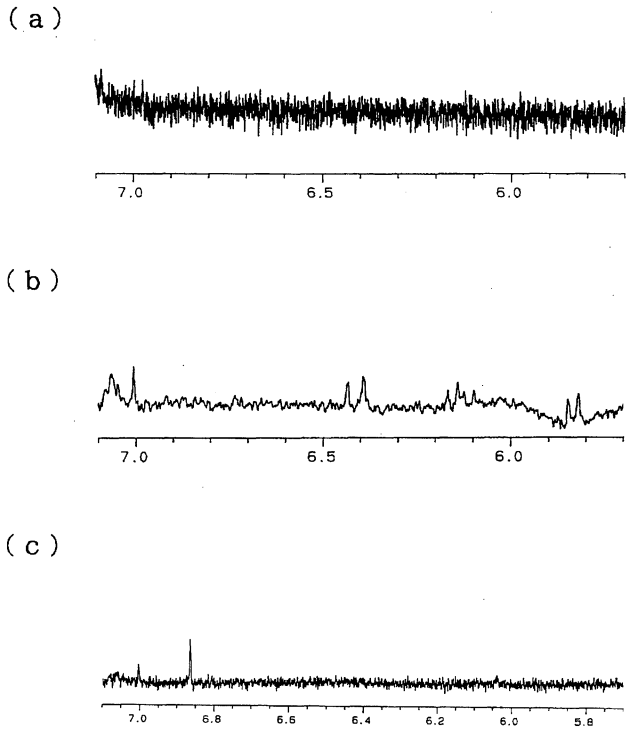
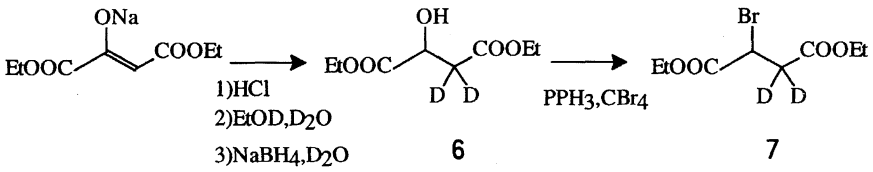


Fig. 10. ^{1}H NMR spectra of irradiated samples: (a) (*R*)-**1d**, (b) (*R*)-**2d**, and (c) (*R*)-**3d**.

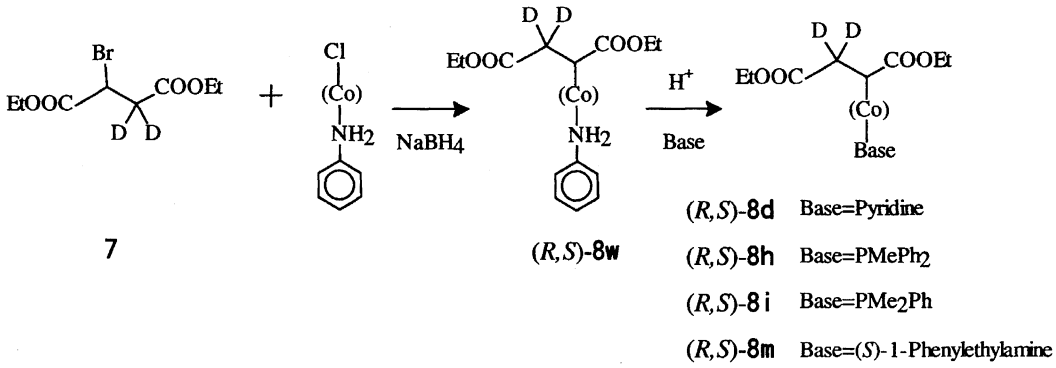
racemization rate and the time for the olefin to be detected: the racemization rates for (*R*)-**2c**, (*R*)-**2d**, and (*R*)-**3h** are relatively large, but olefins are not detected by the time $(T_{1/3})\times 3$. On the other hand, in the case of (*R*)-**3l** which has a relatively small racemization rate (1.89×10^{-4} s^{-1}), olefinic protons are already detected by the time $(T_{1/3})\times 3$. The results show that racemization for 1-(methoxycarbonyl)ethyl and 1,2-bis(alkoxycarbonyl)ethyl complexes may involve path (B) to some extent, but it is not clear whether the racemization through olefin is the major path. Further, the geometry of the detected olefins was unexpectedly (*E*) in every case of 1,2-bis(alkoxycarbonyl)ethylcobaloximes examined: In order to explain such a rather high racemization rate for 1,2-disubstituted ethyl complexes having large substituents, we first postulated[1b] path (C) for the racemization mechanism of these complexes in which racemization could proceed through only smaller motions of (*Z*)-olefins without out-of-plane rotation of radicals or olefins. The above fact also cast some doubt on the possibility of path (C) as the major path for the racemization mechanism of 1,2-bis(alkoxycarbonyl)ethyl complexes. These results prompted us to examine whether 1,2-isomerization occurred or not, and, if it occurred, to measure the isomerization rate.

For this purpose, 2,2-dideuterio-1,2-bis(ethoxycarbonyl)-ethyl complexes ((*RS*)-**8d**, (*RS*)-**8h**, and (*RS*)-**8i**) were synthesized as follows. Diethyl 2-hydroxy-3,3-dideuteriobutanedioate, **6**, was prepared by treating diethyl oxalacetate sodium salt with a (2 : 1) mixture of C_2H_5OD and D_2O for 7 d, and successive reduction with $NaBH_4$ in D_2O. Bromination of **6** by triphenylphosphine and carbon tetrabromide gave diethyl 2-bromo-3,3-dideuteriobutanedioate, **7**. (Aniline)[2,2-dideuterio-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)cobalt(III), (*RS*)-**8w**, was prepared by the reaction of **7** with (aniline)bis(dimethylglyoximato)cobalt(I) anion which was produced by reducing (aniline)chlorobis(dimethylglyoximato)cobalt(III) with $NaBH_4$. (*RS*)-**8d**, (*RS*)-**8h**, and (*RS*)-**8i** were prepared by axial ligand displacement of (*RS*)-**8w** with pyridine, methyldiphenylphosphine, and dimethylphenylphosphine, respectively (Scheme 1). (*RS*)-**8m** prepared by axial ligand displacement of (*RS*)-**8w** with (*S*)-1-phenylethylamine via aqua complex, was recrystallized from 2-propanol/hexane several times to produce optically active (*R*)-**8m**. (*R*)-**8i** was prepared by axial ligand displacement of (*R*)-**8m** with dimethylphenylphosphine (Scheme 2).

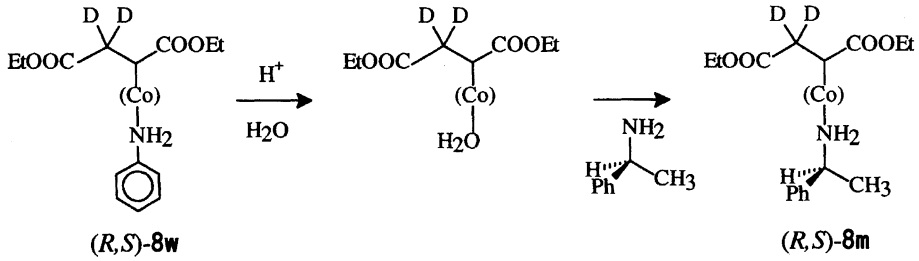
If 1,2-isomerization occurs, (*RS*)-**8d**, (*RS*)-**8h**, (*RS*)-**8i**, (*R*)-**8i**, and (*R*)-**8m** should afford the corresponding 1,2-

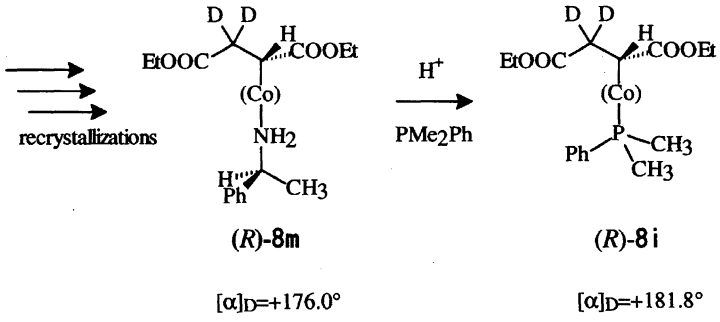


solvent	time	deuterium content
EtOD:D_2O=15:1	1day	0.4
EtOD:D_2O=15:1	7days	0.6
MeOD:D_2O=4:1	1day	1.4
EtOD:D_2O=5:1	7days	1.7
EtOD:D_2O=2:1	7days	1.9



Scheme 1.





Scheme 2.

dideuterio-1,2-bis(ethoxycarbonyl)ethyl complex, respectively, and hydrogen content at α-carbon should decrease (Fig. 11). Consequently, we can estimate the isomerization rates by ^1H and ^{13}C NMR spectra of the photo-irradiated samples. The isomerization rates for deuterium-labeled (*RS*)-**8d**, (*RS*)-**8i**, (*R*)-**8i**, and (*R*)-**8m** were measured. As the isomerization rate for (*RS*)-**8h** was very slow, the rate constant could not be calculated. The results are shown in Table 7 with the corresponding racemization rate. The results showed that isomerization occurred, but the isomerization rates of (*RS*)-

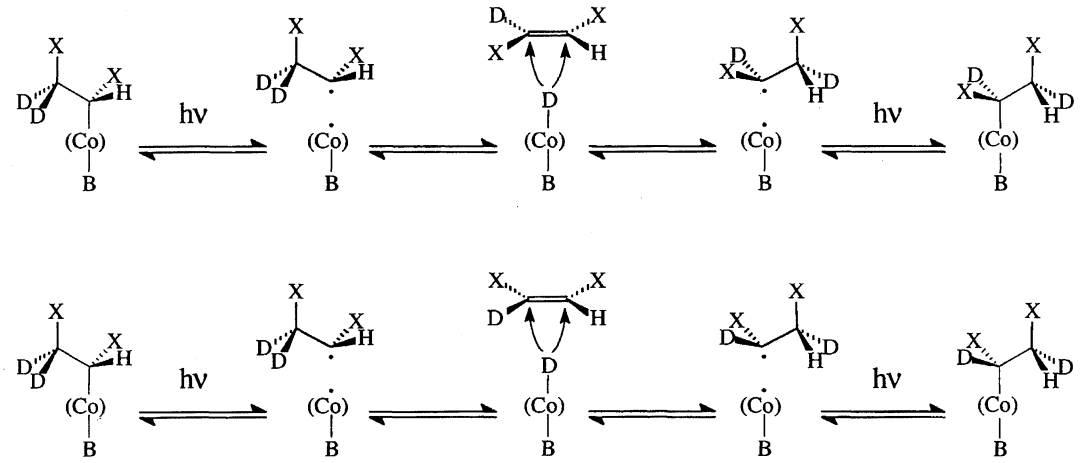


Fig. 11. 1,2-Isomerization reaction of 1,2-disubstituted complexes.

Table 7. Rate Constants of Photoisomerization and Photoracemization for (Base)[1,2-di(ethoxycarbonyl)ethyl]-bis(dimethylglyoximato)cobalt(III) in the Solid-State

Complex	Axial ligand	Rate constant/s^{-1}	
	B	Isomerization	Racemization
(*R*,*S*)-**8d**	Pyridine	3.1×10^{-6}	
(*R*)-**4d**	Pyridine		2.48×10^{-3}
(*R*,*S*)-**8h**	Methyldiphenylphosphine	Very slow	
(*R*)-**4h**	Methyldiphenylphosphine		2.18×10^{-5}
(*R*,*S*)-**8i**	Dimethylphenylphosphine	2.8×10^{-6}	
(*R*)-**4i**	Dimethylphenylphosphine		6.51×10^{-3}
(*R*)-**8i**	Dimethylphenylphosphine	3.7×10^{-6}	1.03×10^{-2}
(*R*)-**8m**	(*S*)-1-Phenylethylamine	2.9×10^{-6}	1.07×10^{-3}

8d, (*RS*)-**8i**, (*R*)-**8i**, and (*R*)-**8m** were extremely slow compared with the corresponding racemization rates: The ratios of racemization rates of the (*R*)-**4d**, (*R*)-**4i**, (*R*)-**8i**, and (*R*)-**8m** to the corresponding isomerization rates of (*RS*)-**8d**, (*RS*)-**8i**, (*R*)-**8i**, and (*R*)-**8m** were about 800, 2300, 2800, and 370 respectively. This fact clearly indicates that the contribution of path (C) to the racemization of 1,2-bis(alkoxycarbonyl)ethyl complexes was negligibly small.

Thus, out-of-plane rotations of radicals and (*E*)-olefins remain as the candidates for the racemization mechanism of 1-(methoxycarbonyl)ethyl and 1,2-bis(alkoxycarbonyl)ethyl cobaloxime complexes. When the 180° out-of-plane rotation of an (*E*)-olefin occurs, both substituents on C(1) and C(2) must make a large movement, and they are therefore subject to much steric hindrance from the surrounding molecules. In the case of the rotation of radicals, however, only the 180° out-of-plane rotation of substituents on C(1) is required (without substantial movement of substituents on C(2)), with some small angle of rotation about the axis C(2)–COOR and the axis Co–C(1) with which the reactive group is favorably accommodated in the reaction cavity. Consequently, the out-of-plane rotation of radicals is overwhelmingly easier than that of (*E*)-olefins (Fig. 12).

By the above mechanism, we can understand the following facts: while the rate constants of a series of complexes (*R*)-**2** (having a large substituent, methoxycarbonyl, on the C(1) of the reactive group) are smaller, by one or two orders of magnitude, than those of a series of complexes (*R*)- or (*S*)-**1** (having a small substituent, cyano, on the C(1) of the reactive group), the rate constants of a series of complexes (*R*)-**3** (having an additional substituent, methoxycarbonyl, on the C(2) of the reactive group of complexes (*R*)-**2**) are in almost the same range (10^{-3}—10^{-4}) as those of a series of complexes (*R*)-**2**, when there is no hydrogen bond and no solvent molecule in the crystal lattice.

Thus, the racemization for chiral 1-(methoxycarbonyl)-ethyl and 1,2-bis(alkoxycarbonyl)ethyl complexes is also considered to proceed mainly through path (A), though it probably involves path (B) and/or path (C) to some extent as minor paths (Fig. 13).

The above mechanism was also supported by rationalization of the interesting and unusual isotope effect that the rate constants of racemization for D-labeled complexes (*R*)-**8i** and (*R*)-**8m** were larger than those for unlabeled complexes (*R*)-**4i** and (*R*)-**4m**, respectively (Table 8). Since out-of-plane rotation of olefin is assumed to be difficult, as already discussed above, the racemization rate should mainly depend on the concentration of the radicals. Since the rate of C(2)–H abstraction by Co(II) is much faster than that of

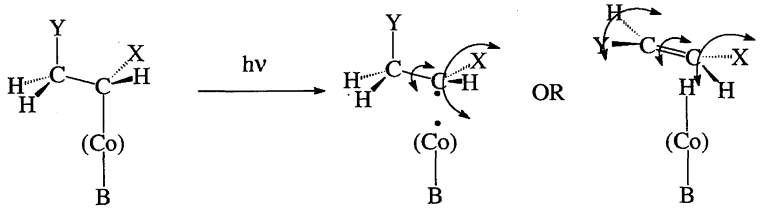


Fig. 12. The 180° out-of-plane rotation of reactive group.

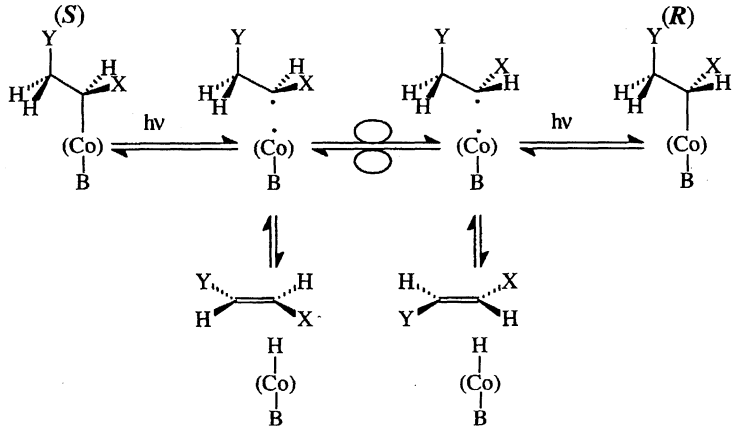


Fig. 13. Mechanism of solid-state photoracemization.

Table 8. Comparison of Photoracemization Rates of D-Labeled and Unlabeled (Base)[1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)cobalt(III) in the Solid-State

Axial ligand	Rate constant of racemization/s^{-1}	
	Unlabeled complex	D-Labeled complex
	(*R*)-**4i**	(*R*)-**8i**
Dimethylphenylphosphine	6.51×10^{-3}	1.03×10^{-2}
	(*R*)-**4m**	(*R*)-**8m**
(*S*)-1-Phenylethylamine	1.48×10^{-4}	1.07×10^{-3}

C(2)–D abstraction, the leakage of the radical species of unlabeled complexes to olefins is proportionately much larger, compared with that of the D-labeled complexes. Thus, the radical concentration in a photo-steady state for D-labeled complexes should be much higher than those in the photo-steady state for unlabeled complexes, and in turn, the racemization rates for D-labeled complexes should be faster than those for unlabeled complexes.

Conclusion

Solid-state photoracemization was observed in every case of 1-cyanoethyl, 1-(methoxycarbonyl)ethyl, 1,2-bis(methoxycarbonyl)ethyl, 1,2-bis(ethoxycarbonyl)ethyl, and 1,2-bis(allyloxycarbonyl)ethyl cobaloxime complexes coordinated with various axial ligands. The racemization of all these complexes proceeds with 180° out-of-plane rotation of the alkyl radical formed by photohomolysis.

The rate of racemization was not controlled by intramolecular electronic character, but by the shape and volume of the cavity for the reactive group, flexibility around the reactive group, and intermolecular interactions such as hydrogen bonding, the last of which is most overwhelming.

Experimental

The IR spectra were recorded on a Perkin–Elmer 1720 spectrometer. The NMR spectra were obtained by JEOL FX-200 and α-400 spectrometers, using TMS as the internal standard. The optical rotations were measured on a Perkin–Elmer 241 polarimeter. A WACOM Solar Simulator WX-105H (Flux density: 100 mW cm^{-2}), was used as the light source for the photoracemizations. All of the operations, except for photoracemizations, were carried out in the dark.

Materials. Each series of chiral cobaloxime complexes coordinated with various axial ligands were prepared by ligand exchange reactions of [(*R*)-1-cyanoethyl]bis(dimethylglyoximato)-[(*S*)-1-phenylethylamine]cobalt(III), (*R*)-**1m**, [(*S*)-1-cyanoethyl]-bis(dimethylglyoximato)[(*S*)-1-phenylethylamine]cobalt(III), (*S*)-**1m**, bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl) ethyl][(*R*)-1-phenylethylamine]cobalt(III), (*R*)-**2l**, [(*R*)-1,2-bis(methoxycarbonyl)ethyl]bis(dimethylglyoximato)[(*S*)-1-phenylethylamine]-cobalt(III), (*R*)-**3m**, [(*R*)-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)[(*S*)-1-phenylethylamine]cobalt(III), (*R*)-**4m**, and [(*S*)-1,2-bis(allyloxycarbonyl)ethyl]bis(dimethylglyoximato)[(*S*)-1-phenylethylamine]cobalt(III), (*S*)-**5m** with the corresponding ligand, respectively.

Preparations of (*R*)-**1a**,[5] (*R*)-**1d**,[9] (*R*)-**1g**,[5] (*R*)-**1j**,[5] (*R*)-**1m**,[9] (*R*)-**2d**,[9] (*R*)-**2g**,[6] (*R*)-**2l**,[9] (*R*)-**2m**,[9] and (*R*)-**2v**[9] were reported in previous papars. Preparation of (*R*)-**1h** was published simply, and the details are published in this paper. (*S*)-**1u**, (*R*)-**2a**, and (*R*)-**2e** were prepared from (*S*)-**1m**, (*R*)-**2l**, and (*R*)-**2l** by the same methods as those for preparation of the enantiomers, (*R*)-**1u**,[5] (*S*)-**2a**,[6] and (*S*)-**2e**,[6] respectively, and were confirmed by ^{1}H NMR, IR, and optical rotations. The preparations of (*R*)-**3d** and (*R*)-**3m** were simply described in a previous paper[16] and the details will be published later.

(3-Aminopyridine)[*R*-1-cyanoethyl]bis(dimethylglyoximato) cobalt(III), [(*R*)-1c]. 2.00 g of (*R*)-**1m** ($[\alpha]_{589} = +59.8°$) was dissolved in methanol (100 cm^3) and H_2O (10 cm^3) and ion-exchange resin (Dowex 50W-X2: 10 g) were added to the solution. The mixture was stirred for 45 h at room temperature, and then filtered to remove ion-exchange resin. A methanol solution of 3-aminopyridine (0.45 g/10 cm^3) was added to the filtered solution. The mixed solution was stirred for 1 h at room temperature, and then concentrated in vacuo. The crude product was recrystallized from methanol–water to give crystals of (*R*)-**1c** (1.652 g); $[\alpha]_{589} = +58.9°$, $[\alpha]_{578} = +61.6°$, and $[\alpha]_{546} = +71.5°$ (*c* 0.151, $CHCl_3$); IR (KBr) 3335, 3224, 2206, 1562, 1236, 1089, and 737 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 7.96$ (d, 1H, $J = 2.2$ Hz, pyridine), 7.84 (d, 1H, $J = 5.1$ Hz, pyridine), 7.01 (dd, 1H, $J = 8.5$ Hz, pyridine), 6.95 (m, 1H, pyridine), 4.02 (broad, 2H, NH_2), 2.26 (s, 6H, CH_3 of Hdmg), 2.24 (s, 6H, CH_3 of Hdmg), 2.12 (q, 1H, $J = 7.3$ Hz, Co–CH–), 0.55 (d, 3H, Co–CH–CH_3). Found: C, 43.76; H, 5.34; N, 22.57%. Calcd for $C_{16}H_{24}CoN_7O_4$: C, 43.94; H, 5.53; N, 22.42%.

[(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)(1-methylimida-

zole)cobalt(III), [(*R*)-1f′]. (*R*)-**1f′** was prepared from (*R*)-**1m** (1.5 g, $[\alpha]_{589}=+57.4°$) by a method similar to that for the preparation of (*R*)-**1c**, except for using 1-methylimidazole (0.6 cm^3) as the axial ligand. The crude product was recrystallized from benzene–methanol–hexane to give crystals of (*R*)-**1f′** (0.282 g); $[\alpha]_{589}=+61.3°$, $[\alpha]_{578}=+64.1°$, and $[\alpha]_{546}=+73.0°$ (*c* 0.181, $CHCl_3$); IR (KBr) 3134, 2957, 2199, 1569, 1235, and 1093 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta=7.40$ (m, 1H, imidazole), 6.89 (t, 1H, $J=1.2$ Hz, imidazole), 6.78 (t, 1H, $J=1.2$ Hz, imidazole), 3.65 (s, 3H, N–CH_3), 2.26 (s, 6H, CH_3 of Hdmg), 2.24 (s, 6H, CH_3 of Hdmg), 2.03 (q, 1H, $J=7.3$ Hz, Co–CH–), 0.59 (d, 3H, Co–CH–C<u>H</u>$_3$). Found: C, 42.21; H, 5.72; N, 23.28%. Calcd for $C_{15}H_{24}CoN_7O_4$: C, 42.36; H, 5.69; N, 23.05%.

[(*R*)- 1- Cyanoethyl]bis(dimethylglyoximato)(methyldiphenylphosphine)cobalt(III), [(*R*)-1h]. 2.03 g of (*R*)-**1m** ($[\alpha]_{589}=+56.3°$) was dissolved in methanol (100 cm^3). To the solution were added methyldiphenylphosphine (0.81 cm^3) and ion-exchange resin (6.0 g). The mixture was stirred for 2 d at room temperature, and then filtered to remove ion-exchange resin. The crude product was purified by column chromatography on silica gel (solvent: benzene–methanol) and was recrystallized from ethanol–hexane to give crystals of (*R*)-**1h** (1.014 g); $[\alpha]_{589}=+54.3°$, $[\alpha]_{578}=+56.3°$, and $[\alpha]_{546}=+65.1°$ (*c* 0.103, $CHCl_3$); IR (KBr) 2916, 2200, 1559, 1433, 1236, 1091, 757, 743, 700, and 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta=7.42$ (m, 10H, aromatic), 2.32 (m, 1H, Co–CH–), 1.90 (d, 3H, $J=8.5$ Hz, P–CH_3), 1.89 (d, 6H, $J=3.0$ Hz, CH_3 of Hdmg), 1.85 (d, 6H, $J=3.0$ Hz, CH_3 of Hdmg), 0.65 (dd, 3H, $J=6.4$ Hz and $J=7.3$ Hz, Co–CH–C<u>H</u>$_3$). Found: C, 52.92; H, 5.90; N, 12.78%. Calcd for $C_{24}H_{31}CoN_5O_4P$: C, 53.04; H, 5.75; N, 12.89%.

[(*S*)-1-Cyanoethyl]bis(dimethylglyoximato)(dimethylphenylphosphine)cobalt(III), [(*S*)-1i]. 2.00 g of (*S*)-**1m** was dissolved in methanol (40 cm^3). To the solution were added dimethylphenylphosphine (0.91 cm^3) and 2 mol dm^{-3} HCl (2.2 cm^3). The mixture was stirred for 1 d at room temperature under Ar atmosphere and the solution was neutralized with K_2CO_3. After water (5 cm^3) was added to the solution, it was cooled. Crude crystals (1.45 g) which deposited were filtered and recrystallized from methanol–water to give crystals of (*S*)-**1i** (1.06 g); $[\alpha]_{589}=-54.2°$, $[\alpha]_{578}=-57.1°$, and $[\alpha]_{546}=-63.1°$ (*c* 0.1034, $CHCl_3$); IR (KBr) 2998, 2987, 2952, 2915, 2860, 2196, 1557, 1236, 748, and 693 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta=7.40$ (m, 3H, aromatic), 7.14 (m, 2H, aromatic), 2.18 (m, 1H, Co–CH–), 2.06 (d, 6H, $J=2.9$ Hz, CH_3 of Hdmg), 2.03 (d, 6H, $J=2.9$ Hz, CH_3 of Hdmg), 1.43 (d, 6H, $J=10.3$ Hz, CH_3 of PMe_2Ph), 0.71 (dd, 3H, $J=6.1$ Hz and $J=7.3$ Hz, Co–CH–C<u>H</u>$_3$). Found: C, 47.48; H, 6.27; N, 14.51%. Calcd for $C_{19}H_{29}CoN_5O_4P$: C, 47.41; H, 6.07; N, 14.55%.

(Allylamine)[(*R*)-1-cyanoethyl]bis(dimethylglyoximato)-cobalt(III), [(*R*)-1q]. (*R*)-**1q** was prepared from (*R*)-**1m** (1.50 g) by a method similar to that for the preparation of (*R*)-**1c** except for using allylamine (1.43 cm^3) as the axial ligand. The crude product was recrystallized from methanol–water to give crystals of (*R*)-**1q** (0.767 g); $[\alpha]_{589}=+61.0°$, $[\alpha]_{578}=+64.0°$, and $[\alpha]_{546}=+68.4°$, (*c* 0.136, $CHCl_3$); IR (KBr) 3450, 3258, 3162, 2960, 2865, 2195, 1652, 1570, 1236, and 1088 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta=5.73$ (ddt, 1H, $J=6.1$ Hz, $J=10.5$ Hz, and $J=17.2$ Hz, –CH_2–C<u>H</u>=CH_2), 5.14, (dd, 1H, $J=1.0$ Hz, –CH=C<u>H</u>H), 5.10 (dd, 1H, –CH=C<u>H</u>H), 2.74 (q, 2H, –C<u>H</u>$_2$–CH=CH_2), 2.36 (s, 6H, CH_3 of Hdmg), 2.35 (s, 6H, CH_3 of Hdmg), 1.98 (q, 1H, $J=7.3$ Hz, Co–C<u>H</u>–CH_3), 1.76 (broad, 2H, –NH_2), 0.51 (d, 3H, Co–CH–C<u>H</u>$_3$). Found: C, 41.82; H, 6.13; N, 21.05%. Calcd for $C_{14}H_{25}CoN_6O_4$: C, 42.00; H, 6.29; N, 20.99%.

(4-Chloropyridine)bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III), [(*R*)-2b]. (*R*)-**2b** was prepared from (*R*)-**2l** ($[\alpha]_{578}=+200.7°$) by a method similar to that for the preparation of (*R*)-**1c**, except for using HCl and 4-chloropyridine as acid and the axial ligand. (*R*)-**2b**; $[\alpha]_{589}=+109.0°$, $[\alpha]_{578}=+120.0°$, and $[\alpha]_{546}=+140.0°$ ($CHCl_3$); IR (KBr) 3090, 2940, 1670, 1588, 1240, and 719 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta=8.34$ (d, 3H, $J=6.5$ Hz, aromatic), 7.18 (d, 2H, aromatic), 3.44 (s, 3H, –OCH_3), 2.18 (s, 12H, CH_3 of Hdmg), 2.18 (m, 1H, Co–CH–), 0.35 (d, 3H, $J=7.2$ Hz, Co–CH–C<u>H</u>$_3$). The structure of this complex was confirmed by X-ray structural analysis.[4a)]

(3-Aminopyridine)bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III), [(*R*)-2c]. (*R*)-**2c** was prepared from (*R*)-**2l** (2.0 g, $[\alpha]_{589}=+191.9°$) by a method similar to that for the preparation of (*R*)-**1c**, except for using 3-aminopyridine (0.401 g) as the axial ligand. The crude product was recrystallized from methanol–water to give crystals of (*R*)-**2c** (1.13 g); $[\alpha]_{589}=+138.7°$, $[\alpha]_{578}=+153.6°$, and $[\alpha]_{546}=+185.8°$ (*c* 0.155, $CHCl_3$); IR (KBr) 3327, 3219, 2949, 2859, 1680, 1559, 1447, and 1236 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta=7.95$ (d, 1H, $J=2.5$ Hz, pyridine), 7.88 (d, 1H, $J=5.2$ Hz, pyridine), 6.99 (dd, 1H, $J=8.2$ Hz, pyridine), 6.92 (dd, 1H, pyridine), 3.89 (broad s, 2H, NH_2), 3.47 (s, 3H, –OCH_3), 2.21 (s, 6H, CH_3 of Hdmg), 2.20 (s, 6H, CH_3 of Hdmg), 2.12 (q, 1H, $J=7.0$ Hz, Co–CH–), 0.38 (d, 3H, Co–CH–C<u>H</u>$_3$). Found: C, 43.20; H, 5.59; N, 17.62%. Calcd for $C_{17}H_{27}CoN_6O_6$: C, 43.41; H, 5.79; N, 17.87%. Second crops of crystals (0.21 g) were obtained from the mother liquor.

Bis(dimethylglyoximato)(imidazole)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III), [(*R*)-2f]. (*R*)-**2f** was prepared from (*R*)-**2l** (1.50 g) by a method similar to that for the preparation of (*R*)-**1h**, except for using imidazole (0.23 g) as the axial ligand. The crude product was recrystallized from methanol–water to give crystals of (*R*)-**2f** (0.30 g); $[\alpha]_{589}=+158.3°$, $[\alpha]_{578}=+175.4°$, and $[\alpha]_{546}=+232.5°$ (*c* 0.0998, $CHCl_3$); IR (KBr) 3146, 2947, 1689, 1566, 1235, and 1079 cm^{-1}; ^{1}H NMR (200 MHz, CD_3OD) $\delta=7.48$ (m, 1H, imidazole), 7.02 (t, 1H, $J=1.3$ Hz, imidazole), 6.81 (t, 1H, $J=1.3$ Hz, imidazole), 3.44 (s, 3H, –OCH_3), 2.19 (s, 6H, CH_3 of Hdmg), 2.18 (s, 6H, CH_3 of Hdmg), 2.04 (q, 1H, $J=7.1$ Hz, Co–CH–), 0.43 (d, 3H, Co–CH–C<u>H</u>$_3$). Found: C, 40.43; H, 5.54; N, 19.00%. Calcd for $C_{15}H_{25}CoN_6O_6$: C, 40.55; H, 5.67; N, 18.91%.

Bis(dimethylglyoximato)(dimethylphenylphosphine)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III), [(*R*)-2i]. (*R*)-**2i** was prepared from (*R*)-**2l** (1.50 g, $[\alpha]_{589}=+189.4°$) by a method similar to that for the preparation of (*R*)-**1h**, except for using dimethylphenylphosphine (0.45 cm^3) as the axial ligand. The crude product was recrystallized from methanol–water to give crystals of (*R*)-**2i** (1.02 g); $[\alpha]_{589}=+149.6°$, $[\alpha]_{578}=+161.9°$, and $[\alpha]_{546}=+216.7°$ (*c* 0.122, $CHCl_3$); IR (KBr) 2948, 1683, 1556, 1236, 1171, 754, and 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta=7.35$ (m, 3H, aromatic), 7.12 (m, 2H, aromatic), 3.43 (s, 3H, –OCH_3), 2.20—2.00 (m, 1H, Co–CH–), 2.00 (d, 6H, $J=3.2$ Hz, CH_3 of Hdmg), 1.98 (d, 6H, $J=3.2$ Hz, CH_3 of Hdmg), 1.39 (d, 6H, $J=9.5$ Hz, P–C<u>H</u>$_3$), 0.62 (t, 3H, $J=7.2$ Hz, Co–CH–C<u>H</u>$_3$). Found: C, 46.74; H, 6.38; N, 10.91%. Calcd for $C_{20}H_{32}CoN_4O_6P$: C, 46.70; H, 6.27; N, 10.89%.

Bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl][tris-(2-cyanoethyl)phosphine]cobalt(III), [(*R*)-2k]. (*R*)-**2k** was prepared from (*R*)-**2l** (1.50 g, $[\alpha]_{589}=+189.4°$) by a method similar to that for the preparation of (*R*)-**1h**, except for using tris(2-cyanoethyl)phosphine (0.61 g) as the axial ligand. The crude product was recrystallized from acetone–water to give crystals of (*R*)-**2k** (1.25 g); $[\alpha]_{589}=+132.2°$, $[\alpha]_{578}=+139.6°$, and $[\alpha]_{546}=+167.0°$ (*c* 0.1347, $CHCl_3$: MeOH = 9 : 1); IR (KBr) 2969, 2939, 2247, 1689, 1555, 1422, 1232, and 1108 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$)

δ = 3.47 (s, 3H, –OCH_3), 2.67 (dt, 6H, J = 7.6 Hz and J = 7.8 Hz, P(CH_2–C$\underline{H_2}$–)$_3$), 2.33 (d, 6H, J = 3.7 Hz, CH_3 of Hdmg), 2.32 (d, 6H, J = 3.7 Hz, CH_3 of Hdmg), 2.30—2.10 (m, 1H, Co–CH–), 1.85 (q, 6H, J = 7.6 Hz, P($C\underline{H_2}$–)$_3$), 0.51 (dd, 3H, J = 7.2 Hz, and J = 8.9 Hz, Co–CH–C$\underline{H_3}$). Found: C, 44.58; H, 5.94; N, 17.35%. Calcd for $C_{21}H_{33}CoN_7O_6P$: C, 44.29; H, 5.84; N, 17.22%.

(Butylamine)bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III), [(*R*)-2n]. (*R*)-**2n** was prepared from (*R*)-**2l** (1.54 g, $[\alpha]_{589}$ = +191.2°) by a method similar to that for the preparation of (*R*)-**1c**, except for using butylamine (1.05 cm^3) as the axial ligand. The crude product was recrystallized from benzene–hexane to give crystals of (*R*)-**2n** (1.14 g); $[\alpha]_{589}$ = +161.6°, $[\alpha]_{578}$ = +178.5°, and $[\alpha]_{546}$ = +221.1° (*c* 0.1126, $CHCl_3$); IR (KBr) 3246, 3162, 2960, 2862, 1681, 1560, 1237, and 1093 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.45 (s, 3H, –OCH_3), 2.32 (s, 6H, CH_3 of Hdmg), 2.30 (s, 6H, CH_3 of Hdmg), 2.04 (m, 2H, –C$\underline{H_2}$–NH_2), 1.93 (q, 1H, J = 7.1 Hz, Co–CH–), 1.45 (broad, 2H, NH_2), 1.32—1.15 (m, 4H, –C$\underline{H_2}$C$\underline{H_2}$–CH_2NH_2), 0.82 (t, 3H, J = 7.1 Hz, CH_3 of butylamine), 0.37 (d, 3H, Co–CH–C$\underline{H_3}$). Found: C, 42.56; H, 7.46; N, 15.75%. Calcd for $C_{16}H_{32}CoN_5O_6$: C, 42.76; H, 7.18; N, 15.58%.

Bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]-(propylamine)cobalt(III), [(*R*)-2o]. (*R*)-**2o** was prepared from (*R*)-**2l** (1.50 g, $[\alpha]_{589}$ = +191.2°) by a method similar to that for the preparation of (*R*)-**1c**, except for using propylamine (0.85 cm^3) as the axial ligand. The crude product was recrystallized from ethyl acetate–hexane to give crystals of (*R*)-**2o** (0.68 g); $[\alpha]_{589}$ = +171.5°, $[\alpha]_{578}$ = +191.3°, and $[\alpha]_{546}$ = +232.4° (*c* 0.1166, $CHCl_3$); IR (KBr) 3542, 3465, 3297, 3272, 3240, 2963, 2862, 1686, 1673, 1559, 1237, and 1090 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.45 (s, 3H, –OCH_3), 2.33 (s, 6H, CH_3 of Hdmg), 2.31 (s, 6H, CH_3 of Hdmg), 2.02 (m, 1H, Co–CH–), 1.99 (m, 2H, –C$\underline{H_2}$–NH_2), 1.45 (broad, 2H, –NH_2), 1.35 (m, 2H, CH_3C$\underline{H_2}$–CH_2NH_2), 0.78 (t, 3H, J = 7.1 Hz, –CH_3 of propylamine), 0.37 (d, 3H, J = 7.1 Hz, Co–CH–C$\underline{H_3}$). Found: C, 41.00; H, 7.13; N, 16.12%. Calcd for $C_{15}H_{30}CoN_5O_6$: C, 41.38; H, 6.95; N, 16.09%.

Bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]-(methylamine)cobalt(III), [(*R*)-2p]. (*R*)-**2p** was prepared from (*R*)-**2l** (1.50 g, $[\alpha]_{589}$ = +191.2°) by a method similar to that for the preparation of (*R*)-**1c**, except for using methylamine (commercially available: 40% aqueous solution, 6.0 equiv) as the axial ligand. The crude product was recrystallized from methanol–benzene–hexane to give crystals of (*R*)-**2p** (0.39 g); $[\alpha]_{589}$ = +171.5°, $[\alpha]_{578}$ = +191.5°, and $[\alpha]_{546}$ = +236.1° (*c* 0.0449, $CHCl_3$); IR (KBr) 3273, 3165, 2949, 2850, 1665, 1568, 1254, 1237, and 1071 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.45 (s, 3H, –OCH_3), 2.32 (s, 6H, CH_3 of Hdmg), 2.30 (s, 6H, CH_3 of Hdmg), 2.01 (m, 1H, Co–CH–), 1.93 (t, J = 6.7 Hz, 3H, C$\underline{H_3}$–NH_2), 0.38 (d, 3H, J = 7.0 Hz, Co–CH–C$\underline{H_3}$). Found: C, 38.30; H, 6.24; N, 17.21%. Calcd for $C_{13}H_{26}CoN_5O_6$: C, 38.34; H, 6.43; N, 17.19%.

(Benzylamine)bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III), [(*R*)-2r]. (*R*)-**2r** was prepared from (*R*)-**2l** (2.02 g, $[\alpha]_{589}$ = +184.8°) by a method similar to that for the preparation of (*R*)-**1c**, except for using benzylamine (0.47 cm^3) as the axial ligand. The crude product was recrystallized from benzene–hexane to give crystals of (*R*)-**2r** (0.41 g); $[\alpha]_{589}$ = +167.3°, $[\alpha]_{578}$ = +184.3°, and $[\alpha]_{546}$ = +219.0° (*c* 0.153, $CHCl_3$); IR (KBr) 3293, 3258, 2996, 2946, 1681, 1559, 1238, and 739 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.29 (m, 3H, aromatic), 7.08 (m, 2H, aromatic), 3.46 (s, 3H, –OCH_3), 3.23 (m, 2H, Ph–C$\underline{H_2}$–NH_2), 2.32 (s, 6H, CH_3 of Hdmg), 2.30 (s, 6H, CH_3 of Hdmg), 2.02 (q, 1H, J = 7.2 Hz, Co–CH–), 1.82 (broad, 2H, –NH_2), 0.38 (d, 3H, Co–CH–C$\underline{H_3}$). Found: C, 47.17; H, 6.33; N, 14.48%. Calcd for $C_{19}H_{30}CoN_5O_6$: C, 47.21; H, 6.25; N, 14.49%. Second crops of crystals (0.77 g) were obtained from the mother liquor.

(Cyclohexanemethylamine)bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III), [(*R*)-2s]. (*R*)-**2s** was prepared from (*R*)-**2l** (2.00 g, $[\alpha]_{589}$ = +184.8°) by a method similar to that for the preparation of (*R*)-**1c**, except for using cyclohexanemethylamine (0.55 cm^3) as the axial ligand. The crude product was recrystallized from methanol–water to give crystals of (*R*)-**2s** (1.34 g); $[\alpha]_{589}$ = +149.7°, $[\alpha]_{578}$ = +166.2°, and $[\alpha]_{546}$ = +204.8° (*c* 0.145, $CHCl_3$); IR (KBr) 3272, 3133, 2922, 2852, 1693, 1561, 1239, and 1179 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.45 (s, 3H, –OCH_3), 2.32 (s, 6H, CH_3 of Hdmg), 2.30 (s, 6H, CH_3 of Hdmg), 1.97 (q, J = 7.1 Hz, 1H, Co–CH), 1.91 (m, 2H, C$\underline{H_2}$–NH_2), 1.66—0.74 (m, 13H, $C_6\underline{H_{11}}$–CH_2–N$\underline{H_2}$), 0.36 (d, 3H, Co–CH–C$\underline{H_3}$). Found: C, 46.37, H, 7.77; N, 13.96%. Calcd for $C_{19}H_{36}CoN_5O_6 \cdot 1/3CH_3OH$: C, 46.43; H, 7.52; N, 14.00%.

(Cyclohexylamine)bis(dimethylglyoximato)[(*R*)-1-(methoxycarbonyl)ethyl]cobalt(III), [(*R*)-2t]. (*R*)-**2t** was prepared from (*R*)-**2l** (1.36 g, $[\alpha]_{589}$ = +191.2°) by a method similar to that for the preparation of (*R*)-**1c**, except for using cyclohexylamine (1.10 cm^3) as the axial ligand. The crude product was purified by column chromatography on silica gel (solvent: benzene–dichloromethane–methanol) and was recrystallized from benzene to give crystals of (*R*)-**2t** (0.49 g); $[\alpha]_{589}$ = +157.0°, $[\alpha]_{578}$ = +172.4°, and $[\alpha]_{546}$ = +199.6° (*c* 0.1363, $CHCl_3$); IR (KBr) 3289, 3225, 3145, 2929, 2856, 1693, 1557, 1236, 1174, 1091, and 684 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.45 (s, 3H, –OCH_3), 2.32 (s, 6H, CH_3 of Hdmg), 2.30 (s, 6H, CH_3 of Hdmg), 1.97 (m, 1H, Co–CH–), 1.9—0.65 (m, 13H, $C_6H_{11}NH_2$), 0.34 (d, 3H, Co–CH–C$\underline{H_3}$). Found: C, 48.61; H, 7.27; N, 13.77%. Calcd for $C_{18}H_{34}CoN_5O_6 \cdot 1/2C_6H_6$: C, 49.03; H, 7.25; N, 13.61%.

[(R)-1,2-Bis(methoxycarbonyl)ethyl]bis(dimethylglyoximato)(1-methylimidazole)cobalt(III), [(*R*)-3f′]. (*R*)-**3f′** was prepared from (*R*)-**3m** (1.00 g, $[\alpha]_{589}$ = +220.8°) by a method similar to that for the preparation of (*R*)-**1c**, except for using 1-methylimidazole (0.42 cm^3) as the axial ligand. The crude product was recrystallized from benzene–hexane to give crystals of (*R*)-**3f′** (0.51 g); $[\alpha]_{589}$ = +200.9°, $[\alpha]_{578}$ = +223.0°, and $[\alpha]_{546}$ = +299.1° (*c* 0.113, $CHCl_3$); IR (KBr) 3116, 2951, 1734, 1693, 1560, 1238, 1160, and 1094 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.38 (m, 1H, imidazole), 6.89 (t, 1H, J = 1.3 Hz, imidazole), 6.72 (t, 1H, J = 1.3 Hz, imidazole), 3.61 (s, 3H, N–CH_3), 3.55 (s, 3H, –OCH_3), 3.51 (s, 3H, –OCH_3), 2.28 (d, 2H, J = 6.4 Hz, Co–CH–C$\underline{H_2}$), 2.23 (s, 6H, CH_3 of Hdmg), 2.19 (s, 6H, CH_3 of Hdmg), 2.07 (m, 1H, Co–CH–). Found: C, 41.74; H, 5.66; N, 16.41%. Calcd for $C_{18}H_{29}CoN_6O_8$: C, 41.87; H, 5.66; N, 16.27%.

[(*R*)-1,2-Bis(methoxycarbonyl)ethyl]bis(dimethylglyoximato)(methyldiphenylphosphine)cobalt(III), [(*R*)-3h]. (*R*)-**3h** was prepared from (*R*)-**3m** (0.98 g, $[\alpha]_{589}$ = +220.8°) by a method similar to that for the preparation of (*R*)-**1h**, except for using methyldiphenylphosphine (0.50 cm^3) as the axial ligand. The crude product was purified by column chromatography on silica gel (benzene–dichloromethane–metanol) and was recrystallized from ethyl acetate–hexane to give crystals of (*R*)-**3h** (0.88 g); $[\alpha]_{589}$ = +205.0°, $[\alpha]_{578}$ = +225.2°, and $[\alpha]_{546}$ = +293.5° (*c* 0.1288, $CHCl_3$); IR (KBr) 3059, 2939, 1735, 1685, 1558, 1434, 1239, 1203, 1155, 755, and 697 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40 (m, 10H, aromatic), 3.53 (s, 3H, –OCH_3), 3.46 (s, 3H, –OCH_3), 2.27 (m, 3H, Co–CH–CH_2), 1.86 (d, 3H, J = 9.0 Hz, P–CH_3), 1.85 (d, 6H, J = 3.2 Hz, CH_3 of Hdmg), 1.81 (d, 6H, J = 3.2 Hz, CH_3 of Hdmg). Found: C, 51.30; H, 5.76; N, 8.72%. Calcd for $C_{27}H_{36}CoN_4O_8P$: C, 51.11;

H, 5.72; N, 8.83%.

[(*R*)-1,2-Bis(methoxycarbonyl)ethyl]bis(dimethylglyoximato)[(*R*)-1-phenylethylamine]cobalt(III), [(*R*)-3l]. (*R*)-**3l** was prepared from (*R*)-**3m** (1.56 g, $[\alpha]_{589}=+217.0°$) by a method similar to that for the preparation of (*R*)-**1c**, except for using (*R*)-1-phenylethylamine (0.36 cm^3) as the axial ligand. The crude product was purified by column chromatography on silica gel (benzene–methanol) and then recrystallized from ethyl acetate–hexane to give crystals of (*R*)-**3l** (0.73 g); $[\alpha]_{589}=+243.9°$, $[\alpha]_{578}=+267.7°$, and $[\alpha]_{546}=+313.1°$ (*c* 0.130, $CHCl_3$); IR (KBr) 3310, 3267, 3003, 2957, 1718, 1678, 1581, 1243, 1193, 766, and 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta=7.31$ (m, 3H, aromatic), 7.04 (m, 2H, aromatic), 3.61 (tq, 3H, $J=6.6$ Hz and $J=6.6$ Hz, N–CH), 3.53 (s, 3H, $-OCH_3$), 3.49 (s, 3H, $-OCH_3$), 2.22 (s, 6H, CH_3 of Hdmg), 2.18 (s, 6H, CH_3 of Hdmg), 2.13 (d, 2H, $J=8.1$ Hz, Co–CH–C<u>H</u>$_2$), 2.00 (t, 1H, Co–CH–), 1.70 (broad, 1H, NH_2), 1.40 (m, 1H, NH_2), 1.21 (d, 3H, H_2N–CH–C<u>H</u>$_3$). Found: C, 47.61; H, 6.24; N, 12.63%. Calcd for $C_{22}H_{34}CoN_5O_8$: C, 47.57; H, 6.17; N, 12.61%.

[(*R*)-1,2-Bis(methoxycarbonyl)ethyl]bis(dimethylglyoximato)(propylamine)cobalt(III), [(*R*)-3o]. (*R*)-**3o** was prepared from (*R*)-**3m** (1.52 g, $[\alpha]_{589}=+216.4°$) by a method similar to that for the preparation of (*R*)-**1c**, except for using propylamine (0.80 cm^3) as the axial ligand. The crude product was recrystallized from methanol to give crystals of (*R*)-**3o** (0.74 g); $[\alpha]_{589}=+234.4°$, $[\alpha]_{578}=+255.3°$, and $[\alpha]_{546}=+318.6°$ (*c* 0.1042, $CHCl_3$); IR (KBr) 3497, 3278, 3161, 2947, 2883, 1710, 1677, 1562, 1237, and 1091 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) $\delta=3.54$ (s, 3H, $-OCH_3$), 3.48 (s, 3H, $-OCH_3$), 2.34 (s, 6H, CH_3 of Hdmg), 2.30 (s, 6H, CH_3 of Hdmg), 2.16 (d, 2H, $J=7.3$ Hz, Co–CH–C<u>H</u>$_2$), 2.01 (m, 1H, Co–CH–), 2.01 (quintet, 2H, $J=7.6$ Hz, H_2N–C<u>H</u>$_2$–), 1.48 (broad, 2H, $-NH_2$), 1.35 (tq, 2H, $J=7.3$ Hz and $J=7.3$ Hz, H_2N–CH_2–C<u>H</u>$_2$–), 0.78 (t, 3H, $-CH_3$ of propylamine). The structure of this complex was confirmed by X-ray structural analysis.[14,19]

(Aqua)[(*R*)-1,2-bis(methoxycarbonyl)ethyl]bis(dimethylglyoximato)cobalt(III), [(*R*)-3v]. Water (10 cm^3) and ion-exchange resin (dowex 50W-X2: 2.6 g) were added to a solution of (*R*)-**3m** (0.63 g) in methanol (70 cm^3). The mixture was stirred for 2 d at room temperature. After the usual work-up, the crude product was crystallized from acetone to give crystals of (*R*)-**3v** (0.26 g); ^1H NMR (400 MHz, $CDCl_3$) $\delta=3.52$ (s, 3H, $-OCH_3$), 3.38 (s, 3H, $-OCH_3$), 2.4–1.9 (m, 3H, Co–CH–CH_2), 2.25 (s, 6H, CH_3 of Hdmg), 2.24 (s, 6H, CH_3 of Hdmg). As this complex is unstable for elementary analysis, the structure of this complex was confirmed by ^1H NMR.

[(*R*)-1,2-Bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)-[(*S*)-1-phenylethylamine]cobalt(III), [(*R*)-4m]. To a solution of $Co(OCOCH_3)_2\cdot4H_2O$ (25.10 g) in methanol (100 cm^3) was added a hot solution of dimethylglyoxime (24.4 g) in methanol (800 cm^3) under argon atmosphere with stirring. The solution was stirred for 10 min. An aqueous solution of sodium hydroxide (8.5 g) and (*S*)-1-phenylethylamine (13.5 cm^3) were added to the solution on cooling and then the reaction vessel was connected to a hydrogen-gas burret. Diethyl maleate (18.7 cm^3) was added to the reaction vessel by means of a syringe. The reaction mixture was then stirred under hydrogen atmosphere. After the theoretical amount of hydrogen had been absorbed, the product was extracted with dichloromethane (1.5 dm^3) and washed several times with water. The dichloromethane solution was dried over anhydrous sodium sulfate and concentrated in vacuo. The orange crystals was obtained by purification of the residue with column chromatography on silica gel (benzene–chloroform–methanol). The crystals were dissolved in 2-propanol (200 cm^3) on warming slightly. The solution was filtered, and hexane (300 cm^3) was added slowly to the solution. Orange crystals (6.99 g) which deposited were collected by filtration. After five recrystallizations, optically pure crystals (3.53 g) of (*R*)-**4m** were obtained; $[\alpha]_{589}=+180.1°$, $[\alpha]_{578}=+197.9°$, and $[\alpha]_{546}=+241.4°$ (*c* 0.151, $CHCl_3$); IR (KBr) 3279, 3249, 3170, 2970, 2930, 1713, 1686, 1563, 1239, 1208, 1092, 765, and 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta=7.31$ (m, 3H, aromatic), 7.03 (m, 2H, aromatic), 3.98 (m, 2H, O–C<u>H</u>$_2$–), 3.92 (dq, 1H, $J=7.2$ Hz and $J=10.9$ Hz, O–C<u>H</u>H–), 3.82 (dq, 1H, $J=7.2$ Hz, O–CH<u>H</u>–), 3.60 (m, 1H, H_2N–C<u>H</u>–Ph), 2.22 (s, 6H, CH_3 of Hdmg), 2.18 (s, 6H, CH_3 of Hdmg), 2.12 (m, 2H, Co–CH–C<u>H</u>$_2$–), 1.92 (m, 1H, Co–CH–), 1.67 (broad, 1H, $-NH_2$), 1.42 (m, 1H, $-NH_2$), 1.21 (d, 3H, $J=6.1$ Hz, HN–CH–C<u>H</u>$_3$), 1.19 (t, 3H, CH_3 of ethoxy), 1.15 (t, 3H, CH_3 of ethoxy). Found: C, 49.91; H, 7.34; N, 10.92%. Calcd for $C_{24}H_{38}CoN_5O_8\cdot3/4C_3H_8O$: C, 50.16; H, 7.05; N, 11.14%.

[(*R*)-1,2-Bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)-(pyridine)cobalt(III), [(*R*)-4d]. (*R*)-**4d** was prepared from (*R*)-**4m** (1.50 g, $[\alpha]_{589}=+180.1°$) by a method similar to that for the preparation of (*R*)-**1h**, except for using pyridine (10 cm^3) as the axial ligand. The crude product was purified by column chromatography on silica gel (benzene–pyridine–methanol) and was recrystallized from methanol–water to give crystals of (*R*)-**4d** (1.08 g); $[\alpha]_{589}=+178.4°$, $[\alpha]_{578}=+198.0°$, and $[\alpha]_{546}=+248.0°$ (*c* 0.148, $CHCl_3$); IR (KBr) 2979, 2950, 1727, 1684, 1563, 1452, 1373, 1239, 1197, 1153, 767, and 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta=8.50$ (dt, 2H, $J=1.5$ Hz and $J=4.9$ Hz, pyridine), 7.69 (tt, 1H, $J=1.5$ Hz and $J=7.6$ Hz, pyridine), 7.27 (m, 2H, pyridine), 4.01 (m, 2H, O–CH_2–), 3.97 (m, 1H, O–C<u>H</u>H–), 3.89 (dq, 1H, $J=7.2$ Hz and $J=10.6$ Hz, O–CH<u>H</u>–), 2.25 (m, 2H, –Co–CH–C<u>H</u>$_2$), 2.22 (s, 6H, CH_3 of Hdmg), 2.18 (s, 6H, CH_3 of Hdmg), 2.15 (m, 1H, Co–CH–), 1.24 (t, 3H, $J=7.1$ Hz, CH_3 of ethoxy), 1.17 (t, 3H, $J=7.1$ Hz, CH_3 of ethoxy). Found: C, 46.35; H, 6.17; N, 13.02%. Calcd for $C_{21}H_{32}CoN_5O_8$: C, 46.59; H, 5.96; N, 12.93%.

[(*R*)-1,2-Bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)-(methyldiphenylphosphine)cobalt(III), [(*R*)-4h]. (*R*)-**4h** was prepared from (*R*)-**4m** (1.58 g, $[\alpha]_{589}=+180.1°$) by a method similar to that for the preparation of (*R*)-**1h**, except for using methyldiphenylphosphine (1.1 cm^3) as the axial ligand. The crude product was purified by column chromatography on silica gel (benzene–methanol) and was recrystallized from ethanol–hexane to give crystals of (*R*)-**4h** (1.21 g); $[\alpha]_{589}=+168.8°$, $[\alpha]_{578}=+187.0°$, and $[\alpha]_{546}=+251.0°$ (*c* 0.192, $CHCl_3$); IR (KBr) 3070, 2973, 2920, 1732, 1683, 1561, 1240, 1179, 754, and 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta=7.42$ (m, 10H, aromatic), 3.98 (m, 2H, O–CH_2–), 3.90 (m, 1H, O–C<u>H</u>H–), 3.82 (dq, 1H, $J=7.2$ Hz and $J=10.6$ Hz, O–CH<u>H</u>–), 2.26 (m, 2H, –Co–CH–C<u>H</u>$_2$), 2.19 (m, 1H, –Co–C<u>H</u>–CH_2–), 1.85 (d, 3H, $J=9.3$ Hz, P–CH_3), 1.84 (d, 6H, $J=3.2$ Hz, CH_3 of Hdmg), 1.81 (d, 6H, $J=3.2$ Hz, CH_3 of Hdmg), 1.19 (t, 3H, $J=7.2$ Hz, CH_3 of ethoxy), 1.14 (t, 3H, $J=7.2$ Hz, CH_3 of ethoxy). Found: C, 52.45; H, 6.34; N, 8.62%. Calcd for $C_{29}H_{40}CoN_4O_8P$: C, 52.57; H, 6.08; N, 8.46%.

[(*R*)-1,2-Bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)-(dimethylphenylphosphine)cobalt(III), [(*R*)-4i]. (*R*)-**4i** was prepared from (*R*)-**4m** (1.46 g, $[\alpha]_{589}=+176.0°$) by a method similar to that for the preparation of (*R*)-**1h**, except for using dimethylphenylphosphine (0.75 cm^3) as the axial ligand. The crude product was purified by column chromatography on silica gel (benzene–methanol) and was recrystallized from 2-propanol–hexane to give crystals of (*R*)-**4i** (0.88 g); $[\alpha]_{589}=+179.4°$, $[\alpha]_{578}=+196.0°$, and $[\alpha]_{546}=+264.0°$ (*c* 0.175, $CHCl_3$); IR (KBr) 2980, 2928, 1730, 1683, 1558, 1239, 1189, 1152, 1091, 749, and 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta=7.42$ (m, 1H, aromatic), 7.35 (m, 2H, aro-

matic), 7.12 (m, 2H, aromatic), 3.99 (m, 2H, O–CH_2–), 3.91 (m, 1H, O–C<u>H</u>H–), 3.81 (dq, 1H, J=7.0 Hz and J=10.5 Hz, O–CH<u>H</u>–), 2.30 (m, 2H, Co–CH–C<u>H</u>$_2$), 2.09 (m, 1H, Co–CH–), 2.00 (d, 6H, J=3.2 Hz, CH_3 of Hdmg), 1.96 (d, 6H, J=3.2 Hz, CH_3 of Hdmg), 1.384 (d, 3H, J=10.2 Hz, P–CH_3), 1.380 (d, 3H, J=10.2 Hz, P–CH_3), 1.19 (t, 3H, J=7.2 Hz, CH_3 of ethoxy), 1.15 (t, 3H, J=7.2 Hz, CH_3 of ethoxy). Found: C, 47.82; H, 6.52; N, 9.44%. Calcd for $C_{24}H_{38}CoN_4O_8P$: C, 48.00; H, 6.38; N, 9.33%.

[(*R*)-1,2-Bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)(propylamine)cobalt(III), [(*R*)-4o]. (*R*)-**4o** was prepared from (*R*)-**4m** (1.50 g, $[\alpha]_{589}$=+176.0°) by a method similar to that for the preparation of (*R*)-**1c**, except for using propylamine (0.33 cm^3) as the axial ligand. The crude product was recrystallized from benzene–hexane to give crystals of (*R*)-**4o** (0.97 g); $[\alpha]_{589}$=+198.1°, $[\alpha]_{578}$=+221.7°, and $[\alpha]_{546}$=+287.3° (*c* 0.157, $CHCl_3$); IR (KBr) 3299, 3257, 2971, 2930, 1722, 1680, 1596, 1562, 1241, 1191, and 1164 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.99 (m, 2H, O–CH_2–), 3.94 (dq, 1H, J=7.3 Hz and J=10.7 Hz, O–C<u>H</u>H–), 3.82 (dq, 1H, J=7.2 Hz, O–CH<u>H</u>–), 2.33 (s, 6H, CH_3 of Hdmg), 2.29 (s, 6H, CH_3 of Hdmg), 2.15 (m, 2H, Co–CH–C<u>H</u>$_2$), 2.00 (m, 3H, Co–CH– and N–CH_2), 1.44 (broad, 2H, –NH_2), 1.35 (tq, 2H, J=7.3 Hz and J=7.3 Hz, N_2N–CH_2–C<u>H</u>$_2$–), 1.20 (t, 3H, CH_3 of ethoxy), 1.15 (t, 3H, CH_3 of ethoxy), 0.78 (t, 3H, J=7.3 Hz, –CH_3 of propylamine). Found: C, 43.64; H, 7.22; N, 13.55%. Calcd for $C_{19}H_{36}CoN_5O_8$: C, 43.76; H, 6.96; N, 13.43%.

[(*S*)-1,2-Bis(allyloxycarbonyl)ethyl]bis(dimethylglyoximato)[(*S*)-1-phenylethylamine]cobalt(III), [(*S*)-5m]. To a solution of $Co(OCOCH_3)_2{\cdot}4H_2O$ (37.5 g) in acetonitrile (120 cm^3) and methanol (30 cm^3) was added a hot solution of dimethylglyoxime (35.1 g) in acetonitrile (600 cm^3) and methanol (180 cm^3) under argon atmosphere with stirring. The solution was stirred for 5—10 min. The reaction vessel was then connected to a hydrogen-gas buret. Diallyl maleate (277 cm^3) was added to the reaction vessel by means of a syringe. The reaction mixture was the stirred under hydrogen atmosphere. After the theoretical amount of hydrogen had been absorbed, the reaction mixture was neutralized by an aqueous solution of sodium hydroxide (12 g) on cooling. To the resulting solution, (*S*)-1-phenylethylamine (19.5 cm^3) was added. The product was extracted with dichloromethane (1.5 dm^3) and washed several times with water. The dichloromethane solution was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography on silica gel (benzene–methanol) to give dark red crystals (12.8 g). The crystals dissolved in benzene (100 cm^3) on warming slightly. The solution was filtered, and hexane (65 cm^3) was added slowly to the solution. Dark red crystals (10.2 g) which deposited were collected by filtration. After four recrystallizations, optically pure crystals (4.1 g) of (*S*)-**5m** were obtained; $[\alpha]_{589}$=−195.8°, $[\alpha]_{578}$=−217.3°, and $[\alpha]_{546}$=−255.4° (*c* 0.146, $CHCl_3$); IR (KBr) 3303, 3231, 2963, 2932, 1741, 1687, 1553, 1241, 1154, 1089, 765, and 706 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ=7.30 (m, 3H, aromatic), 7.04 (m, 2H, aromatic), 5.85 (m, 2H, –CH_2–C<u>H</u>=CH_2), 5.20 (m, 4H, –CH=C<u>H</u>$_2$), 4.33 (m, 4H, –OC<u>H</u>$_2$–CH=C), 3.60 (tq, 1H, J=6.5 Hz and J=6.5 Hz, N–CH), 2.22 (s, 6H, CH_3 of Hdmg), 2.18 (s, 6H, CH_3 of Hdmg), 2.30—1.95 (m, 3H, Co–CH–CH_2), 1.75 (broad, 1H, –NH), 1.39 (m, 1H, –NH), 1.22 (d, 3H, N_2N–CH–C<u>H</u>$_3$). Found: C, 51.16; H, 6.27; N, 11.57%. Calcd for $C_{26}H_{38}CoN_5O_8$: C, 51.40; H, 6.30; N, 11.53%.

[(*S*)-1,2-Bis(allyloxycarbonyl)ethyl]bis(dimethylglyoximato)(4-methylpyridine)cobalt(III), [(*S*)-5e]. (*S*)-**5e** was prepared from (*S*)-**5m** (1.40 g, $[\alpha]_{589}$=−188.8°) by a method similar to that for the preparation of (*R*)-**1h**, except for using 4-methylpyridine (0.91 cm^3) as the axial ligand. The crude product was recrystallized from methanol–water to give crystals of (*S*)-**5e** (0.87 g); $[\alpha]_{589}$=−152.6°, $[\alpha]_{578}$=−170.8°, and $[\alpha]_{546}$=−219.7° (*c* 0.1206, $CHCl_3$); IR (KBr) 2935, 1726, 1560, 1238, 1153, and 1092 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ=8.30 (d, 2H, J=6.4 Hz, 4-methylpyridine), 7.06 (d, 2H, 4-methylpyridine), 5.90 (m, 2H, –CH_2–C<u>H</u>=CH_2), 5.22 (m, 4H, –CH=C<u>H</u>$_2$), 4.42 (m, 4H, –O–C<u>H</u>$_2$–CH=C), 2.31 (s, 3H, CH_3 of 4-methylpyridine), 2.31—2.09 (m, 3H, Co–CH–CH_2), 2.21 (s, 6H, CH_3 of Hdmg), 2.18 (s, 6H, CH_3 of Hdmg). Found: C, 49.53; H, 5.93; N, 11.96%. Calcd for $C_{24}H_{34}CoN_5O_8$: C, 49.74; H, 5.91; N, 12.09%.

Photoracemization. Powdered crystals (0.05 g) were suspended in a liquid (5 cm^3) in which the crystals were insoluble: Most samples were suspended in liquid paraffin and only (*R*)-**2h** was suspended in glycerol. The suspension was irradiated for a definite time by a solar simulator (flux density: 100 mW cm^{-2}). After separation of crystals from insoluble liquid, if the axial base was alkylamine or 4-cyanopyridine, it was displaced with pyridine. Each sample was purified by column chromatography on silica gel and the optical rotation was measured at three wavelengths: 589, 578, and 546 nm. Optical rotations of the samples decreased gradually with irradiation time. The optical rotational change of the early stage fitted first-order rate expression, from which rate constants of solid-state photoracemizations were obtained (see Tables 1, 2, 3, 4, and 5). Most rate constants on these tables are means of three values calculated from optical rotations at three wavelengths respectively. The rate constants of (*R*)-**2f** and (*R*)-**3h** were calculated from optical rotations at 589 nm and the rate constants of (*R*)-**1d**, (*R*)-**2a**, (*R*)-**2b**, (*R*)-**2d**, (*R*)-**2e**, (*R*)-**2l**, (*R*)-**2v**, (*R*)-**3d**, and (*R*)-**3m** were calculated from optical rotations at 578 nm.

NMR Experiments. Powdered crystals (0.010 g) were irradiated in an NMR sample tube (r=2.5 mm) by a solar simulator (flux density: 100 mW cm^{-2}). After irradiation, 0.6 cm^3 of $CDCl_3$ was added to the NMR sample tube and ^{1}H NMR was measured soon under the same conditions at each sample. These results are shown in Table 6.

Diethyl 2-Bromo-3,3-dideuteriobutanedioate (7). A solution of diethyl oxalacetate sodium salt (50.05 g) in water (600 cm^3) was neutralized by 6 mol dm^{-3} HCl (35 cm^3) on cooling. Diethyl oxalacetate was extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was dissolved in ethanol-d_1 (125 cm^3) and water-d_2 (62 cm^3) was added to the solution. The solution was stirred for a week at room temperature. To the solution was added a solution of sodium borohydride (3.05 g) in water-d_2 (8 cm^3) while cooling. After being stirred for 2 min, the solution was neutralized by 6 mol dm^{-3} HCl (10 cm^3) on cooling. After the solution was concentrated in vacuo to remove ethanol, residue was purified by column chromatography on silica gel (hexane–ethyl acetate) to give a syrup of diethyl 2-hydroxy-3,3-dideuteriobutanedioate (8.58 g), **6**. This syrup was dissolved in *N*,*N*-dimethylformamide (DMF) (100 cm^3). To the solution were added a solution of triphenylphosphine (23.56 g) in DMF (60 cm^3) and a solution of tetrabromomethane (16.38 g) in DMF (30 cm^3) on cooling. The solution was stirred for 1 d and concentrated in vacuo. After the residue was purified roughly by column chromatography on silica gel (hexane–ethyl acetate), this syrup was distilled in vacuo (80—94 °C/5 mmHg, 1 mmHg = 133.322 Pa) to give syrup of **7** (8.58 g). Deuterium content was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ=4.55 (m, 1H, H-1), 4.25 (dq, 2H, J=0.7 Hz and J=7.2 Hz, –O–CH_2–), 4.17 (dq, 2H, J=0.7 Hz and J=7.2 Hz, –O–CH_2–), 3.25 (m, 0.046H, H-2), 2.96 (m, 0.055H, H-2′), 1.31 (t, 3H, –CH_3), 1.26 (t, 3H, –CH_3).

[(*R*,*S*)-2,2-Dideuterio-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)(pyridine)cobalt(III), [(*R*,*S*)-8d]. (Aniline)(chloro)bis(dimethylglyoximato)cobalt(III) (1.32 g) was suspended in methanol (50 cm^3) under argon atmosphere. To the reaction mixture was added a solution of sodium borohydride (0.47 g) in water (8 cm^3), and the mixture was stirred for 15 min. To the solution was added acetone (4 cm^3) and the mixture was stirred for 10 min. A solution of **7** (0.71 g, deuterium content 1.7) in methanol (15 cm^3) was added to the solution. After we stirred the sample for 2 d, the product was extracted by dichloromethane and washed with water. Dichloromethane solution was dried over anhydrous sodium sulfate and concentrated in vacuo to give dark red crystals: 0.65 g.

To a solution of crude crystals (0.65 g) in methanol (50 cm^3) were added ion-exchange resin (4.0 g) and pyridine (2 cm^3). The reaction mixture was stirred for 20 min and was filtered to remove ion-exchange resin. The solution was concentrated in vacuo and crude crystals were recrystallized from methanol–water to give crystals of (*R*,*S*)-**8d** (0.17 g); IR (KBr) 2979, 2928, 1724, 1683, 1563, 1451, 1368, 1239, 1182, and 1092 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 (m, 2H, pyridine), 7.69 (tt, 1H, J = 1.5 Hz and J = 7.6 Hz, pyridine), 7.27 (m, 2H, pyridine), 4.01 (m, 2H, O–CH_2–), 3.96 (m, 1H, O–CHH–), 3.89 (dq, 1H, J = 7.2 Hz and J = 10.4 Hz, O–CHH–), 2.25 (m, 0.3H, –Co–CH–$CH_{0.3}D_{1.7}$–), 2.22 (s, 6H, CH_3 of Hdmg), 2.18 (s, 6H, CH_3 of Hdmg), 2.09 (m, 1H, Co–CH–), 1.24 (t, 3H, J=7.1 Hz, CH_3 of ethoxy), 1.17 (t, 3H, J=7.1 Hz, CH_3 of ethoxy). Found: C, 46.43; HD, 6.15; N, 12.90%. Calcd for $C_{21}H_{30.28}D_{1.72}CoN_5O_8$: C, 46.44; HD, 6.25; N, 12.89%.

[(*R*,*S*)-2,2-Dideuterio-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)(methyldiphenylphosphine)cobalt(III), [(*R*,*S*)-8h]. (Aniline)(chloro)bis(dimethylglyoximato)cobalt(III) (1.02 g) was suspended in methanol (50 cm^3) under argon atmosphere. To a reaction mixture was added a solution of sodium borohydride (0.46 g) in water (5 cm^3) and the mixture was stirred for 20 min. To the solution was added acetone (4 cm^3) and the mixture was stirred for 7 min. A solution of **7** (0.54 g, deuterium content 1.43) in methanol (10 cm^3) was added to the solution. After stirring for 8 h, the product was extracted by dichloromethane and washed with water. Dichloromethane solution was dried over anhydrous sodium sulfate and concentrated in vacuo to give dark red crystals; 0.586 g.

To a solution of crude crystals (0.586 g) in methanol (12 cm^3) were added ion-exchange resin (3.0 g) and methyldiphenylphosphine (0.294 cm^3). The reaction mixture was stirred for 2 h and the solution was filtered. After concentration, the crude crystals was purified by column chromatography on silica gel (benzene–methanol), and then were recrystallized from ethanol–hexane to give crystals of (*R*,*S*)-**8h** (0.18 g); IR (KBr) 2979, 1721, 1687, 1553, 1435, 1236, 1176, 1093, 752, and 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (m, 10H, aromatic), 3.98 (m, 2H, O–CH_2–), 3.89 (m, 1H, O–CHH–), 3.83 (m, 1H, O–CHH–), 2.19 (m, 1.57H, –Co–CH–$CH_{0.57}D_{1.43}$), 1.86 (d, 3H, J = 8.1 Hz, P–CH_3), 1.84 (d, 6H, J = 3.1 Hz, CH_3 of Hdmg), 1.82 (d, 6H, J = 3.2 Hz, CH_3 of Hdmg), 1.19 (t, 3H, J = 7.2 Hz, CH_3 of ethoxy), 1.14 (t, 3H, J = 7.1 Hz, CH_3 of ethoxy). Found: C, 52.43; H, 6.01; H, 8.64%. Calcd for $C_{29}H_{38.57}D_{1.43}CoN_4O_8P$: C, 52.46; H, 6.29; N, 8.44%.

[(*R*,*S*)-2,2-Dideuterio-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)(dimethylphenylphosphine)cobalt(III), [(*R*,*S*)-8i]. (Aniline)(chloro)bis(dimethylglyoximato)cobalt(III) (1.51 g) was suspended in methanol (150 cm^3) under argon atmosphere. To a reaction mixture was added a solution of sodium borohydride (0.57 g) in water (6 cm^3) and this was stirred for 10 min. To the solution was added acetone (5 cm^3) and the mixture was stirred for 7 min. A solution of **7** (1.87 g, deuterium content 1.92) in methanol (30 cm^3) was added to the solution. After stirring for 2 h, product was extracted by dichloromethane and washed with water. Dichloromethane solution was dried over anhydrous sodium sulfate and concentrated in vacuo to give dark red crystals; 2.17 g.

To a solution of crude crystals (2.17 g) in methanol (100 cm^3) were added ion-exchange resin (5.0 g) and water (5 cm^3). The reaction mixture was stirred for 15 min and was filtered to remove ion-exchange resin. To a solution was added dimethylphenylphosphine (0.52 cm^3). The reaction mixture was stirred for 80 min and then the solution was concentrated in vacuo. The crude crystals was purified by column chromatography on silica gel (benzene–methanol), and then were recrystallized from 2-propanol–hexane to give crystals of (*R*,*S*)-**8i** (0.57 g); IR (KBr) 2981, 1725, 1672, 1556, 1435, 1235, 1175, 1089, 909, 748, and 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (m, 1H, aromatic), 7.35 (m, 2H, aromatic), 7.11 (m, 2H, aromatic), 3.99 (m, 2H, O–CH_2–), 3.91 (m, 1H, O–CHH–), 3.81 (dq, 1H, J = 7.1 Hz and J = 10.5 Hz, O–CHH–), 2.27 (m, 0.08H, –Co–CH–$CH_{0.08}D_{1.92}$–), 2.08 (d, 1H, J = 6.8 Hz, Co–CH), 2.00 (d, 6H, J = 3.0 Hz, CH_3 of Hdmg), 1.96 (d, 6H, J = 3.0 Hz, CH_3 of Hdmg), 1.384 (d, 3H, J = 10.0 Hz, P–CH_3), 1.380 (d, 3H, J = 10.0 Hz, P–CH_3), 1.19 (t, 3H, J = 7.3 Hz, CH_3 of ethoxy), 1.15 (t, 3H, J = 7.2 Hz, CH_3 of ethoxy). Found: C, 47.54; H, 6.36; N, 9.11%. Calcd for $C_{24}H_{36.08}D_{1.92}CoN_4O_8P$: C, 47.85; H, 6.67; N, 9.30%.

[(*R*)-2,2-Dideuterio-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)[(*S*)-1-phenylethylamine]cobalt(III) and [(*S*)-2,2-Dideuterio-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)[(*R*)-1-phenylethylamine]cobalt(III), [(*R*)-8m and (*S*)-8l]. (Aniline)(chloro)bis(dimethylglyoximato)cobalt(III) (2.86 g) was suspended in methanol (300 cm^3) under argon atmosphere. To a reaction mixture was added a solution of sodium borohydride (1.03 g) in water (10 cm^3) and this was stirred for 10 min. To the solution was added acetone (4 cm^3) and the mixture was stirred for 5 min. A solution of **7** (2.61 g, deuterium content 1.92) in methanol (80 cm^3) was added to the solution. After stirring for 2 h, product was extracted by dichloromethane and washed with water. Dichloromethane solution was dried over anhydrous sodium sulfate and concentrated in vacuo to give dark red crystals; 5.39 g.

To a solution of crude crystals (5.39 g) in methanol (100 cm^3) were added ion-exchange resin (8.0 g) and water (8 cm^3). The reaction mixture was stirred for 80 min and was filtered to remove ion-exchange resin. To a solution was added (*S*)-1-phenylethylamine (1.19 cm^3). The reaction mixture was stirred for 30 min and the solution was concentrated in vacuo. The crude crystals was purified by column chromatography on silica gel (benzene–methanol) to give crystals of (*R*,*S*)-**8m** (1.67 g).

The crystals were dissolved in 2-propanol (22 cm^3) of slight warming. The solution was filtered, and hexane (44 cm^3) was added slowly to the solution. Dark red crystals (0.73 g) which deposited were collected by filtration. After two recrystallizations, optically pure crystals (0.55 g) of (*R*)-**8m** were obtained; $[\alpha]_{589}$ = +176.0°, $[\alpha]_{578}$ = +194.2°, and $[\alpha]_{546}$ = +236.4° (*c* 0.121, $CHCl_3$); IR (KBr) 3279, 3249, 2971, 2928, 1712, 1685, 1562, 1458, 1367, 1235, 1184, 766, and 706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (m, 3H, aromatic), 7.03 (m, 2H, aromatic), 3.98 (m, 2H, O–CH_2–), 3.91 (m, 1H, O–CHH–), 3.82 (dq, 1H, J = 7.1 Hz and J = 10.5 Hz, O–CHH–), 3.60 (m, 1H, N–CH–), 2.22 (s, 6H, CH_3 of Hdmg), 2.18 (s, 6H, CH_3 of Hdmg), 1.92 (s, 1H, Co–CH–), 1.62 (broad, 1H, NH), 1.42 (m, 1H, NH), 1.21 (d, 3H, J = 6.1 Hz, N–CH–CH_3), 1.19 (t, 3H, J = 7.1 Hz, CH_3 of ethoxy), 1.15 (t, 3H, J = 7.1 Hz, CH_3 of ethoxy). Found: C, 49.95; H, 7.25; N, 10.56%. Calcd for $C_{24}H_{36.08}D_{1.92}CoN_5O_8 \cdot C_3H_8O$: C, 50.24; H, 7.47; N, 10.85%. Crude (*S*)-**8m** was obtained by concentration of the mother liquor

at the first recrystallization. (*S*)-**8l** was prepared from the crude (*S*)-**8m** by a method similar to that for the preparation of (*R*)-**1c**, except for using (*R*)-1-phenylethylamine as the axial ligand. The crude crystals was purified by column chromatography on silica gel (benzene–methanol) and recrystallized from 2-propanol–hexane. After two recrystallizations, optically pure crystals of (*S*)-**8l** were obtained; $[\alpha]_{589} = -173.4°$, $[\alpha]_{578} = -191.6°$, and $[\alpha]_{546} = -232.2°$ (*c* 0.143, $CHCl_3$); IR (KBr) 3279, 3249, 2971, 2928, 1712, 1685, 1565, 1457, 1367, 1235, 1184, 766, and 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.29$ (m, 3H, aromatic), 7.03 (m, 2H, aromatic), 3.98 (m, 2H, O–CH_2–), 3.91 (m, 1H, O–C<u>H</u>H–), 3.82 (dq, 1H, J=7.1 Hz and $J = 10.8$ Hz, O–CH<u>H</u>–), 3.60 (tq, 1H, $J = 6.4$ and $J = 6.4$ Hz, N–CH–), 2.22 (s, 6H, CH_3 of Hdmg), 2.18 (s, 6H, CH_3 of Hdmg), 1.92 (s, 1H, Co–CH–), 1.62 (broad, 1H, NH), 1.43 (m, 1H, NH), 1.21 (d, 3H, J=6.2 Hz, N–CH–C<u>H</u>$_3$), 1.19 (t, 3H, J=7.2 Hz, CH_3 of ethoxy), 1.15 (t, 3H, J=7.1 Hz, CH_3 of ethoxy). Found: C, 50.21; H, 7.15; N, 10.63%. Calcd for $C_{24}H_{36.08}D_{1.92}CoN_5O_8 \cdot 0.95(C_3H_8O)$: C, 50.19; H, 7.45; N, 10.90%.

[(*R*)-2,2-Dideuterio-1,2-bis(ethoxycarbonyl)ethyl]bis(dimethylglyoximato)(dimethylphenylphosphine)cobalt(III), [(*R*)-8i]. (*R*)-**8i** was prepared from (*R*)-**8m** (0.82 g, $[\alpha]_{589} = +176.0°$) by a method similar to that for the preparation of (*R*)-**1h**, except for using dimethylphenylphosphine (0.27 cm^3) as the axial ligand and ethanol as the reaction solvent. The crude product was purified by column chromatography on silica gel (benzene–methanol) and recrystallized from 2-propanol–hexane to give crystals of (*R*)-**8i** (0.58 g); $[\alpha]_{589} = +181.8°$, $[\alpha]_{578} = +197.7°$, and $[\alpha]_{546} = +266.7°$ (*c* 0.132, $CHCl_3$); IR (KBr) 2980, 1728, 1683, 1554, 1436, 1235, 1180, 1091, 747, and 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 7.42$ (m, 1H, aromatic), 7.35 (m, 2H, aromatic), 7.11 (m, 2H, aromatic), 3.99 (m, 2H, O–CH_2–), 3.91 (m, 1H, O–C<u>H</u>H–), 3.81 (dq, 1H, $J = 7.2$ Hz and $J = 10.5$ Hz, O–CH<u>H</u>–), 2.27 (m, 0.09H, –Co–CH–C<u>H</u>$_{0.09}D_{1.91}$–), 2.08 (d, 1H, $J = 6.9$ Hz, Co–CH), 2.00 (d, 6H, $J = 2.9$ Hz, CH_3 of Hdmg), 1.96 (d, 6H, $J = 3.2$ Hz, CH_3 of Hdmg), 1.384 (d, 3H, $J = 10.2$ Hz, P–CH_3), 1.380 (d, 3H, $J = 10.2$ Hz, P–CH_3), 1.19 (t, 3H, $J = 7.2$ Hz, CH_3 of ethoxy), 1.15 (t, 3H, $J = 7.2$ Hz, CH_3 of ethoxy). Found: C, 47.68: H, 6.41; N, 9.16%. Calcd for $C_{24}H_{36.08}D_{1.92}CoN_4O_8P$: C, 47.85; H, 6.67; N, 9.30%.

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