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Preparation and Reaction of Optically Active Organotransition Metal Complexes. II.[1] Preparation and Photoracemization of Optically Active (1-Cyanoethyl)cobaloxime Complexes Coordinated with Various Axial Ligands

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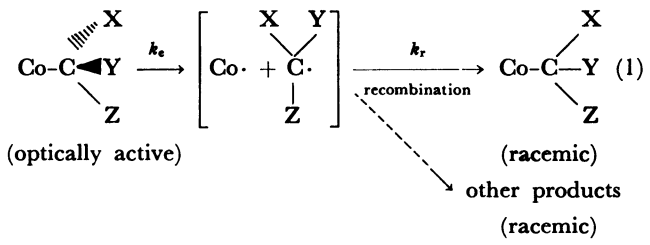
Optically active (1-cyanoethyl)cobaloxime complexes coordinated with various pyridines, phosphines and amines etc. as axial ligands were prepared and their photoracemization rates were measured in a solution state. It was found that the steric factor, rather than the electronic, of the axial ligand controlled, predominantly, the rate of Co–C bond homolysis in these alkylcobaloximes.

Syntheses and reactions of chiral alkyl transition metal complexes can provide a clearer description of the elementary process of catalytic reactions involving alkyl transition metal intermediates. We have shown various useful properties of optically active alkyl cobalt complexes for an elucidation of solution-state and solid-state reactions of the Co–C bond formation and cleavage.[1-4,7]

In relation to coenzyme B_{12} chemistry, extensive investigations on the reactions of alkyl cobalt complexes, including thermal and photochemical decompositions, have been made by UV-VIS and NMR spectroscopies using achiral complexes. However, spectroscopic methods involving achiral complexes include, in general, possibilities for underestimating or overestimating the rate of Co–C bond cleavage unless an elaborated kinetic treatment is made.[4] A chiroptical measurement using optically active alkyl metal complexes provides a more simple, precise evaluation of the forward rate, since alkyl radicals formed by bond homolysis are "planar or rapidly inverting pyramid".[5] Thus, recombinations of these species with Co(II) and all other subsequent reactions such as radical coupling, beta-elimination etc., will give substantially racemic or achiral products (Eqs. 1 and 2).[4]



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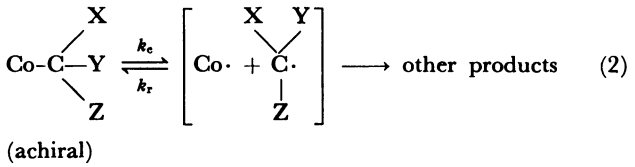


(2)

Consequently, Eqs. 3 and 4 were established for the Co–C bond homolysis of the optically active alkyl complexes:

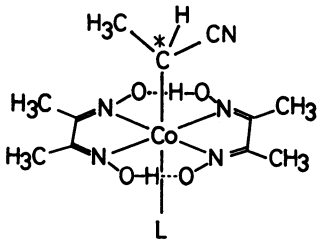
$$-d[R]/dt = k_c[R] \quad (3)$$

and

$$-d\alpha/dt = k_c\alpha. \quad (4)$$

Here, k_c is the rate constant for the Co–C bond cleavage, k_r the rate constant for the recombination, [R] the concentration of the reactant and α the optical rotation.

We wish to describe here the preparation of optically active (1-cyanoethyl)bis(dimethylglyoximato)-cobalt(III) complexes which have chirality at the carbon bound directly to the cobalt atom (Fig. 1) as well as the influence of the axial ligand on the rate of the photochemical Co–C bond homolysis.



L: pyridines
phosphines
amines
etc.

Fig. 1. Chiral (1-cyanoethyl)cobaloximes coordinated with various axial ligands.

Results and Discussion

Preparation of Optically Active (1-Cyanoethyl)-cobaloximes. Optically active (1-cyanoethyl)cobaloximes which are coordinated with various axial ligands were prepared according to the method described in a previous paper.[1] The newly prepared

Table 1. ^{1}H NMR Chemical Shifts of Chiral (1-Cyanoethyl)cobaloximes Coordinated with Various Axial Ligands

Cobaloxime	Axial ligand	^{1}H NMR chemical shift δ/ppm[a]		
		$\underline{CH_3}CHCo$	$CH_3\underline{CH}Co$	CH_3(DMG)
2	4-Cyanopyridine	0.545		2.221
	(4-CN-Py)	(d, 3H)	nc[b]	2.247 (12H)
3	4-Chloropyridine	0.550		2.233
	(4-Cl-Py)	(d, 3H)	nc	2.259 (12H)
4	4-Methylpyridine	0.564		2.22
	(4-Me-Py)	(d, 3H)	nc	2.25 (12H)
5	Triethylphosphine	0.663	2.089	2.286, 2.301
	(PEt_3)	(q, 3H)	(m, 1H)	2.315 (12H)
6	Tributylphosphine	0.656	2.043	2.271, 2.286
	($P(n\text{-}Bu)_3$)	(q, 3H)	(m, 1H)	2.301 (12H)
7	Diethyl(phenyl)phosphine	0.645	2.1	2.002, 2.017
	(PEt_2Ph)	(q, 3H)	(m, 1H)	(12H)
8	Diphenylmethylphosphine	0.654	2.314	1.830, 1.842
	($PMePh_2$)	(t, 3H)	(m, 1H)	1.864, 1.880 (12H)
9	Diphenylethylphosphine	0.617	2.28	1.893, 1.908
	($PEtPh_2$)	(q, 3H)	(m, 1H)	1.915, 1.930 (12H)
10	Triphenylphosphine	0.539	2.40	1.875, 1.890
	(PPh_3)	(t, 3H)	(m, 1H)	1.912, 1.956 (12H)
11	Tris(*p*-chlorophenyl)phosphine	0.526	2.30	1.917, 1.932
	($P(p\text{-}ClC_6H_4)_3$)	(t, 3H)	(m, 1H)	1.950, 1.964 (12H)
12	Triethyl phosphite	0.688	2.14	2.258, 2.277
	($P(OEt)_3$)	(q, 3H)	(m, 1H)	2.296 (12H)
13	Piperidine	0.459		2.373, 2.386
		(d, 3H)	nc	(12H)
14	Pyrrolidine	0.505		2.345, 2.355
		(d, 3H)	nc	(12H)
15	H_2O	0.205		2.246, 2.27
		(3H)	nc	2.315, 2.325 (12H)

a) Solvent: $CDCl_3$; Internal standard: TMS. b) nc: The chemical shift is not clear because of overlapping with the signals of methyl protons of dimethylglyoximes.

complexes were characterized by elemental analyses as well as IR and NMR spectra. The ^{1}H NMR spectra and main bands of the IR spectra are shown in Tables 1 and 2. Their configurations and specific rotations are given in Table 3.

Photoracemization Reaction for (4-Substituted Pyridine)-Coordinated Cobaloximes. The optical rotations of a methanol solution of the optically active (1-cyanoethyl)cobaloxime complexes coordinated with various 4-substituted pyridines gradually decreased owing to Co–C bond cleavage upon visible-light irradiation. ln α vs. time were approximately linear. The k_c values obtained from the slopes of these first-order rate plots decreased only slightly with increasing pK_a value of the axial ligand (Table 4). This trend coincides with that in a thermal reaction,[4] and shows that the electron-donation ability of 4-substituted pyridine ligand influences, to some degree, the rate of the Co–C bond photolysis. However, the effect is very small in this series.

Photoracemization Reaction of Phosphine-Coordinated Cobaloximes. A photoracemization reaction of the optically active (1-cyanoethyl)cobaloxime complexes coordinated with various phosphines was carried out under the same conditions as that of (4-substituted pyridine)-coordinated complexes, except for the use of chloroform as the solvent.

The ^{1}H NMR spectrum of the PPh_3-coordinated complex solution suggested that the equilibrium accompanying an axial ligand dissociation existed in this system (Eq. 5).

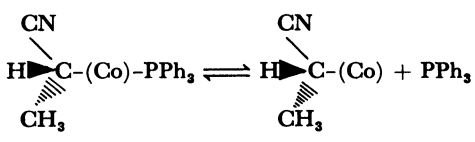


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Table 2. Main IR Absorption Data of (1-Cyanoethyl)cobaloximes

Cobaloxime	IR absorption data/cm^{-1} a)			
	Cyanoethyl ν(C=N)	Glyoxime ν(C=N)	Glyoxime ν(O-H)	Others
2	2202	1555	3440	pyridine ν(C=C): 1606
3	2198	1555	3440	pyridine ν(C=C): 1592
4	2205	1550	3410	pyridine ν(C=C): 1620
5	2189	1580	3440	
6	2194	1553	3440	
7	2193	1575	3450	
8	2197	1540	3440	
9	2200	1580	3450	
10	2195	1555	3440, 3530	

a) KBr disk.

Table 3. Configurations and Specific Optical Rotations of Chiral (1-Cyanoethyl)cobaloximes Coordinated with Various Axial Ligands

Cobaloxime	Configuration	$[\alpha]^{RT}_{578}$	
		CH_3OH soln	$CHCl_3$ soln
2	*R*	+61.8	
3	*R*	+53.4	
4	*R*	+48.6	
5	*S*	−44.8	−53.3
6	*R*	+37.6	+46.6
7	*R*	+52.3	+54.0
8	*R*	+44.1	+24.1
9	*R*	+46.4	+50.0
10	*R*	+52.5	+73.1
11	*R*		+57.0
12	*R*	+47.8	+57.6
13	*R*	+50.5	+61.1
14	*R*		+70.2

In order to obtain the rate for the "ligand-on" form, free phosphine was added to the cobaloxime solution and photoracemization experiments were carried out. The value of k_c increased with increasing added free PPh_3 and reached a maximum in the case of the PPh_3 complex **10** (Fig. 2). This phenomenon shows that the rate of racemization is faster in "ligand-on" form than in "ligand-off" form, because addition of PPh_3 will promote the formation of "ligand-on" complex. A similar phenomenon was also observed in the P(*p*-$ClC_6H_4)_3$-coordinated complex **11** (Fig. 2). On the contrary, the addition of free phosphine did not substantially affect the photoracemization rate in the case of complexes coordinated with PEt_3, P(*n*-Bu)$_3$, $PMePh_2$, and $PEtPh_2$ (**5**, **6**, **8**, and **9**) (Fig. 3). These

Table 4. k_c Values for Photoracemization of (4-Substituted Pyridine)-Coordinated Cobaloximes

Cobaloxime	**2**	**3**	**4**
$k_c \times 10^5/s^{-1}$	6.1	5.7	5.1
Axial ligand	4-CN-Py	4-Cl-Py	4-Me-Py
pK_a(at 25 °C)a)	1.86	3.83	6.03

a) A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, **1964**, 3591.

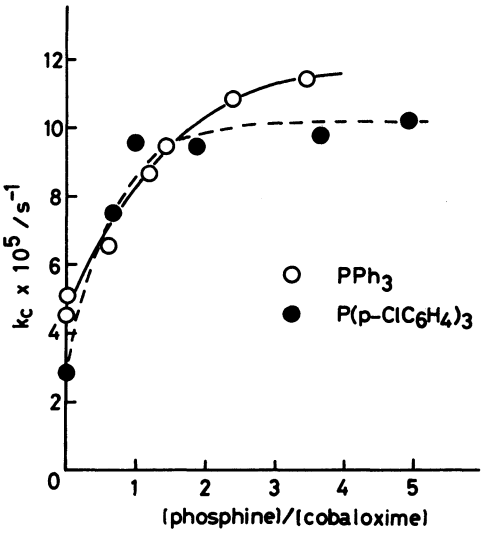

Fig. 2. Increase of k_c with addition of free phosphine to the PPh_3 and P(*p*-$ClC_6H_4)_3$-coordinated cobaloximes.

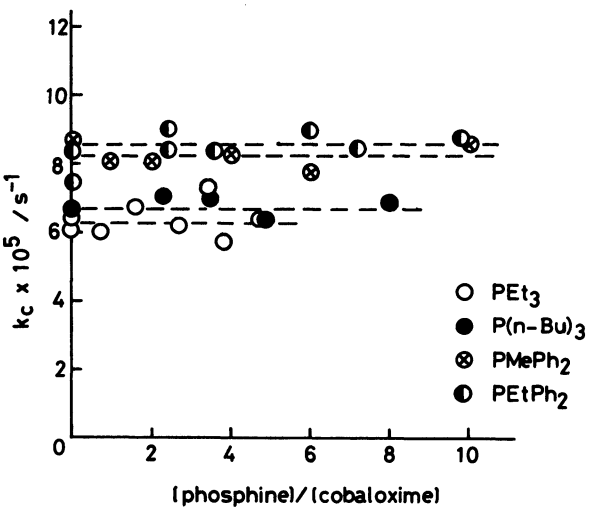

Fig. 3. Relationship between k_c and the mole ratio of added free phosphine to the cobaloximes coordinated with PEt_3, P(*n*-Bu)$_3$, $PMePh_2$, and $PEtPh_2$.

results show that the degree of ligand dissociation is negligibly small in the latter complexes, even without the addition of free phosphine since these phosphines have both stronger basicities and smaller steric

Table 5. $k_{c,max}$ Values for Photoracemization of Phosphine-Coordinated Cobaloximes

Cobaloxime	5	6	8	9	11	10
$k_{c,max} \times 10^5/s^{-1}$	6.2	6.7	8.3	8.6	10	11
Axial ligand	PEt_3	$P(n\text{-}Bu)_3$	$PMePh_2$	$PEtPh_2$	$P(p\text{-}ClC_6H_4)_3$	PPh_3
Cone angle/°	132[a]	132[a]	136[a]	140[a]	145[b]	145[a]
pK_a[c]	8.65	8.43	4.65	4.91	2.86	2.73

a) Ref. 6. b) Estimated value. c) Ref. 9.

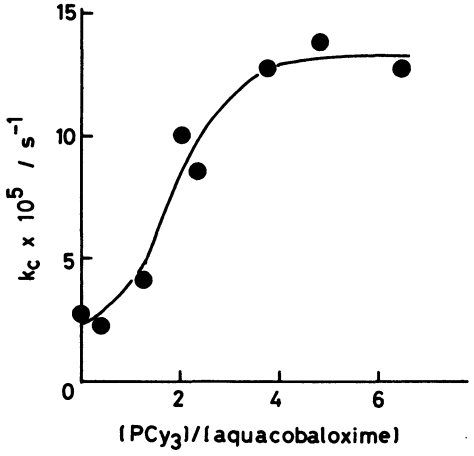

Fig. 4. Increase of k_c with addition of free PCy_3 to the aquacobaloxime.

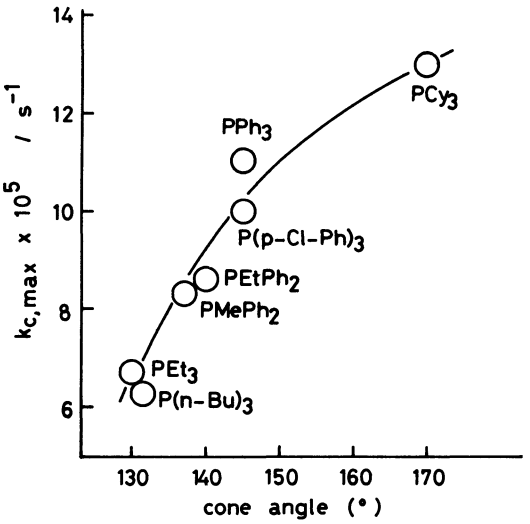

Fig. 5. Relationship between $k_{c,max}$ and the cone angle for phosphine-coordinated cobaloximes.

hindrances than PPh_3 and $P(p\text{-}ClC_6H_4)_3$. This can be seen from Table 5, which shows the large pK_a values of the conjugated acids and the small Tolman's cone angles[6] on these phosphines. On the other hand, the Co–P bonds in the former complexes (**10** and **11**) are weakened owing to the weak basicity and steric bulkiness of the triarylphosphines; therefore, ligand dissociation will be promoted.

Steric Influence of the Axial Phosphine on the Co-C Bond Photocleavage. Table 5 gives $k_{c,max}$, the maximum value of photoracemization rate constant obtained for the "ligand-on" form whose formation was promoted by the addition of free phosphine. The value of $k_{c,max}$ increased in the following order: $PEt_3 \lesssim P(n\text{-}Bu)_3 < PMePh_2 \lesssim PEtPh_2 < P(p\text{-}ClC_6H_4)_3 < PPh_3$. Either the electronic or steric factor of the phosphine ligand is responsible for this order. As can be seen from Table 5, the value of $k_{c,max}$ increased with an increase in the cone angle as well as a decrease in the pK_a value. Therefore, it cannot be determined whether the electronic or the steric effect acts as a dominant factor in influencing the value of $k_{c,max}$.

Tricyclohexylphosphine (PCy_3) has maximum values with respect to both the cone angle (170° [6]) and pK_a (9.70[9]), compared with preceding phosphines. Therefore, if the electronic factor is dominant in the case of the PCy_3-coordinated complex, the photoracemization rate will be minimum. On the contrary, if the steric factor is dominant, the maximum photoracemization rate will be obtained. Unfortunately, a PCy_3-coordinated complex could not be isolated, perhaps owing to its instability. However, the PCy_3-coordinated complex was formed in situ by the addition of PCy_3 to a chloroform solution of the aqua-coordinated complex **15**. This was confirmed by the ^1H NMR spectrum. The photoracemization experiment on this solution revealed that $k_{c,max}$ is $13 \times 10^{-5}\ s^{-1}$ (Fig. 4); this is the largest value obtained for all the cobaloxime complexes coordinated with pyridines and phosphines.

Consequently, as revealed by Fig. 5, these experimental data clearly demonstrate that the cone angle of a phosphine ligand is a dominant factor influencing the value of $k_{c,max}$ (the rate of Co–C bond photocleavage).††

In Table 6, the structural parameters around the Co atom based on the X-ray crystallographic analyses[7] are summarized for the complexes coordinated with $P(n\text{-}Bu)_3$, $PEtPh_2$, and PPh_3 (**6**, **9**, and **10**). The values of θ (the acute dihedral angle between the planes of the two glyoximato groups), d (the displacement of the Co

†† Recently Halpern et al. have reported a similar result in thermal reaction for the alkylcobaloximes.[8]

Table 6. Comparisons of Crystallographic Data[a] for **6**, **9**, and **10**

Complex	**6**	**9**	**10**
Axial ligand	$P(n\text{-}Bu)_3$	$PEtPh_2$	PPh_3
θ/°[b]	1.5	4.8	9.4
d/Å[c]	0.026	0.048	0.078
Co-P/Å	2.316	2.370	2.410
Co-C/Å	2.089	2.098	2.08

a) Ref. 7. b) The acute dihedral angle between the planes of the two glyoximato groups. The bending is toward the 1-cyanoethyl group. c) The displacement of the Co atom toward the P atom from the mean plane composed of four nitrogen atoms in the equatorial ligand.

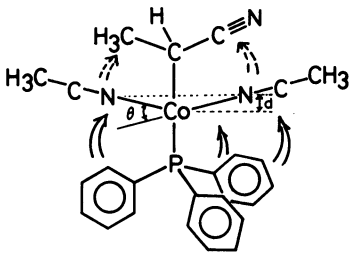

Fig. 6. Repulsive interaction in the PPh_3-coordinated cobaloxime.

atom toward the P atom from the mean plane composed of four nitrogen atoms in the equatorial ligand), and the Co–P distances increased with an increase in the cone angle of the phosphine ligand, probably in order to avoid the shortest contacts between the substituents of the phosphine ligand and the cobaloxime moiety. On the other hand, the Co–C bond length varied little. Therefore, with increasing steric bulkiness of the phosphine ligand, the 1-cyanoethyl group and the cobaloxime moiety come so close together that their mutual repulsion increases and the Co–C bond becomes strongly strained. This situation is depicted in Fig. 6 using, as an example, the PPh_3-coordinated cobaloxime.

In a solution state, the steric effect of the phosphine ligand on the Co–C bond may operate in a similar manner as that of the above description regarding a crystalline state. Thus, it is concluded that the acceleration of the photocleavage of the Co–C bond is responsible for the increase of the strain on this bond, *arising from an increase in the steric bulkiness of the* phosphine ligand. The electronic effect of the axial ligand on the Co–C bond photocleavage is found to be much smaller than the steric effect and, therefore, to be masked by the steric factor within this series.

Experimental

Apparatus. The IR spectra were recorded on a JASCO A-3 spectrometer using KBr disks. The ^1H NMR spectra were obtained on a JEOL FX-200 spectrophotometer, using TMS as the internal standard.

The optical rotations were measured on a Perkin-Elmer 241 polarimeter.

Photoracemization. The sample for photoracemization was dissolved under dim light at ca. 2×10^{-3} mol dm^{-3} in chloroform which was freed from dissolved oxygen by bubbling with a stream of argon for about 30 min. The sample solution was placed in a glass (Pyrex) cell for a measurement of the optical rotation; photoreactions were carried out under the conditions of visible-light irradiation using four 40-W fluorecent lamps "white" (Matsushita Elec. Ind. Co.) at 25±2 °C. The cell was placed at the distance of ca. 3.0 m from the light source; at that distance the radiation intensity was 0.008 mW cm^{-2}. The optical rotations (α), which gradually decreased upon irradiation, were measured at regular time intervals. In the dark conditions, the optical rotation didn't vary while standing overnight.

Materials. All chemicals were reagent grade commercial materials and used without further purification.

All chiral (1-cyanoethyl)cobaloximes coordinated with various pyridines, phosphines, amines etc. were prepared by a ligand exchange reaction for [(*R*) or (*S*)-1-cyanoethyl]bis-(dimethylglyoximato)[(*S*)-1-phenylethylamine]cobalt(III) (**1**-(*R*) or **1**(*S*)) prepared according to a preceding paper.[1] All the preparative operations were performed in the dark.

[(*R*)-1-Cyanoethyl](4-cyanopyridine)bis(dimethylglyoximato)cobalt(III) (2): To a methanol solution (10 cm^3) of 0.50 g of **1**(*R*) were added 0.8 cm^3 of 2 mol dm^{-3} hydrochloric acid and 0.17 g of 4-cyanopyridine. After standing for 4 h at 30 °C, water (10 cm^3) was added to the reaction mixture; the solution was then cooled overnight. Deposited dark brown crystals were collected by filtration; 0.44 g (91%). The crude product was recrystallized several times from acetone–water to give plates. Found: C, 45.34; H, 5.10; N, 22.14%. Calcd for $C_{17}H_{22}N_7O_4Co$: C, 45.64; H, 4.96; N, 21.92%.

(4-Chloropyridine)[(*R*)-1-cyanoethyl]bis(dimethylglyoximato)cobalt(III) (3) and [(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)(4-methylpyridine)cobalt(III) (4): These were similarly prepared for **2** by using 4-chloropyridine and 4-methylpyridine, respectively, in place of 4-cyanopyridine. For **3**: Crude yield, 71%. Brown needles (acetone–water). Found: C, 42.14; H, 5.08, N, 18.71%. Calcd for $C_{16}H_{22}N_6O_4ClCo$: C, 42.07; H, 4.85; N, 18.40%. For **4**: Crude yield, 74%. Brown needles (acetone–water). Found: C, 46.37; H, 5.82; N, 19.34%. Calcd for $C_{17}H_{25}N_6O_4Co$: C, 46.79; H, 5.77; N, 19.26%.

[(*S*)-1-Cyanoethyl]bis(dimethylglyoximato)(triethylphosphine)cobalt(III) (5): To a acetone (30 cm^3) solution of a 1.5 g of **1**(*S*) were added 1.62 cm^3 of 2 mol dm^{-3} hydrochloric acid and 0.72 cm^3 of PEt_3. After having been stirred for 20 h under a nitrogen atmosphere at room temperature, a 10 cm^3 *of water was added to the solution. The resulting solution* was concentrated under reduced pressure. Deposited orange crystals were collected by filtration; 1.25 g (84%). The crude product was recrystallized from methanol–water to give columns. Found: C, 44.09; H, 7.53; N, 15.07%. Calcd for $C_{17}H_{33}N_5O_4CoP$: C, 44.25; H, 7.21; N, 15.18%.

[(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)(triphenylphosphine)cobalt(III) (10): A 0.50 g of **1**(*R*) was dissolved in methanol (20 cm^3) and then 0.42 g of PPh_3 and 0.54 cm^3 of

2 mol dm^{-3} hydrochloric acid were added. The reaction mixture was stirred overnight under an argon atmosphere at room temperature. Then, 10 cm^3 of water was added and the resulting solution was cooled. Deposited dark brown crystals were collected by filtration; 0.57 g (87%). The crude product was recrystallized several times from methanol–water to give flakes. Found: C, 56.66; H, 5.79; N, 11.26%. Calcd for $C_{29}H_{33}N_4O_5CoP$: C, 57.52; H, 5.49; N, 11.57%.

[(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)(tributylphosphine)cobalt(III) (6) and [(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)(diphenylmethylphosphine)cobalt(III) (8): These complexes were similarly prepared for **10** by using P(*n*-Bu)$_3$ and PMePh$_2$ respectively in place of PPh$_3$. For **6**: Crude yield, 56%. Orange columns (methanol–water). Found: C, 50.85; H, 8.85; N, 12.85%. Calcd for $C_{23}H_{45}N_5O_4CoP$: C, 50.64; H, 8.31; N, 12.84%. For **8**: Crude yield, 68%. Brown plates (acetone–water). Found: C, 52.97; H, 5.82; N, 12.97%. Calcd for $C_{24}H_{31}N_5O_4CoP$: C, 53.04; H, 5.75; N, 12.89%.

[(*R*)-1-Cyanoethyl][diethyl(phenyl)phosphine]bis(dimethylglyoximato)cobalt(III) (7): 1.0 g of **1**(*R*) was dissolved in methanol (30 cm^3) and then 0.6 cm^3 of PEt$_2$Ph and 1.08 cm^3 of 2 mol dm^{-3} hydrochloric acid were added. The solution was stirred for 46 h under a nitrogen atmosphere at room temperature and then concentrated under reduced pressure. 10 cm^3 of acetone was added to the residual syrup. After the deposited white needles were removed by filtration, water was added to the filtrate and the resulting solution was cooled. Deposited brown crystals were collected by filtration; 0.70 g (64%). The crude product was recrystallized several times from acetone–water. Found: C, 49.34; H, 6.72; N, 13.67%. Calcd for $C_{21}H_{33}N_5O_4CoP$: C, 49.51; H, 6.53; N, 13.75%.

[(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)(diphenylethylphosphine)cobalt(III) (9): 1.0 g of **1**(*R*) was dissolved in acetone (20 cm^3) and then 0.77 cm^3 of PEtPh$_2$ and 1.08 cm^3 of 2 mol dm^{-3} hydrochloric acid were added. The solution was stirred for 23 h under a nitrogen atmosphere at room temperature and then dried under reduced pressure. To the acetone solution of the residue was added water. Deposited brown crystals were collected by filtration; 0.76 g (63%). The crude product was recrystallized twice from acetone–water to give plates. Found: C, 53.74; H, 6.09; N, 12.55%. Calcd for $C_{25}H_{33}N_5O_4CoP$: C, 53.86; H, 5.97; N, 12.56%.

Aqua[(*R*)-1-cyanoethyl]bis(dimethylglyoximato)cobalt(III) (15): To a methanol (20 cm^3) solution of 4.0 g of **1**(*R*) was added 8.6 cm^3 of 2 mol dm^{-3} hydrochloric acid and the solution was stirred for 16 h under a nitrogen atmosphere at room temperature. A 17 cm^3 of 6 mol dm^{-3} hydrochloric acid was added. The resulting aqua complex was extracted with three 60 cm^3 portions of dichloromethane. The extract was neutralized by adding solid potassium carbonate. After standing overnight, the dichloromethane was dried under reduced pressure to give a crystalline mass of **15**; 2.2 g (87%). This complex was satisfactorily used for further syntheses of **11**, **13**, and **14**. The structure of **15** was confirmed by the ^{1}H NMR spectrum.

[(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)[tris(*p*-chlorophenyl)phosphine]cobalt(III) (11): A 0.65 g of **15** was dissolved in dichloromethane and 0.70 g of P(*p*-ClC$_6$H$_4$)$_3$ was added. The solution was stirred for 7 h under a nitrogen atmosphere at room temperature and then the solvent was removed under reduced pressure. To the resulting syrup acetone (20 cm^3) and a small amount of water were added. After the white precipitate had been removed by filtration, the filtrate was cooled. The deposited brown crystals were collected by filtration. The crude product was recrystallized from acetone–water. The structure of **11** was confirmed by the ^{1}H NMR spectrum. The pattern of spectrum was analogous to that of **10**.

[(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)(piperidine)cobalt(III) (13): A 0.80 g of **15** was dissolved in methanol (5 cm^3) and 0.38 cm^3 of piperidine was added. The solution was allowed to stand overnight at room temperature. A 5 cm^3 of water was added and the resulting solution was cooled overnight to give dark brown flakes; 0.55 g (58%). The crude product was recrystallized several times from methanol–water. The structure of **13** was confirmed by the ^{1}H NMR spectrum.

[(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)(pyrrolidine)cobalt(III) (14): This complex was similarly prepared for **13** by using pyrrolidine in place of piperidine. Crude yield, 0.25 g (45%). Dark brown plates (methanol–water). The structure of **14** was confirmed by the ^{1}H NMR spectrum.

[(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)(triethylphosphite)cobalt(III) (12): A 0.35 g of **2** was dissolved in dichloromethane (3 cm^3) and 0.15 cm^3 of P(OEt)$_3$ was added. After having been stood for 1 h at room temperature, the solution was dried under reduced pressure. To the residual syrup were added 0.5 cm^3 of methanol and successively 2 cm^3 of water and then the solution was cooled overnight to give yellow leaflets; 0.12 g (30%). The crude product was recrystallized from methanol–water. The structure of **12** was confirmed by the ^{1}H NMR spectrum.

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