Synthesis of Chiral Square Planar Cobalt(III) Complexes and Catalytic Asymmetric Epoxidations with these Complexes

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The chiral square planar cobalt(III) complexes, Na[Co(η⁴-(*R*)-HMBA-DMP)] (**2**), {H_4(*R*)-HMBA-DMP = (−)2,4-bis[(*R*)-2-hydroxy-2-methylbutyramido]-2,4-dimethylpentan-3-one} and complexes with two or four chiral centres, Co{[OC(R)R'C(O)N]$_2$L}[(**3**; R = Et, R' = Ph, L = CMe_2COCMe_2); (**4**; R = Et, R' = Me, L = *o*-phenylene); (**5**; R = Et, R' = Me, L = $CH(Me)CH_2CHMe$); (**6**; R = Et, R' = Ph, L = $CH(Me)CH_2CHMe$)] have been prepared and characterized by ^{1}H NMR spectroscopy, solution magnetic properties, and X-ray crystallography. Asymmetric epoxidations of styrenes with these chiral cobalt(III) complexes and iodosylbenzene have been investigated. Various substituted styrenes were epoxidized with chemical yields of (25–86%) and enantiomeric excesses between 0 and 17%.

We have reported that the square planar cobalt(III) complexes of oxidation-resistant polyanionic (PAC) ligands catalysed the epoxidation of styrene using iodosylbenzene as a mono-oxygen donor.[1] In these cytochrome-450-like oxygen-transfer reactions, the cobalt(V)–oxo complex of these PAC ligands has been tentatively proposed as an active species. Of five complexes used for the catalysis of epoxidation, complex (**1**) was found to be most effective as a catalyst for epoxidation of styrene.[1]

Asymmetric epoxidations of simple alkenes with optically active complexes have been investigated using an optically active molybdenum(VI) peroxo complex,[2a] 'basket-handle'[2b] and 'picket' iron–porphyrin complexes,[2c] chiral diphosphine-modified platinum(II) complexes,[2d] and chiral dioxirane intermediates.[2e] The above reactions with simple alkenes did not seem to be so successful as reactions with activated alkenes such as allyl alcohols[3] or conjugated ketones.[4] Such reactions involving enzyme systems[5] are rare cases in which the asymmetric epoxidation of simple alkenes with a high degree of stereoselectivity has been achieved. In the present work, we attempted the asymmetric epoxidation of various styrenes with optically active square planar cobalt(III) complexes containing amido-*N*- and alkoxido-donors similar to those of complex (**1**), namely, (**2**)–(**6b**). It was reasoned that chiral centres of the ligands held close to the cobalt reaction centre might assist chiral recognition of substrates, such as simple alkenes.

Synthesis and Characterization of Chiral Square Planar Cobalt(III) *Complexes.*—The optically active square planar cobalt(III) complexes which we have synthesized and used as catalysts for epoxidations of styrenes are depicted below.

As shown, complexes (**2**), (**4**), and (**3**) have two chiral centres at alkyl-(aryl-)oxy groups, and complexes (**5a**, **5b**) and (**6a**, **6b**) have four chiral centres at both amide and alkyl-(aryl-)oxy groups. All complexes were prepared according to the methods described in the literature[6,7] using the corresponding optically active ligand and $Co(OAc)_2$ (1 equiv.) with an excess of NaOH in ethanol under air. Optically active ligand complements, [*R*-(−)-2-hydroxy-2-methylbutyric acid,[8] (*R*)-(−)-2-hydroxy-2-phenylbutyric acid,[9] and (*R*,*R*)-(−)- and (S,S) − (+)-pentane-2,4-diamine[12]] were synthesized by known methods.

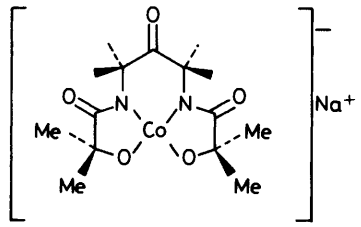
^{1}H NMR data for the cobalt(III) complexes synthesized are summarized in Table 1.

The ^{1}H resonance spectra of these complexes extend over a range of *ca.* −25 ppm for (**4**), to 125 ppm for (**6b**). These unusually large variations in the shielding of the hydrogen nuclei indicate that these cobalt(III) complexes are paramagnetic, like complex (**1**).[7] The ^{1}H NMR spectra of complex (**2**), and a complex in which the alkoxy groups of the ligand component were prepared from racemic 2-hydroxy-2-methylbutyric acid, are shown in Figure 1(*a*) and (*b*), respectively.

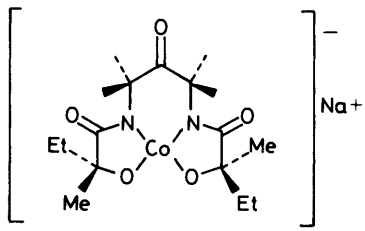
The assignment of the two methyl signals of complex (**2**) has tentatively been made on the basis of a comparison with ^{1}H NMR spectra of complex (**1**)[7] (Table 1). The resonances due to the methylene and methyl protons of the ethyl group were assigned on the basis of the number of protons. In the spectra for the non-chiral counterpart of (**2**), [Figure 1(*b*)], the resonances due to the two methyl-group and the methylene-group protons in the alkoxy group and the methyl protons in the amide group appear as two singlets and doublets, respectively. These ^{1}H NMR spectra indicate that complex (**2**) was made from a ligand of single configuration. The optical purity of the other complexes was confirmed by comparison of each ^{1}HNR spectrum with that of the corresponding racemic complex in the same manner as complex (**2**). The assignment of aromatic protons, H_a and H_b in complex (**4**) was made on the basis of comparison with ^{1}H NMR spectra shown in the literature.[6] The tentative assignment of aromatic protons in complexes (**3**), (**6a**), and (**6b**) and the bridging propylene protons in (**5a**), (**5b**), (**6a**), and (**6b**) were made by reference to the ^{1}H NMR data previously observed for paramagnetic osmium(IV) complexes.[11]

Magnetic Susceptibility Measurements.—Magnetic moments (294 K) of these complexes were measured in D_2O or CD_3OD according to the method in the literature,[12] and are listed in the experimental section. The values are in the range 3.7–4.0 μ_{eff} except for complex (**4**) (μ_{eff} = 5.1 μ_B),* suggesting that in these solvents all complexes except for (**4**) are in a spin triplet state (S = 1), while (**4**) is in a high-spin quintet (S = 2) state.

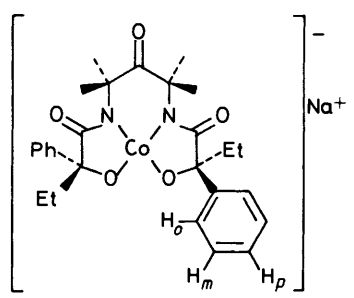
* $\mu_B = 9.274 \times 10^{-24}$ J T^{-1}.



(1)



(2)



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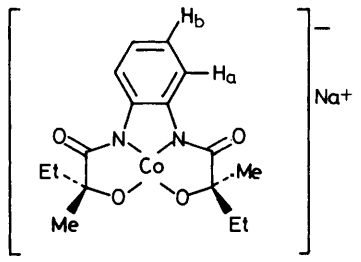

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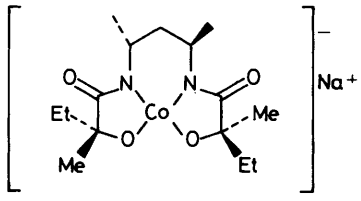
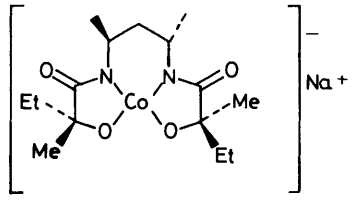
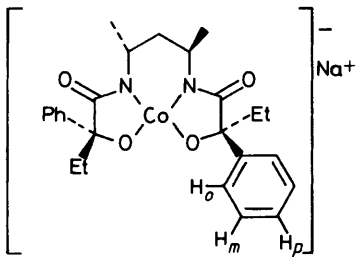


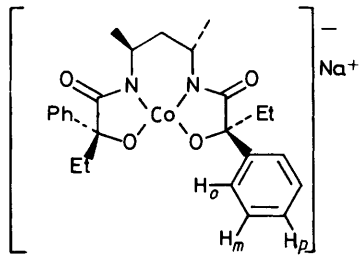
(5a)



(5b)



(6a)



(6b)

X-Ray Crystal Structure Determination of Complex (**2**).—The result of an X-ray crystal-structure determination for complex (**2**)·1.5THF is depicted in Figure 2. Experimental data for the structure determination of complex (**2**) are listed in the Experimental section.

The X-ray crystal-structure determination reveals a square-planar environment for the metal centre. The bond distances within the ligand framework are comparable to those of complex (**1**)[7] or Na[Co(η⁴-HMPA-B)], [H_4HMPA-B = 1,2-bis(2-hydroxy-2-methylpropionamido)benzene][6] and are shorter than is usual for cobalt(III) complexes of PAC ligands.[13]

Catalytic Epoxidation of Styrenes.—Epoxidation of styrenes was performed in acetonitrile at −2 to 0 °C under nitrogen gas with mechanical stirring. The results are summarized in Table 2.

Catalyst turnover numbers and the amounts of complex remaining unchanged after a reaction time of 24 h are listed in the Experimental section. The oxidation reaction, followed by GLC, showed that iodobenzene was formed together with epoxy compounds. In the case of styrene, phenylacetaldehyde was formed in addition to styrene oxide. The ratio styrene oxide: phenylacetaldehyde as determined by GLC was *ca.* 3.20:1. The ^{1}H NMR spectra of the separated products, however, indicated that the ratio was 4.75:1. These observations show that the rearrangement of styrene oxide into phenylacetaldehyde took place, to some extent, in the GLC injection port, and this was ascertained by the injection of standard styrene oxide. In some oxidations of substituted styrenes, small amounts of the corresponding benzaldehyde were formed, probably by autoxidation of the styrenes by the residual molecular oxygen in the reaction mixture. The ^{1}H NMR spectrum of the complex isolated from solution after oxidation of complex (**5a**) was identical with that of complex (**5a**). When iodosylbenzene was added to the solution after oxidation of the styrene, the yield of the styrene oxide was found to increase further for all complexes. The configuration of the predominant enantiomer was determined by polarimetry and the optical purity of the isolated styrene oxide was analysed by reduction to 1-phenylethanol by lithium aluminum hydride, and conversion of this into a mixture of stereoisomeric esters with (*R*)-2-phenylpropionyl chloride. Optical yields for these epoxidations were conveniently measured by ^{1}H NMR spectroscopy with use of a chiral reagent, tris[3-heptafluoropropyl(hydroxy)methylene-(+)-camphorato]europium(III) [Eu(hfc)$_3$].

The chemical yields for epoxides are generally good, but the asymmetric inductions are rather poor. Though no clear effect on enantiometic induction was observed upon changing the substituent on the phenyl group of the styrenes, the con-

Table 1. ^{1}H NMR (90 MHz) data[a] for chiral cobalt(III) complexes.

Complex	H_o	H_m	H_p	$OC(CH_3)$	$OC(CH_2CH_3)$	$OC(CH_2CH_3)$	$NC(CH_3)$	$NCHCH_3$	$C(CH_2)C$	H_a	H_b
(2)	—	—	—	16.2 (6 H)	32.8 (2 H) 4.1 (2 H)	−8.3 (6 H)	2.2 (6 H) −2.1 (6 H)	—	—	—	—
(3)	2.9 (4 H) $J_{o,p}$ 7 Hz; $J_{m,p}$ 7 Hz	7.7 (4 H)	5.7 (2 H)	—	39.7 (2 H) 9.4 (2 H)	−5.8 (6 H)	1.1 (6 H) −1.0 (6 H)	—	—	—	—
(4)	—	—	—	8.1 (6 H)	28.1 (2 H) 5.2 (2 H)	−9.8 (6 H)	—	—	—	0.8 (2 H)	−24.5 (2 H)
(5a)	—	—	—	21.6 (6 H)	22.2 (2 H) 0.6 (2 H)	−15.7 (6 H)	−3.4 (6 H)	12.5 (2 H)	87.9 (2 H)	—	—
(5b)	—	—	—	1.8 (6 H)	49.0 (2 H) 11.5[b]	−4.0 (6 H)[c]	−1.0 (6 H)[c]	11.5[b]	92.2 (2 H)	—	—
(6a)	−1.3 (4 H)	5.7 (4 H)	0.9 (2 H)	—	45.2 (2 H) 12.5 (2 H)[c]	−3.8 (6 H)	−0.9 (6 H)	10.8 (2 H)[c]	84.2 (2 H)	—	—
(6a)[d]	1.7 (4 H)	6.4 (4 H)	4.8[e]	—	34.4 (2 H) 11.9[b]	−1.9 (6 H)	−0.5 (6 H)	11.9[b]	99.7 (2 H)	—	—
(6b)	0.8 (4 H)	9.8 (4 H)	6.2 (2 H)	—	18.3 (2 H) 7.3 (2 H)	−15.5 (6 H)	−3.5 (6 H)	12.7 (2 H)	101.2 (2 H)	—	—
(6b)[d]	0.8 (4 H)	9.8[f]	6.5 (2 H)	—	10.4 (2 H) 9.8[f]	−11.0 (6 H)	−1.8 (6 H)	11.7 (2 H)	125.1 (2 H)	—	—
(1)[g]	—	—	—	12.3 (6 H)	—	—	−1.2 (12 H)	—	—	—	—

[a] Measured in D_2O unless otherwise stated. All shifts are in ppm relative to that of the residual protons in D_2O or CD_3OD, and are slightly concentration dependent. [b] Corresponds to four protons from one of the methylene groups and $NCH(CH_3)$. [c] Assignment may be reversed. [d] Measured in CD_3OD. [e] Overlaps with the residual protons in CD_3OD. [f] Corresponds to six protons from H_m and one of the methylene protons. [g] Quoted from ref. 7.

Table 2. Catalytic asymmetric epoxidation with cobalt(III) complexes.[a]

Styrenes	% Chemical yield[b] ee,[c] (Configuration)						
	(2)	(3)	(4)	(5a)	(6a)	(5b)	(6b)
Styrene	66/4 (*R*)-(+)	70/13 (*S*)-(−)	58/6 (*R*)-(+)	45/2 (*R*)-(+)	57/7 (*S*)-(−)	43/6 (*R*)-(+)	55/6 (*S*)-(−)
p-Cl	63/3 (+)	64/13 (−)	49/5 (+)	27/1 (+)	33/14 (−)	27/0	31/8 (−)
m-Cl	80/7 (+)	65/13 (−)	50/3 (+)	31/0	35/6 (−)	25/7 (+)	31/1 (−)
o-Cl	69/4 (+)	70/12 (−)	74/2 (+)	49/2 (+)	46/17 (−)	47/6 (+)	51/7 (−)
p-Me	65/6 (+)						
p-NO_2	65/5 (+)						
m-NO_2	58/2 (+)						
(Z) Stilbene 68 [(*cis*) Stilbene oxide][d]							
(*E*)-Stilbene 43 [(*trans*)-Stilbene oxide][d]							

[a] Reactions in acetonitrile at −2 to 0 °C with iodosylbenzene (40 mmol dm^{-3}), substrate (600 mmol dm^{-3}) and a complex (1 mmol dm^{-3}). [b] Determined by GLC based on the iodosylbenzene consumed. [c] From integration of the ^1H NMR resonance due to the epoxide proton. [d] Determined by HPLC (see the Experimental section).

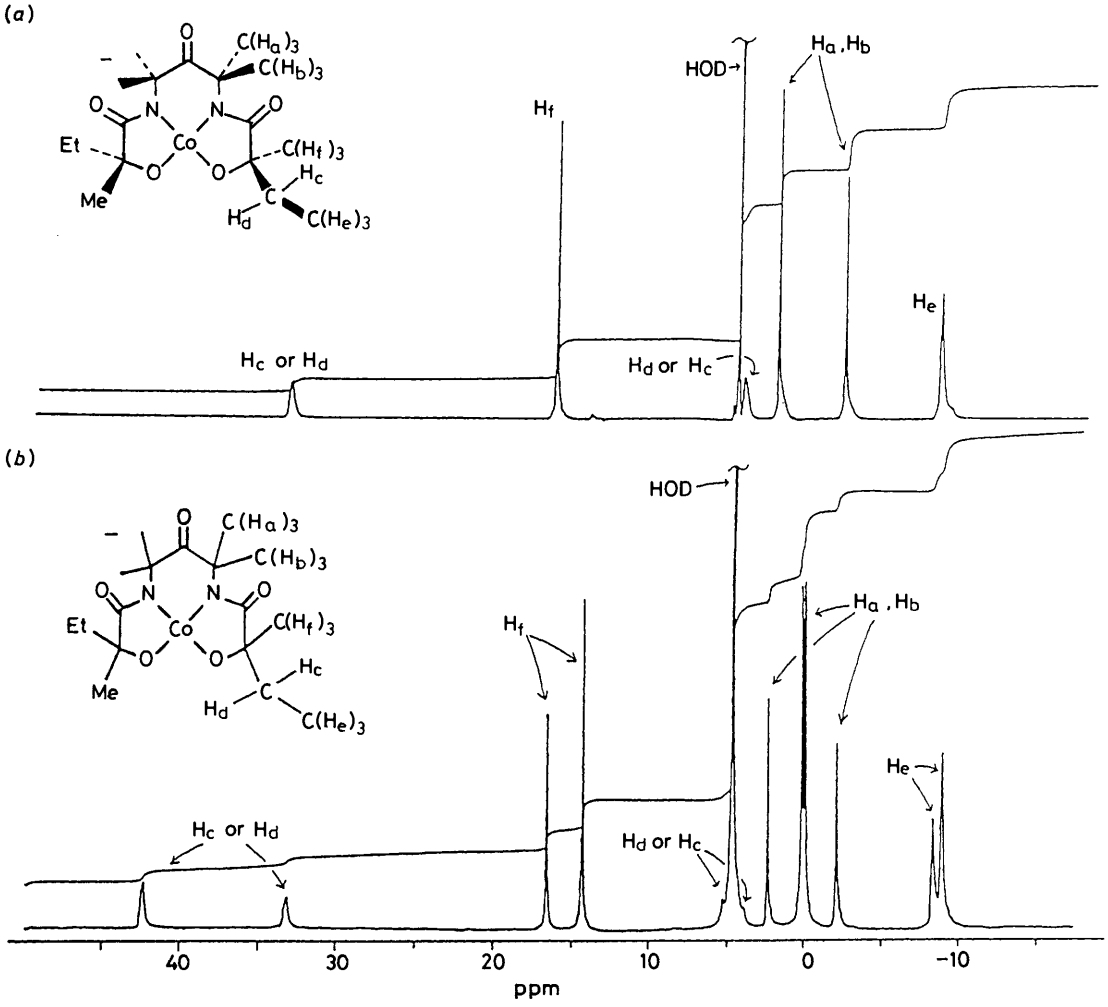


Figure 1. ^1H NMR spectra of complex (2) and non-chiral counterpart of (2).

figuration of major enantiomer definitely depended on the structure of the alkoxy groups and not on that of amide groups in the present complexes. By way of an evaluation of the factors that determine the extent of asymmetric induction, the mechanism of the catalytic epoxidation reaction by these cobalt complexes has been proposed as follows. It has been reported that iodosylbenzene and cumenyl hydroperoxide affect the oxidation of alkenes by cobalt(II) nitrate or trifluoromethanesulphonate[14] and chloro(tetraphenylporphyrinato)cobalt(III),[15] respectively. In these oxidations, possible pathways include a mechanism similar to that for cytochrome-P-450-catalysed oxidations; a radical mechanism has been proposed for the formation of both the epoxide and the radical cation. The present results, namely that (*a*) (*Z*)-stilbene is more reactive than (*E*)-stilbene towards epoxidation, and configurations of both (*Z*)- and (*E*)-stilbene were completely retained and (*b*) the

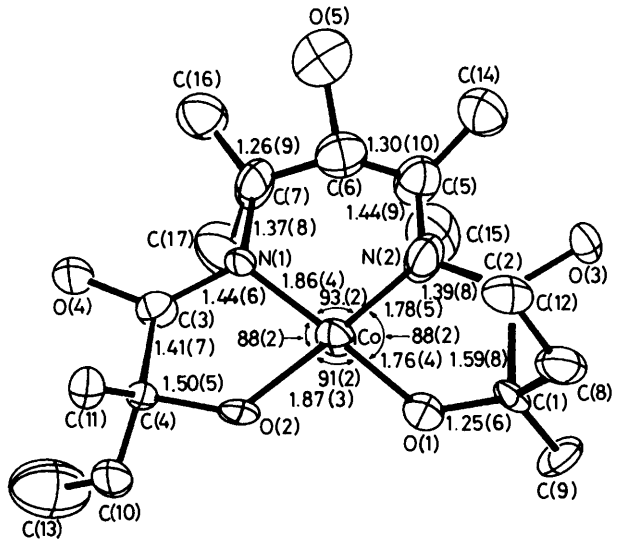


Figure 2. Structure of the ion $[Co(\eta^4\text{-}(R)\text{-HMBA-DMP})]^-$ in $Na[Co(\eta^4\text{-}(R)\text{-HMBA-DMP})]\cdot 1.5THF$.

extent of asymmetric induction and the configuration of the major enantiomer is dependent on the structure of the complexes, and no asymmetric induction was observed in control experiments using a non-chiral complex (**1**), suggest that the radical mechanism proposed in the literature[14,15] is unlikely to be the main mechanism, and that degradation products could not be the active catalysts in this system.

In the light of studies on the epoxidation of alkenes (stilbene) catalysed by iron– or manganese–porphyrin complexes,[2c,16] a cobalt(v)–oxo complex, or some equivalent, could be regarded as one of the most probable active intermediates in the present system, which itself is derived from oxygen transfer from iodosylbenzene to the square-planar cobalt(III) complexes. A enantiomeric excess of the epoxides would be produced by preferential oxygen-atom transfer from the possible chiral cobalt(v)–oxo complex to either the *Si* or *Re* face of the styrenes which approach to the oxocobalt group from the side and parallel to the plane of the complex in a manner similar to that reported for (porphinato) iron complexes.[16a,b,17] The high chemical yields of epoxides observed in reactions with complexes (**1**), (**2**), (**3**), and (**4**) suggest that the ligands of these complexes are sufficiently resistant to oxidation and have large donor capacities such that unusually high oxidation states in the cobalt complexes can be produced. The relatively low asymmetric induction observed with these cobalt complexes indicates that the free-energy difference between the diastereoisomeric intermediates leading to asymmetric discrimination is not large enough. In this case evaluation of the factors that determine the extent of asymmetric induction or the preferential approach mode of styrenes to the oxocobalt group is difficult. But the results on the configuration of epoxides suggest that there are two preferential approach modes of styrenes depending on the structure of complexes as shown in Figure 3.

These figures indicate that in reactions involving (**2**), (**4**), and (**5a,b**) styrenes approach the oxocobalt centre of the complex from the alkoxy-group side of the complex, keeping their phenyl groups to the less hindered side, *i.e.* towards the methyl group, to give (*R*)-(+)-epoxides [Figure 3(*a*)]. On the other hand styrenes approach the oxocobalt centre of complexes (**3**), (**6a,b**) (in which the alkoxy groups which contain both phenyl and ethyl components) such that their phenyl groups are kept on the same side as the phenyl group of the alkoxide group, to give (*S*)-(−)-epoxides [Figure 3(*b*)]. It is probable that π–π interactions

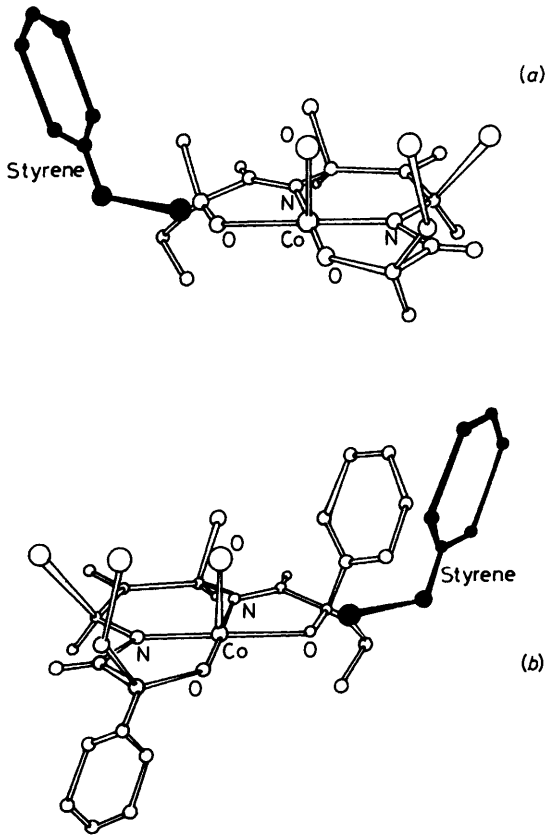


Figure 3. Approach modes of styrene to (*a*) complex (**2**) and (*b*) complex (**3**).

between the two phenyl groups make it possible for styrene phenyl groups to approach the alkoxy groups in this manner. On the basis that the distance between the two alkoxy groups is greater than those between other chiral centres, the main approach of styrenes from the alkoxy-group side seems very probable and is reflected by the observation that the predominant configuration of the resulting epoxides is not dependent on the configuration of the amide groups in the complexes. These modes of approach of styrenes to the oxocobalt also account for the inversion of the predominant configuration in the epoxides, in the reaction with these cobalt complexes which have same (*R*)-configuration in alkoxides groups. Improvement of the % ee is possible by increasing the difference in the bulk between the two alkyl components of the alkoxide groups and by introducing bulkier groups into the amide function in order to make the approach from this side to oxocobalt more difficult.

At the present time, the structure and reactivity of higher-valent cobalt complexes such as cobalt(IV)–[13,18] and cobalt(v)–oxo complexes are poorly understood, in contrast with those of (porphinato)–chromium(v)[19] (porphinato)–iron(v),[20,16b] and (porphinato)–manganese(v) complexes.[21,16d]

It has been suggested that in the reaction of chloro(tetraphenylporphinato) cobalt(III) with peroxycarboxylic acids, initial transfer of the oxygen atom to cobalt(III) yields a cobalt(v) species, which by rapid internal electron transfer, results in a dicationic porphyrin species of cobalt(III).[22] Attempts to characterize intermediates, high-valent cobalt complexes in the present oxidation reaction are in progress.

Experimental

Instrumentation.—Gas chromatographic analyses (GLC) were performed on a JEOL JGC-20K chromatograph with a

PEG 20M glass column (2 m; 3 mm diameter) or a Shimadzu GC-8A chromatograph fitted with HiCap CPBI M25-025. GLC integrations were measured with a Takeda Riken TR-2215A integrator. NMR spectra were taken on a JEOL FX-90Q, or a Hitachi R-600 instrument. Chemical shifts are reported relative to Me_4Si or residual protons of deuteriated NMR solvents. IR spectra were taken on a JASCO A 202 instrument. Visible and UV spectra were taken on a Hitachi 124 spectrophotometer. Rotations were measured on a Perkin-Elmer 241 polarimeter. High performance liquid chromatography (HPLC) was performed on a Shimadzu LC-5A fitted with a Water Associates Radial-Pak μ Bondapak C_{18} column and equipped with an SPD-2A spectrophotometric detector.

Materials.—*p*-Chlorostyrene, *m*-chlorostyrene, *o*-chlorostyrene, *p*-methylstyrene, *p*-nitrostyrene, 2-phenylethanol, and diisopropyl ketone were purchased from Tokyo Kasei Kogyo Co., Ltd. Phenylacetaldehyde, DL-1-phenylethanol, benzaldehyde, iodobenzene, styrene oxide, (*R*)-styrene oxide, tiglic acid, *N*-bromosuccimide, zinc bromide, methyl iodide and t-butyl alcohol were purchased from Nacalai Tesque, Inc. Styrene, cobalt(II) acetate tetrahydrate, and L-proline were purchased from Wako Pure Chemical Industries, Ltd. *m*-Nitrostyrene, iodobenzene diacetate, (*R*)-(−)-2-phenylpropionic acid, tris{3-[heptafluoropropyl(hydroxy)methylene]-(+)-camphorato}europium(III), acetylacetone, dibenzoyl-D-tartaric acid, (1*R*,2*S*,5*R*)-(−)-menthanol, phenylene-1,2-diamine and 2-hydroxy-2-methylbutyric acid were purchased from Aldrich. Styrenes were ascertained by GLC to be free from the corresponding oxides prior to use in oxidations and other agents were used as received. Acetonitrile was dried over K_2CO_3 and purified by successive distillations over CaH_2 and P_2O_5. Iodosylbenzene was prepared according to the method in the literature.[23]

Syntheses.—Epoxy compounds were prepared by four methods: A,[24] B,[25] C,[26] and D.[27]

p-*Chlorostyrene oxide:* method B (28%), b.p. 47–49 °C at 0.2 mmHg (lit.,[28] 72 °C at 0.5 mmHg); δ($CDCl_3$) 2.73 (1 H, dd), 3.12 (1 H, dd), 3.82 (1 H, dd), and 7.24 (4 H, m).

m-*Chlorostyrene oxide:* method B (26%), b.p. 34–35 °C at 0.2 mmHg (Found: C, 62.0; H, 4.55; Cl, 23.1. Calc. for C_8H_7ClO: C, 62.13; H, 4.57; Cl, 22.93%); δ($CDCl_3$) 2.72 (1 H, dd), 3.11 (1 H, dd), 3.80 (1 H, dd), and 7.23 (4 H, m).

o-*Chlorostyrene oxide:* method C (74%) (Found: C, 62.15; H, 4.55; Cl, 22.95. Calc. for C_8H_7ClO: C, 62.47; H, 4.46; Cl, 22.80%); δ($CDCl_3$) 2.60 (1 H, dd), 3.13 (1 H, dd), 4.15 (1 H, dd), and 7.20 (4 H, m).

p-*Methylstyrene oxide:* method B (94%), b.p. 50 °C at 1 mmHg (lit.,[28] 54 °C at 1.2 mmHg); δ($CDCl_3$) 2.31 (3 H, s), 2.75 (1 H, dd), 3.08 (1 H, dd), and 7.18 (4 H, s).

p-*Nitrostyrene oxide:* method D (53%), m.p. 84–85 °C (lit.,[27] 84–85 °C); δ($CDCl_3$) 2.78 (1 H, dd), 3.22 (1 H, dd), 3.94 (1 H, dd), and 7.30, 7.50, 8.08, and 8.26 (4 H, each s).

m-*Nitrostyrene:* method D (72%), b.p. 96–98 °C at 0.4 mmHg (lit.,[28] 101 °C at 0.5 mmHg); δ($CDCl_3$) 2.81 (1 H, dd), 3.22 (1 H, dd), 3.97 (1 H, dd), and 7.61 and 8.11 (2 H and 2 H, s).

(*R*)-(−)-2-Hydroxy-2-methylbutyric acid, (*R*)-HMBA was prepared according to the method in the literature[8] by asymmetric bromolactonisation of (*S*)-*N*-tigloylproline $[\alpha]_D$ −73.0° (*c* 1.00 in MeOH), {lit.,[8] $[\alpha]_D^{20}$ − 72.7° (*c* 1.00 in MeOH} as a key step. (*R*)-HMBA was obtained as colourless needles from EtOAc–hexane, m.p. 69–72 °C (lit.,[8] 72–74 °C), $[\alpha]_D^{24}$ −8.7° (*c* 3.30 in $CHCl_3$), {lit.,[8] $[\alpha]_D^{25}$ − 8.9(*c* 2.97 in $CHCl_3$)}.

(R)-(−)-2-Hydroxy-2-phenylbutyric acid, [(R)-HPBA] was prepared according to the method in literature[9] by selective addition of an ethyl group to (−)-methylphenyl glyoxalate $[\alpha]_D$ − 45.3° (*c* 1.44 in abs. EtOH,) {lit.,[9] $[\alpha]_D^{25}$ − 46.2° (*c* 0.66 in abs. EtOH} using diethylzinc[9] in a key step. (*R*)-HPBA was obtained as an amorphous solid from benzene–light petroleum which sublimed at 97 °C, $[\alpha]_D$ − 24.8° (*c* 0.98 in EtOH) {lit.,[9] $[\alpha]_D^{22}$ − 24° (*c* 0.8 in EtOH}.

Preparation[29] and resolution[10] of racemic pentane-2,4-diamine was performed by the method given in the literature. (2*R*,4*R*)-Pentane-2,4-diamine·2HCl was obtained as white needles from methanolic HCl–EtOH, $[\alpha]_D$ + 16.6° (*c* 1.06 in 1 mol dm^{-3} HCl) (lit.,[10] $[\alpha]_D$ +17° 1% in 1 mol dm^{-3} HCl).

2,4-Diamino-2,4-dimethylpentan-3-one was prepared by the method given in the literature[30] using 2,4-dimethylpentan-3-one as the starting material. The crude amine was obtained as a brown oil, ν_{max}(film) 3 400 (NH_2) and 1 600 cm^{-1} (CO), δ($CDCl_3$) 1.35 (12 H, s, CH_3) and 2.30 (4 H, br s, NH_2).

Chiral ligands of the cobalt complexes depicted were synthesized by the methods described in the literature[6,31] using (*R*)-(−)-2-hydroxy-2-methyl-(or phenyl)-butyric acid and (2*R*, 4*R*)- or (2*S*,4*S*)-pentane-2,4-diamine, 2,4-diamino-2,4-dimethylpentan-3-one, or *o*-phenylenediamine.

H_4(R)-*HMBA-DMP:* an amorphous solid, (2.5 g, 40% based on the starting diamine) m.p. 117–118 °C (from THF–hexane) (Found: C, 58.8; H, 9.55; N, 7.95. $C_{17}H_{32}N_2O_5$ requires C, 59.2; H, 9.37; N, 8.13%); $[\alpha]_D$ +32.6° (*c* 1.18 in MeOH); ν_{CO} 1 710 (ketone) and 1 650 cm^{-1} (amide); δ($CDCl_3$) 0.88 (6 H, t, CH_2CH_3), 1.39 (6 H, s, OCH_3), 1.62 (12 H, s, $NCCH_3$), 1.4–2.1 (4 H, m, CH_2CH_3), 2.89 (2 H, br s, OH), and 7.57 (2 H, br s, NH).

H_3(R)-*HMBA-B:* an amorphous solid, (1.35 g, 49% based on the starting diamine) m.p. 131–135 °C (from acetone–hexane) (Found: C, 62.15; H, 7.85; N, 8.85. $C_{16}H_{24}N_2O_4$ requires C, 62.32; H, 7.84; N, 9.09%); $[\alpha]_D$ +57.8° (*c* 1.11 in MeOH); ν_{max} 1 655 cm^{-1} (CO); δ($CDCl_3$) 0.85 (6 H, t, CH_2CH_3), 1.32 (6 H, s, CH_3), 1.3–1.9 (4 H, m, CH_2CH_3), 5.45 (2 H, br s, OH), 7.0–7.6 (4 H, m, ArH), and 9.46 (2 H, br s, NH).

H_4(R)-*HMBA*-(2R,4R)*P:* an amorphous solid, (90 mg, 12% base on the starting diamine), $[\alpha]_D$ +14.1° (*c* 1.09 in MeOH); ν_{max} 1 638 cm^{-1} (CO); δ($CDCl_3$) 0.90 (6 H, t, CH_2CH_3), 1.21 (6 H, d, $NCHCH_3$), 1.40 (6 H, t, OCH_3), 1.70 (2 H, br s, OH), 1.5–1.9 (4 H, m, CH_2CH_3), 3.92 (2 H, m, $NCCH_2CN$), and 7.74 (2 H, br d, NH).

H_4(R)-*HPBA*-(2R,4R)*P*: an amorphous solid, (1.02 g, 20% based on the starting diamine), m.p. 161–162 °C (from acetone–hexane) (Found: C, 69.0; H, 8.0; N, 6.4. $C_{25}H_{34}N_2O_4$ requires C, 70.06; H, 8.46; N, 6.54%); $[\alpha]_D$ +13.7° (*c* 0.76 in MeOH); ν_{max} 1 658 cm^{-1} (CO); δ[$(CD_3)_2SO$] 0.88 (6 H, t, CH_2CH_3), 1.05 (6 H, d, $NCHCH_3$), 1.3–1.8 (2 H, m, $NCCH_2CN$), 1.7–2.4 (4 H, m, CH_2CH_3), 3.7 (2 H, m, $NCHCH_3$), 3.95 (2 H, br s, OH), and 6.9–7.7 (6 H, m, ArH and NH).

H_4(R)-*HPBA*-(2S,4S)*P:* an amorphous solid, (0.66 g, 35% based on the starting diamine), m.p. 186–187 °C (from THF–hexane); $[\alpha]_D$ +18.7° (*c* 0.74 in EtOH); ν_{max} 1 658 cm^{-1} (CO). The ^1H NMR spectrum is identical with that of H_4(*R*)-HPBA-(2*R*,4*R*)P.

All complexes were synthesized according to the methods in the literature[6,7] using purified chiral ligands except for H_4(*R*)-HMBA-(2*S*,4*S*)P. Crude H_4(*R*)-HMBA-(2*S*,4*S*)P was used for the synthesis of the cobalt complex (**5b**). All yields are based on the corresponding ligand unless otherwise stated.

Complex (**2**): Na[Co(η⁴-(*R*)-HMBA-DMP)] was obtained as orange crystals, m.p. 265–268 °C (from acetone–CH_2Cl_2) (Found: C, 47.94; H, 6.61; N, 6.70. $C_{17}H_{28}CoN_2NaO_5$ requires C, 48.34; H, 6.68; N, 6.63%); $[\alpha]_D$ − 845° (*c* 0.21 in MeOH); μ_{eff} = 3.9 μ_B; ν_{CO} 1 605 (amide) and 1 701 cm^{-1} (ketone); $\lambda_{max}(CH_3CN)$ 387 (ε 5 000 dm^3 mol^{-1} cm^{-1}) and 466 nm (5 400). For the ^1H NMR spectrum, see Table 1.

Complex (**3**): Na[Co(η⁴-(*R*)-HPBA-DMP)]·H_2O was obtained as red crystals, (1.54 g, 64%), m.p. 260–265 °C (decomp.) (from EtOAc–CH_2Cl_2) (Found: C, 57.8; H, 5.95; N,

4.6. $C_{27}H_{32}CoN_2NaO_5 \cdot H_2O$ requires C, 57.44; H, 6.07; N, 4.96%); $[\alpha]_D$ −620° (*c* 0.19 in MeOH); μ_{eff} = 3.7 μ_B (D_2O); ν_{CO} 1 602 (amide) and 1 703 cm^{-1} (ketone); $\lambda_{max}(CH_3CN)$ 401 (ε 4 900 $dm^3\ mol^{-1}\ cm^{-1}$) and 466 nm (5 100). For the ^1H NMR spectrum, see Table 1.

Complex (**4**): Na[Co(η⁴-(*R*)-HMBA-B)]·THF·H_2O was obtained as dark green crystals, (1.35 g, 88%), m.p. > 300 °C (from THF–hexane) (Found: C, 49.85; H, 5.7; N, 5.85. $C_{16}H_{20}CoN_2NaO_4 \cdot THF \cdot H_2O$ requires C, 50.4; H, 6.35; N, 5.58%); $[\alpha]_D$ +273° (*c* 0.02 in MeOH); μ_{eff} = 5.0 μ_B (D_2O); ν_{max} 1 624 cm^{-1} (CO); λ_{max} (CH_3CN) 424 (ε 5 600 $dm^3\ mol^{-1}\ cm^{-1}$) and 551 nm (1 600). For the ^1H NMR spectrum see Table 1.

Complex (**5a**): Na[Co(η⁴-(*R*)-HMBA-(2*R*,4*R*)P)] was obtained as orange crystals, (75 mg, 70%), m.p. 284–285 °C (from acetone–CH_2Cl_2) (Found: C, 46.5; H, 6.7; N, 7.4. $C_{15}H_{26}CoN_2NaO_4$ requires C, 47.4; H, 6.90; N, 7.37%); $[\alpha]_D$ −1 400° (*c* 0.21 in MeOH); μ_{eff} = 3.6 μ_B (D_2O); ν_{CO} 1 604 cm^{-1}; $\lambda_{max}(CH_3CN)$ 380 (ε 4 100 $dm^3\ mol^{-1}\ cm^{-1}$) and 461 nm (5 800). For the ^1H NMR spectrum, see Table 1.

Complex (**5b**): Na[Co(η⁴-(*R*)-HMBA-(2*S*,4*S*)P)] was obtained as orange crystals, (54 mg, 7% based on the starting diamine), m.p. 284–285 °C (from acetone–CH_2Cl_2); $[\alpha]_D$ +1 850° (*c* 0.125 in MeOH); $\lambda_{max}(CH_3CN)$ 382 (ε 4 100 $dm^3\ mol^{-1}\ cm^{-1}$) and 463 nm (5 800); μ_{eff} = 3.9 μ_B (D_2O). For the ^1H NMR spectrum see Table 1.

Complex (**6a**): Na[Co(η⁴-(*R*)-HPBA-(2*R*,4*R*)P)] was obtained as orange crystals, (610 mg, 49%) m.p. > 300 °C (from acetone–CH_2Cl_2) (Found: C, 59.0; H, 5.95; N, 5.35. $C_{25}H_{30}CoN_2NaO_4$ requires C, 59.5; H, 5.99; N, 5.55%); $[\alpha]_D$ −1 260° (*c* 0.19 in MeOH); μ_{eff} = 3.2 μ_B (CD_3OD); ν_{CO} 1 602 cm^{-1}; $\lambda_{max}(CH_3CN)$ 381 (ε 3 600 $dm^3\ mol^{-1}\ cm^{-1}$) and 464 nm (5 400). For the ^1H NMR spectrum see Table 1.

Complex (**6b**): Na[Co(η⁴-(*R*)-HPBA-(2*S*,4*S*)P)]·H_2O was obtained as orange crystals, (330 mg, 42%) m.p. > 300 °C (from acetone–CH_2Cl_2–hexane) (Found: C, 58.0; H, 5.8; N, 5.25. $C_{25}H_{30}CoN_2NaO_4 \cdot H_2O$ requires C, 57.5; H, 6.17; N, 5.36%); $[\alpha]_D$ +1 490° (*c* 0.19 in MeOH); μ_{eff} = 3.3 μ_B (CD_3OD); ν_{CO} 1 602 cm^{-1}; $\lambda_{max}(CH_3CN)$ 381 (ε 3 600 $dm^3\ mol^{-1}\ cm^{-1}$) and 464 nm (5 400); ^1H NMR see Table 1.

Oxidation of Substituted Styrenes by Cobalt(III) *Complexes and Iodosylbenzene.*—To acetonitrile (15 cm^3) was added the cobalt complex (15 μmol), iodosylbenzene (600 μmol) and styrene (9 mmol) (or substituted styrene). The reaction mixture was cooled to between −2 and 0 °C under nitrogen and the reaction was allowed to stir for 24 h. The chemical yield of products was determined by GLC (PEG 20M, 2 m glass column or methylsilicone, 25 m capillary). The amount of the complex remaining unchanged after reaction for 24 h was determined by measuring the UV–VIS absorption of the reaction mixture. The catalytic turnover for the epoxidations was determined from the amount of iodosylbenzene used. The amounts of recovered complex from the oxidation of styrene and (turnover for epoxidation) are as follows: complex (**2**) 69% (23); complex (**3**) 64% (24); complex (**4**) 58% (24); complex (**5a**) 45% (9); complex (**5b**) 43% (8); complex (**6a**) 57% (9); complex (**6b**) 55% (10).

Oxidation products were separated by column chromatography on silica gel; iodobenzene and styrenes were eluted with hexane and then styrenes and phenylacetaldehyde were eluted hexane–AcOEt (50:1; 7:1). The optical purity of the isolated styrene oxide was analysed according to the method in the literature[2] by reduction of *ca.* 50 mg of separated products to 1-phenylethanol (67%) and 2-phenylethanol (33%) with $LiAlH_4$ under nitrogen and conversion of these into a mixture of stereoisomeric esters with (*R*)-2-phenylpropanoyl chloride (0.93 g, 83% optically pure). The diastereoisomeric esters were analysed by GLC. The ratio of two peaks assigned to the esters of (*R*)- and (*S*)-1-phenylethanols indicated that a 7% ee had been achieved in the epoxidation reaction with complex (**2**). The optical yields listed in Table 1 were measured by ^1H NMR spectroscopy with the chiral shift reagent [Eu(hfc)$_3$] using the crude products separated by column chromatography.

In the case of styrene oxide obtained *via* complex (**2**), a small discrepancy in %ee was observed between the ^1H NMR spectroscopic method (4%) and the GLC method (7%). The retention of configuration in the epoxidation of (*Z*)- and (*E*)-stilbenes was confirmed by ^1H NMR spectroscopy of the crude products separated by column chromatography, and determined by HPLC.

X-Ray Crystal-structure Determination of Complex (**2**).—*Crystal data.* $C_{15}H_{28}N_2O_5 \cdot 1.5C_4H_8O$, *M* 530.5; monoclinic; space group, *C*2; *a* = 15.827(6), *b* = 15.689(7), *c* = 13.787(5) Å, β = 125.00(2)°, *V* = 2 804(2) Å^3 (by least-squares refinement on diffractometer angles for 25 automationally centred reflections); *Z* = 4; *F*(000) = 1 128; D_x (*Z* = 4) = 1.257 Mg m^{-3}; orange, air-sensitive irregular tetrahedron; crystal size, 0.08 × 0.08 × 0.08 mm; Cu-K_α = 5.49 mm^{-1}.

Data collection and processing. Rigaku AFC-5R diffractometer, ω–2θ mode with ω scan width 0.8 + 0.15 tan θ, scan speed 4° min^{-1}, graphite-monochromated Cu-K_α radiation (40 kV, 250 mA); 2 286 reflections measured (2θ < 120°) 2 175 unique [merging R_F = 0.036 ($|F_o| > 2\sigma(F_o)$)] after absorption correction[32] (maximum and minimum correction factors = 1.35 and 1.00, respectively)]; to give 1 135 with $|F_o| > 2\sigma(F_o)$; decay < 3%.

Structure analysis and refinement. Direct methods [MULTAN78, all non-hydrogen atoms of complex (**2**)][33] followed by a normal Fourier method (all non-hydrogen atoms of two solvent molecules); full-matrix and block-diagonal least-squares refinements with all non-hydrogen atoms of complex (**2**) (anisotropic) and all non-hydrogen atoms of the solvent (isotropic); *R* and R_w = 0.17 and 0.18, respectively (*w* = 1.0); programs and computer used, UNICS-Osaka[34] and ACOS-850; neutral atomic scattering factors.[35]

The *R* value was high and the accuracy of the refinements was lowered owing to a large number of weak intensities with large errors, particularly in high-angle reflections [of 1 027 in the range 90° < 2θ < 120° only 302 (29%) with $|F_o| > 2\sigma(F_o)$ and 180 (16%) with $|F_o| > 3\sigma(F_o)$], arising from the very small size of the crystal and also the large thermal motion reflecting the slight disorders in the atomic positions of the solvent molecules and the methyl and ethyl carbons in complex (**2**).

The thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England.*

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* For details of the CCDC deposition scheme see 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans 2*, 1990, issue 1.

References

1 T. J. Collins, S. Ozaki, and T. G. Richmond, *J. Chem. Soc., Chem. Commun.*, 1987, 803.

2 (*a*) H. B. Kagan, H. Mimoun, C. Mark, and V. Schurig, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 485; (*b*) D. Mansuy, P. Battioni, J.-P. Renaud, and P. Guerin, *J. Chem. Soc., Chem. Commun.*, 1985, 155; (*c*) J. T. Groves and R. S. Myers, *J. Am. Chem. Soc.*, 1983, **105**, 5791; (*d*) R. Sinigalia, R. A. Michelin, F. Pinna, and G. Strukful,

Organometallics, 1987, **6**, 728; (*e*) R. Curci, M. Fiorentio, and M. R. Serio, *J. Chem. Soc., Chem. Commun.*, 1984, 155.
3 (*a*) T. Katsuki and K. B. Sharpless, *J. Am. Chem. Soc.*, 1980, **102**, 5974; (*b*) B. E. Rossiter, T. Katsuki, and K. B. Sharpless, *ibid.*, 1981, **103**, 464; (*c*) R. M. Hanson and K. B. Sharpless, *J. Org. Chem.*, 1986, **51**, 1922; (*d*) S. Y. Ko, H. Masamune, and K. B. Sharpless, *ibid.*, 1987, **52**, 667; (*e*) Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune, and K. B. Sharpless, *J. Am. Chem. Soc.*, 1987, **109**, 5765.
4 R. Helder, J. C. Hummelen, R. W. Laane, J. S. Wiering, and H. Wynberg, *Tetrahedron Lett.*, 1976, 1831.
5 (*a*) S. W. May and R. D. Schwartz, *J. Am. Chem. Soc.*, 1974, **96**, 4031; (*b*) H. Ohta and H. Tetsukawa, *J. Chem. Soc., Chem. Commun.*, 1978, 849.
6 T. J. Collins, T. G. Richmond, B. D. Santarsiero, and B. G. R. T. Treco, *J. Am. Chem. Soc.*, 1986, **108**, 2088.
7 J. C. Brewer, T. J. Collins, M. R. Smith, and B. D. Santarsiero, *J. Am. Chem. Soc.*, 1988, **110**, 423.
8 S.-S. Jew, S. Terashima, and K. Koga, *Tetrahedron Lett.*, 1979, 2337.
9 (*a*) K. Matsumoto and K. Harada, *J. Org. Chem.*, 1966, **31**, 1956; (*b*) D. Abenhäim, E.-H. Basch, and P. Freon, *Bull. Soc. Chim. France*, 1969, 4038 and 4043; (*c*) G. Boireau, A. Deberly, and D. Abenhäim, *Tetrahedron Lett.*, 1988, 2175.
10 B. Bosnich and J. Macb. Harrowfield, *J. Am. Chem. Soc.*, 1972, **94**, 3425.
11 F. C. Anson, J. A. Christie, J. T. Collins, R. T. Coots, T. T. Furutani, S. L. Gipson, J. K. Keech, T. E. Krafft, B. D. Santarsiero, and G. H. Spies, *J. Am. Chem. Soc.*, 1984, **106**, 4460.
12 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
13 F. C. Anson, J. T. Collins, R. C. Coots, S. L. Gipson, and T. G. Richmond, *J. Am. Chem. Soc.*, 1984, **106**, 5037.
14 R. B. Van Atta, C. C. Franklin, and J. S. Valentine, *Inorg. Chem.*, 1984, **24**, 4121.
15 D. Mansuy, J.-F. Bartoli, and M. Momenteau, *Tetrahedron Lett.*, 1982, 2781.
16 (*a*) J. T. Groves, T. E. Nemo, and R. S. Myers, *J. Am. Chem. Soc.*, 1979, **101**, 1032; (*b*) J. T. Groves, W. J. Kruper, and T. E. Nemo, *J. Mol. Catal.*, 1980, **7**, 169; (*c*) J. R. Lindsay Smith and P. R. Sleath, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1009; (*d*) O. Bartolini and B. Meunier, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1967; (*e*) J. P. Collman, J. I. Brauman, B. Meunier, T. Hayashi, T. Kodadek, and S. A. Raybuck, *J. Am. Chem. Soc.*, 1985, **107**, 2000; (*f*) T. Muto, J. Umehara, T. Miura, and M. Kimura, *Chem. Pharm. Bull.*, 1985, **33**, 4749; (*g*) P. Battioni, J.-P. Renaud, J. F. Bartoli, M.-R. Artiles, M. Fort, and D. Mansuy, *J. Am. Chem. Soc.*, 1988, **110**, 8462.
17 K. A. Jorgensen, *J. Am. Chem. Soc.*, 1987, **109**, 697.
18 (*a*) J. Halpern, J. Topich, and K. I. Zamaraev, *Inorg. Chim. Acta*, 1976, **20**, L21; (*b*) J. Topich and J. Halpern, *Inorg. Chem.*, 1979, **18**, 1339.
19 J. T. Groves and W. J. Krupper, Jr., *J. Am. Chem. Soc.*, 1979, **101**, 7613; (*b*) J. T. Groves, W. J. Kruper, Jr., R. C. Haushalter, and W. M. Bulter, *Inorg. Chem.*, 1982, **21**, 1363; (*c*) E. G. Samsel, K. Srinivasan, and J. K. Kochi, *J. Am. Chem. Soc.*, 1985, **107**, 7606; (*d*) J. Muzart, *Tetrahedron Lett.*, 1986, 3139; (*e*) B. Rihter and J. Masonovi, *J. Chem. Soc., Chem. Commun.*, 1988, 35.
20 (*a*) A. Gold, W. Ivey, and M. Bowen, *J. Chem. Soc., Chem. Commun.*, 1981, 293; (*b*) J. T. Groves, R. C. Haushalter, M. Nakamura, T. E. Nemo, and B. J. Evans, *J. Am. Chem. Soc.*, 1981, **103**, 2884; (*c*) L. Lotos-Granzynski and M. W. Renner, *ibid.*, 1984, **106**, 7779; (*d*) A. C. Balch, L. Lotos-Granzynski, and M. W. Renner, *ibid.*, 1985, **107**, 2983; (*e*) T. S. Calderwood, W. A. Lee, and T. C. Bruice, *ibid.*, 1985, **107**, 8272; (*f*) J. T. Groves and Y. Watanabe, *ibid.*, 1986, **108**, 507.
21 C. L. Hill and B. C. Schardt, *J. Am. Chem. Soc.*, 1980, **102**, 6375; (*b*) J. T. Groves, W. J. Kruper, Jr., and R. C. Haushalter, *ibid.*, 1980, **102**, 6377; (*c*) D. Mansuy, P. Battioni, and J.-P. Renaud, *J. Chem. Soc., Chem. Commun.*, 1984, 1255.
22 W. A. Lee and T. C. Bruice, *Inorg. Chem.*, 1986, **25**, 131.
23 H. Saltzman and J. G. Sharefkin, *Org. Synth.*, Coll. Vol. V, 1973, 658.
24 D. Swern, *Org. React.*, 1953, **7**, 378.
25 D. H. Marshall and R. H. Prager, *Aust. J. Chem.*, 1977, **30**, 141.
26 H. Sawada and M. Saito, *Kokai* (*Japan*), 76, **105**, 24, (*Chem. Abstr.*, **86**, 171234j).
27 M. M. Kayser and P. Morand, *Can. J. Chem.*, 1980, **58**, 302.
28 A. C. Knipe, *J. Chem. Soc., Perkin Trans. 2*, 1973, 589.
29 W. H. Lycan, S. V. Puntambeker, and C. S. Marvel, *Org. Synth.*, Coll. Vol. II, 1943, 318.
30 (*a*) G. Classon and A. Thalen, *Acta Chem. Scand.*, 1963, **17**, 1172; (*b*) W. L. Mack, Ph.D. Thesis, Harvard, Cambridge MA, 1964, p. 128; (*c*) R. J. Bushby and M. D. Pollard, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2401.
31 F. C. Anson, T. J. Collins, T. G. Richmond, B. D. Santarsiero, J. E. Toth, and B. G. R. T. Treco, *J. Am. Chem. Soc.*, 1987, **109**, 2974.
32 A. C. T. North, D. C. Philips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
33 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, MULTAN-78, 'A System of Computer Programs for the Automatic Solution of Crystal Structure from X-Ray Diffraction Data,' Universities of York, England and Louvain, Belgium, 1978.
34 T. Asida, 'The Universal Crystallographic Computing System-Osaka,' Library of Programs, Computing Center, Osaka University, 1979.
35 J. A. Ibers and W. C. Hamilton, 'International Tables for X-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

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