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A Study of the Kinetic Resolution of DL-Propylene Oxide with Optically Active Co(I)(salen) Type Complexes

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An optically active Co(I)(salen) type complex, lithium *N*,*N*′-bis-(salicylaldehyde)-1(*R*),2(*R*)-1,2-*trans*-cyclohexanediiminatocobaltate (I), was prepared by reducing the Co(II) complex, *N*,*N*′-bis-(salicylaldehyde)-1(*R*),2(*R*)-1,2-*trans*-cyclohexanediiminatocobalt(II), with butyllithium. The structure of the Co(I) complex was determined by means of its absorption and circular dichroism (CD) spectra. D-Propylene oxide was found to react preferentially (*e.g.*, $\ll$D/D+L$\gg$=68% in a dioxane solution) in a kinetic resolution of DL-propylene oxide using the above Co(I) complex as a catalyst. On the contrary, L-propylene oxide reacted selectively when Lewis acids were added to the system of the lithium Co(I) complex. The Lewis acids were demonstrated to interact with the Co(I) complex and to play a significant role in the asymmetric selectivity of the Co(I) species.

The square-planar tetradentate Schiff-base complexes of cobalt, such as cobaloxime[1] and Co(salen),[2] have been studied in relation to the coenzyme B$_{12}$. Few studies, however, have been done to explore the possibilities of an optically active Co(salen) type complex as a catalyst for any of the asymmetric reactions.

We reported in one of our previous papers[3] the kinetic resolution of DL-propylene oxide using an optically active Co(I) complex prepared by reducing an optically active Co(II)(salen) type complex, *N*,*N*′-bis(salicylaldehyde)-1(*R*),2(*R*)-1,2-*trans*-cyclohexanediiminatocobalt(II), Co(II)(sal)$_2$(*R*-CHXDA), with LiAlH$_4$; L-propylene oxide* was reacted in 95% selectivity.

In the course of further studies, it was found that D-propylene oxide, instead of the L-isomer, reacted preferentially when the Co(I) complex, prepared by reducing Co(II)(sal)$_2$(*R*-CHXDA) with butyllithium (BuLi), was used as a catalyst. This paper will describe the features of the kinetic resolution of DL-propylene oxide by use of the Co(I) complex prepared with BuLi. The effects of several metal alkyls and solvents on the asymmetric selectivity of the Co(I) complex will also be discussed in comparison with the case of the Co(II)(sal)$_2$(*R*-CHXDA)/LiAlH$_4$ system.

Experimental

Measurements. The absorption spectra were measured using a Shimadzu automatic recording spectrophotometer, Model MPS-50L. The CD spectra were taken on a Jasco Model J-20 spectrometer. The optical rotations were observed using a Perkin-Elmer Polarimeter Model 241. The glc analyses were carried out with a Hitachi Model K-53 Gas Chromatograph equipped with a column containing PEG.

Preparation of Cobalt Complexes. The reagents used were purified by the usual methods, as described elsewhere.[4] BuLi was prepared from *n*-butyl chloride and lithium metal; a cyclohexane solution of BuLi at the concentration of 1.42 mol/l was used. The Co(II)(sal)$_2$(*R*-CHXDA) was prepared by the method described in the previous paper.[3]

The Co(I) complex, Li$^+$[Co(I)(sal)$_2$(*R*-CHXDA)]$^-$, was prepared as follows: 0.05 mmol of Co(II)(sal)$_2$(*R*-CHXDA) was suspended in 50 ml of THF; then an equimolar amount of BuLi in cyclohexane added, and the solution was stirred for 1 hr at room temperature under a dry nitrogen atmosphere. A blue-green solution of the Co(I) complex was thus obtained. The evolved gases were analyzed by glc and calculated based on the amount of BuLi used. The Li$^+$[Co(I)(sal)$_2$(*R*-CHXDA)]$^-$/Lewis acid system was prepared by addition of an equimolar amount of a Lewis acid to the above solution of Li$^+$[Co(I)(sal)$_2$(*R*-CHXDA)]$^-$.

Reaction of the Co(I) Complex with DL-Propylene Oxide. 0.36 mmol of the Co(II) complex was suspended in a benzene (10 ml)/dioxane (5 ml) solvent (Tables 1 and 2) or an appropriate solvent (Tables 1 and 3); to which a cyclohexane solution of BuLi was added at the Co(II)/BuLi ratio of 1.0 or 2.0, after which the mixture was stirred for 2 hr at room temperature under a dry nitrogen atmosphere. In the case of the Co(I)/Lewis acid system (Table 2), a Lewis acid was added to the above solution at the ratio BuLi/Lewis acid=1.0 or 2.0, after which the mixture was stirred for 1 hr. Then 70 mmol of DL-propylene oxide was added to the above Co(I) solution. The mixture was sealed in an ampule under dry nitrogen and allowed to stand at 25 °C. After an appropriate reaction time, the non-reacted epoxide and acetone formed were analyzed by gas chromatography. The optical rotation of the recovered propylene oxide was measured.

The reaction of DL-propylene oxide with the Co(I) species prepared from the Co(II)/LiAlH$_4$ system was carried out similarly.

Results and Discussion

Preparation of Li$^+$[Co(I)(sal)$_2$(R-CHXDA)]$^-$. It has been reported that Co(II)(sal)$_2$(*R*-CHXDA) is a low-spin square-planar cobalt(II) complex with a λ conformation of the central chelate ring.[3] The absorption and CD spectra of the Co(I) species prepared by reducing Co(II)(sal)$_2$(*R*-CHXDA) with an equimolar amount of BuLi are shown in Figs. 1 and 2. The absorption spectrum in Fig. 1 is very similar to those of the reported Co(I) species[3] prepared by reducing Co(II)(sal)$_2$(*R*-CHXDA) with LiAlH$_4$ and with Na sand. The spectrum is also similar to that of Na$^+$[Co(I)(salen)]$^-$ observed by Calderazzo and Floriani.[5] Furthermore, by comparing the CD spectrum of the Co(I) species obtained from the Co(II) complex/BuLi system with that[3] of the Co(II) complex/LiAlH$_4$ system, these two Co(I) complexes are considered to have almost the same structure as to the co-planar ligand.

When the reaction of Co(II)(sal)$_2$(*R*-CHXDA) with

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* L-propylene oxide: (*S*)-L-(−)-propylene oxide, D-propylene oxide: (*R*)-D-(+)-propylene oxide.

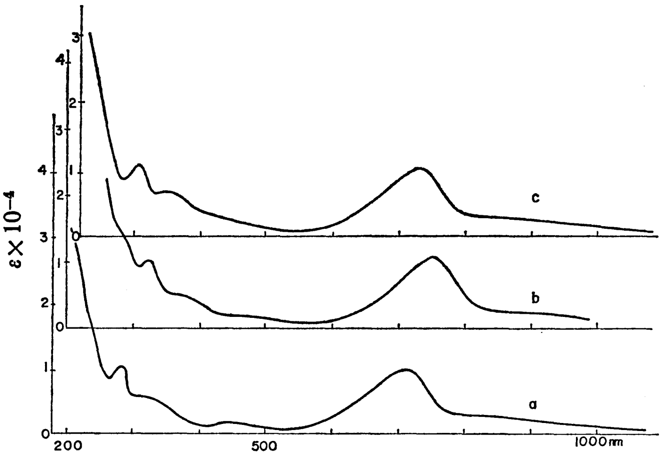

Fig. 1. The absorption spectra of the Co(I) species in THF.
(a) $Co(II)(sal)_2(R\text{-}CHXDA)/BuLi$
(b) $Co(II)(sal)_2(R\text{-}CHXDA)/LiAlH_4$
(c) $Co(II)(sal)_2(R\text{-}CHXDA)/Na$

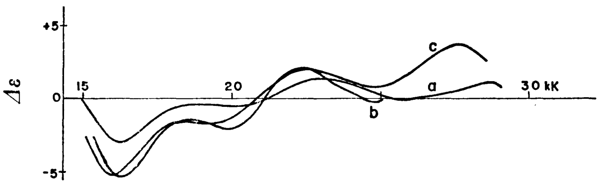

Fig. 2. The CD spectra of the Co(I) species in THF.
(a) $Co(II)(sal)_2(R\text{-}CHXDA)/BuLi$
(b) $Co(II)(sal)_2(R\text{-}CHXDA)/LiAlH_4$
(c) $Co(II)(sal)_2(R\text{-}CHXDA)/Na$

TABLE 1. ASYMMETRIC REACTION OF $Co(II)(sal)_2(R\text{-}CHXDA)/BuLi$ SYSTEM WITH PROPYLENE OXIDE (PO) IN VARIOUS SOLVENTS*

Solvent[a)]	Time (day)	Conv.[b)] (%)	$[\alpha]^{20}_{589}$[c)] (°)	⟪D/D+L⟫[d)] (%)	N[e)]	Acetone formed[f)] (%)
Diox	15	9.9	−0.59	68	20	100
Diox	18	11.3	−0.62	66	23	100
Bz/Diox	15	12.9	−0.33	58	25	95
Bz/Diox	16	14.0	−0.37	58	28	92
Bz/THF	18	14.0	−0.11	52	28	97
Tol	15	15.2	−0.32	56	31	94
o-Xyl	15	16.1	−0.06	51	33	100
m-Xyl	15	16.0	−0.06	51	32	90
Mes	16	16.3	−0.23	54	33	99
Bz/Tol	15	16.2	0	50	33	92
Bz/Tol[g)]	15	13.4	+0.08	(52)[h)]	27	99
Bz	15	16.5	+0.25	(54)[h)]	33	94
Bz/CHAN	18	11.7	+0.09	(52)[h)]	24	100

* $Co(II)/BuLi = 1$(mol/mol), $PO/Co(II) = 200$(mol/mol), temp.: 25 °C.

a) Bz: benzene, Diox: dioxane, THF: tetrahydrofuran, Tol: toluene, *o*-Xyl: *o*-xylene, *m*-Xyl: *m*-xylene, Mes: mesitylene, CHAN: cyclohexane; Bz/Diox = 2(v/v), Bz/THF = 2(w/w), Bz/Tol = 2(w/w), Bz/CHAN = 2(w/w). b) PO consumed(mol)/PO used(mol) × 100. c) $[\alpha]$ for unreacted PO recovered. d) L-PO percent in the total conversion of D- and L-PO. $⟪D/D+L⟫ = 1/2 \left\{1+\left(\frac{D-L}{D+L}\right)\right\} \times 100$, where $\left(\frac{D-L}{D+L}\right)$ is the optical purity of the reacted monomer. The optical purity of the reacted monomer is evaluated by the eq. $\left(\frac{D-L}{D+L}\right) = \frac{[\alpha]}{[\alpha_0]} \times \frac{100-(\text{conv.})}{(\text{conv.})}$, where $[\alpha]/[\alpha_0]$ is the optical purity of the unreacted monomer. $[\alpha_0]^{21}_{589} = +15°$ for D-PO[6)], (*cf.* Ref. 7). e) Recycling number for $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-$. N = PO consumed/$Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-$. Calcd on the assumption $[Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-] = [BuLi]$ used. f) Acetone formed(mol)/PO consumed(mol) × 100. g) Bz/Tol = 2.5(w/w). h) The values for ⟪L/D+L⟫.

BuLi was carried out in a benzene or toluene solvent, butane and 1- and 2-butene were evolved, while butane was evolved quantitatively in a dioxane solution. It is thus concluded that the Co(I) species, $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-$ was prepared with simultaneous formation of the butyl radical by the reaction between $Co(II)(sal)_2(R\text{-}CHXDA)$ and BuLi.

Resolution of DL-*Propylene Oxide with* $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-$. According to a previous study,[3)] L-propylene oxide was reacted selectively in a kinetic resolution of DL-propylene oxide using an optically active Co(I) complex prepared by the reaction of $Co(II)(sal)_2(R\text{-}CHXDA)$ with $LiAlH_4$. The reacted propylene oxide was isomerized to acetone quantitatively in the system at the ratio $Co(II)/LiAlH_4 = 3.0$, where the asymmetric selectivity** was very high, ⟪L/D+L⟫ = 95%. On the other hand, at the ratios $Co(II)/LiAlH_4 = 1.5$ and 1.0 the apparent percentage of acetone formed** and the asymmetric selectivity had lower values. This phenomenon was ascribed to side reactions involving the $LiAlH_4$ which remained in the system because of the incomplete reaction between $LiAlH_4$ and the Co(II) complex.

On the other hand, the reaction of BuLi with the Co(II) complex proceeds almost completely, resulting in the formation of a simple system of the Co(I) complex, which may be anticipated from the spectral similarity to behave as a catalyst similar to the $Co(II)(sal)_2(R\text{-}CHXDA)/LiAlH_4$ system.

In a typical experiment carried out in a benzene/dioxane mixed solvent, the reacted propylene oxide was found to be isomerized to acetone quantitatively even at the Co(II)/BuLi ratio of 1.0, the Co(I) species being recycled as shown by the recycling number of the catalyst, given in Table 1. Contrary to the anticipation from the spectral similarity between the Co(II) complex/$LiAlH_4$ system and the Co(II) complex/BuLi system, D-propylene oxide was preferentially reacted in the reaction with the latter catalyst. Resolution reactions with the Co(II)/BuLi system were carried out in various solvents, as summarized in Table 1. A group of solvents, such as dioxane, tetrahydrofuran, toluene, and cyclohexane, was found to favor the reaction with D-propylene oxide over the L-isomer, whereas benzene exhibited the opposite effect. For comparison, the solvent effect on the reaction with the

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** See the equations in Table 1.

TABLE 2. ASYMMETRIC REACTION OF $Co(II)(sal)_2(R\text{-}CHXDA)/LiAlH_4$ SYSTEM WITH PROPYLENE OXIDE IN VARIOUS SOLVENTS

Co(II)/$LiAlH_4$ (mol/mol)	PO/Co(II) (mol/mol)	Solvent[a]	Temp. (°C)	Time (day)	Conv.[b] (%)	$[\alpha]_{589}^{20}$ [c] (°)	⟨L/D+L⟩[d] (%)
1.0	200	Diox	23	29	13.0	+1.39	81
1.0	100	Diox	28	14	30.2	+2.40	69
1.0	100	THF	22	13	13.2	+0.33	57
1.0	260	Tol	23	14	4.1	+0.30	73
2.0	100	Bz	22	15	11.9	+1.04	76

a), b), c), d) Description as in Table 1.

TABLE 3. ASYMMETRIC REACTION OF $Co(II)(sal)_2(R\text{-}CHXDA)/BuLi/Lewis$ ACID SYSTEM WITH PROPYLENE OXIDE#

Lewis acid[a]	Co(II)/BuLi/Lewis acid (mol/mol/mol)	Time (day)	Conv.[b] (%)	$[\alpha]_{589}^{20}$ [c] (°)	⟪L/D+L⟫[d] (%)	N[e]	Acetone formed[f] (%)
$B(i\text{-}Bu)_3$	2/2/1	15	18.4	+0.07	51	37	96
	2/1/1	16	16.2	+0.16	53	65	94
	1/1/1	16	24.0	+0.75	58	24	94
$Al(i\text{-}Bu)_3$	2/2/1	15	23.0	+0.02	50	46	95
	2/1/1	16	31.5	+0.93	57	126	94
$Zn(n\text{-}Bu)_2$	2/2/1	15	8.7	+0.05	52	18	100
	2/1/1	16	6.5	+0.40	69	26	83
$InEt_3$	2/2/1	16	12.2	−0.29	(57)[g]	25	95
	2/1/1	15	15.2	+0.02	51	61	78
$Co(II)/B(i\text{-}Bu)_3=1$[h]		15	0	0	—	0	0

PO/Co(II) = 200(mol/mol), temp.: 25 °C, Bz/Diox = 2(v/v). a) $B(i\text{-}Bu)_3$: triisobutylborane, $Al(i\text{-}Bu)_3$: triisobutylaluminum, $Zn(n\text{-}Bu)_2$: dibutylzinc, $InEt_3$: triethylindium. b), c), d), e), f) Description as in Table 1. g) The value for ⟪D/D+L⟫. h) $Co(II)(sal)_2(R\text{-}CHXDA)/B(i\text{-}Bu)_3 = 1$(mol/mol) was used as a catalyst.

$Co(II)/LiAlH_4$ system was next examined. The $Co(II)/LiAlH_4$ system was found to attack L-propylene oxide selectively, regardless of the nature of the solvents used, as shown in Table 2. The selectivity is much higher than that of the Co(II)/BuLi system.

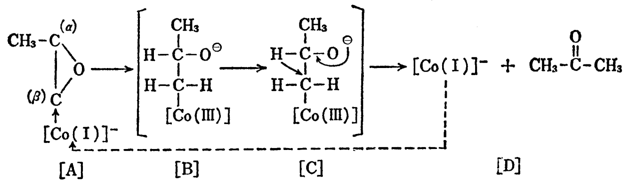
The remarkable difference in asymmetric selectivity between the Co(II)/BuLi and $Co(II)/LiAlH_4$ systems is of particular interest. It might be suspected that the AlH_3 moiety in the $Co(II)/LiAlH_4$ system interacts, as a Lewis acid, with the Co(I) species and plays a significant role in the asymmetric selectivity. Thus, the effect of a Lewis acid on the selectivity of the Co(I) species obtained from the Co(II) complex and BuLi was studied in the dioxane/benzene solvent. The results are summarized in Table 3. As expected, L-propylene oxide was preferentially consumed in a series of reactions involving triisobutylborane, triisobutylaluminum, dibutylzinc, and triethylindium as a Lewis acid, respectively. The results strongly suggest that the Lewis acids interact with the Co(I) species to form a "complex," for instance, $Li^+[Co(I)]^-\cdot$Lewis acid. The selection for L-propylene oxide was observed even at the ratio Co(II)/BuLi/Lewis acid=2/2/1, where comparable amounts of $Li^+[Co(I)]^-$ and $Li^+[Co(I)]^-\cdot$Lewis acid are considered to co-exist, the apparent selectivity ⟪L/D+L⟫ being lowered by the presence of the $Li^+[Co(I)]^-$, which prefers D-propylene oxide. The low selectivity for L-propylene oxide at the ratio $Co(II)/BuLi/InEt_3=2/1/1$ and the selection of D-propylene oxide at the 2/2/1 ratio can be explained by the weak interaction between the Co(I) complex and $InEt_3$ because of the weak Lewis acidity of $InEt_3$.[8]

It has been reported that a Lewis acid such as trialkylaluminum reacts with acetone.[9] In the series of reactions in Table 3, however, the reacted propylene oxide was converted to acetone almost quantitatively, and no further reaction was observed. The Lewis acids may be stabilized by complexation with the Co(I) species, as has been described.

It is considered that the Co(I) species of the $Co(II)/LiAlH_4$ system is present as a complex, $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-\cdot AlH_3$, in accordance with the asymmetric selectivity being similar to that of the Co(II)/BuLi/Lewis acid system.

Mechanism for the Kinetic Resolution of DL-Propylene Oxide. A probable mechanism for the resolution of DL-propylene oxide and the isomerization of propylene oxide to acetone was previously discussed.[3] As shown in Scheme 1, the Co(I) species attacks the β-carbon of propylene oxide by an S_N2 mechanism, thus forming Co–C bonding; this is followed by isomerization of the propylene oxide moiety to acetone, the Co(I) species regenerated being recycled as a nucleophilic reagent.

The kinetic resolution is considered to take place at



Scheme 1.

TABLE 4. THE CD SPECTRA OF $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-$, $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-\cdot Al(i\text{-}Bu)_3$ AND $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-\cdot AlH_3$ IN THF

	$\tilde{\nu}\times 10^{-3}$ cm^{-1} and $\Delta\varepsilon$ in parentheses			
$Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-$	28.3	23.0	19.8	16.1
	(+2.15)	(+1.21)	(−0.95)	(−3.03)
$Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-\cdot Al(i\text{-}Bu)_3$	28.2	22.7	19.4	16.1
	(+1.84)	(+1.21)	(−0.97)	(−2.93)
$Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-\cdot AlH_3$	—	22.4	19.9	16.3
		(+2.08)	(−2.06)	(−5.39)

the stage [A] in Scheme 1. The Co(I) species reacts with either D- or L-propylene oxides preferentially, leaving unreacted propylene oxides containing a higher ratio of the other enantiomer. The CD spectra were measured in order to clarify the difference in asymmetric selectivity between the Co(II)/BuLi system and the Co(II)/BuLi/Lewis acid system. The CD spectra of the Co(II)/$LiAlH_4$ system and the Co(II)/BuLi/Lewis acid systems exhibit shapes similar to, but with slight band shifts[†] compared to, that of the Co(II)/BuLi system, as is shown in Table 4; this indicates that these Co(I) complexes have almost the same structure as to the inplane ligand, with a λ conformation of the central chelate ring similar to that of $Co(II)(sal)_2(R\text{-}CHXDA)$. In the light of the structure of trialkyltin-cobaloxime(I), $Ph_3Sn\text{–}Co(Dmg)_2\cdot$Base, with a bond nature of $Sn^+\text{–}Co(I)^-$ reported by Schrauzer and Kralel,10) it may be considered that the lithium cation is situated above the square plane of the Co(I) complex. Some information has been previously presented as to the site of Lewis acids in Co(salen) complexes. In Co(II)(salen)·$CHCl_3$,11) Co(II)(salen)·InX_3,12) Co(II)(salen)·$SnX_4$13)(X: halogen), and $CH_3\cdot$Co(III)(salen)·H_2O-metal salt complexes,14) it has been reported that $CHCl_3$ is combined with a phenolic oxygen by hydrogen bonding and that the metal atoms of Lewis acids form bonding with two phenolic oxygens.

On the basis of the above discussions, a possible structure for $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-\cdot$Lewis acid including $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-\cdot AlH_3$ is depicted in Fig. 3. It should be easier for an incoming propylene oxide molecule to assume an orientation onto the active site as shown in Fig. 4; the bulky methyl group of propylene oxide and the Schiff-base ligand are far apart, because the left part of the diamine chelate is fixed below the square N_2O_2-plane due to the λ conformation. The chiral steric circumstance around the active site is established by the λ conformation of the central chelate ring, in co-operation with the Lewis acid moiety combined with pehnolic oxygens, which restricts the modes of orientation of the propylene oxide molecule. As shown in Fig. 4, L-propylene oxide would much more easily come to the Co(I) species, resulting in the high selectivity of the Co(II)/$LiAlH_4$ system to the L-isomer. Any orientation of D-propylene oxide could not be so easy as that of L-propylene oxide in Fig. 4 because of the steric hindrance caused by the right part of the diamine chelate fixed above the N_2O_2-plane and by the phenyl-azomethine parts and the AlH_3 placed on the same N_2O_2-plane, which were shown by the molecular-model consideration. In the absence of the Lewis acid moiety, the much smaller steric requirement around the active center would allow an incoming monomer to assume the orientation in a less specific way. According to our observation, D-propylene oxide exhibited a preference to the L-isomer in the reaction with $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-$, though strong steric interaction between the Co(I) complex and the monomer may not be expected.[††] The selection of L-propylene oxide by the Co(II)/BuLi system in benzene seems to be rather strange. Of interest, however, are the results of the X-ray analysis of the Co(II)(BAE)·benzene complex reported by Brückner *et al.*,15) where benzene is fixed to the two phenolic oxygen atoms by the van der Waals distances. If such a specific fixation of benzene around phenolic

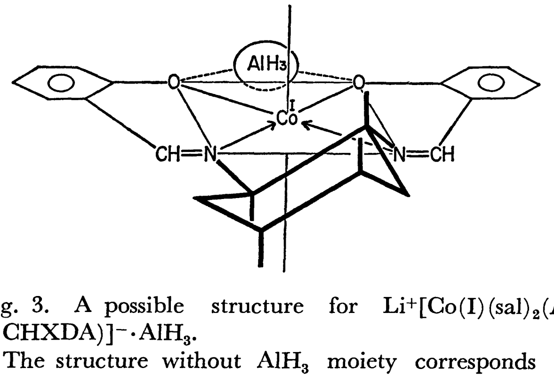


Fig. 3. A possible structure for $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-\cdot AlH_3$.
The structure without AlH_3 moiety corresponds to that for $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-$.

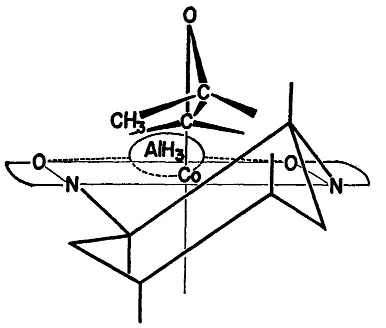


Fig. 4. Probable stereochemistry in the selection of a propylene oxide molecule by $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-\cdot AlH_3$.

[†] The shifts are considered to reflect the interaction between the Co(I) species and Lewis acid.

[††] The selectivities of the Co(II)/BuLi/Lewis acid systems can be interpreted in terms of those of mixed species, $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-\cdot$Lewis acid and $Li^+[Co(I)(sal)_2(R\text{-}CHXDA)]^-$.

oxygens is also present in the Co(II)/BuLi system, a chiral structure similar to that of the $Li^+[Co(I)(sal)_2(R\text{-CHXDA})]^-\cdot$Lewis acid system might be established around the active site.

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