The Enantioselective Dehydrogenation of Racemic Secondary Alcohols Catalyzed by Dimeric Ruthenium(II) Chiral Diphosphine Complexes

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The asymmetric dehydrogenation of racemic alcohols by an effective $Ru_2Cl_4((-)\text{-diop})_3$ (diop=2,3-*O*-isopropylidene-1,4-bis(diphenylphosphino)butane) was investigated with and without unsaturated hydrogen acceptors at 120—195 °C, with particular reference to the enantioselective factors and the reaction mechanism. The magnitude of enantioselectivity was substantially affected by the structures of the alcohols and of the hydrogen acceptors and by the reaction temperature; the hydrogen acceptors ($R^1CH=CHR^2$: $R^1 \neq H$ and $R^2 \neq H$) contributed to the enhancement of the selectivity through the newly formed asymmetric centers which result from their coordination to the chiral Ru(II) complex. The activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) obtained from the linear Arrhenius dependence of the rate constants of each enantiomer (*R*- or *S*-alcohol) established an isokinetic relationship, and the defference in the parameters of the each enantiomer ($\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$) also showed a satisfactorily linear correlationship between them. It is deduced from the present study that the enantioselection of *R*- and *S*-alcohols occurs at different coordination distances toward the chiral Ru(II) complex between the enantiomers under asymmetric circumstances.

Enantio-differentiating reactions with chiral transition-metal complexes have currently received considerable attention in the asymmetric hydrogenation (of prochiral olefins) which was originally developed in 1968.[1,2] Asymmetric induction by chiral metal complexes, especially by rhodium(I) chiral phosphine complexes, in the hydrogenation of prochiral olefins has been extensively investigated by taking notice of the structural effects of chiral ligands or of prochiral olefins on the optical yields of chiral products;[3-13] enantiomeric excesses of 95—96% are now possible in the asymmetric hydrogenation of α-(acylamino)acrylic acids by [Rh(1,5-cyclooctadiene)biphosphine]$^+BF_4^-$ (biphosphine=1,2-bis[(*o*-methoxyphenyl)phenylphosphino]ethane).[7,12]

On the other hand, the catalytic enantioselection of racemates with chiral metal complexes is also of interest and significant in connection with the asymmetric synthesis of chiral compounds with metal complexes. In our laboratory, Ru(II) chiral phosphine complexes were found catalytically effective for the enantioselective dehydrogenation of racemic alcohols with or without hydrogen acceptors.[14] Ru(II) chiral phosphine complexes have hitherto been the objects of only a limited investigation in terms of an examination of their asymmetric catalyses. In regard to chiral phosphine ligands, a diphosphine of (+)- or (−)-2,3-*O*-isopropylidene-1,4-bis(diphenylphosphino)butane (diop) has recently been accepted as an efficient chiral ligand when used in the rhodium-[5,8,15-24] and ruthenium-[25,26] catalyzed asymmetric hydrogenation of prochiral olefins, and it is also extensively used as a polymer-attached active phosphine ligand.[27-30] Therefore, we examined the efficiency of the diphosphine (diop) as a chiral ligand of ruthenium in the enantioselective dehydrogenation of racemic secondary alcohols (RR'CHOH) by $Ru_2Cl_4((-)\text{-diop})_3$[5] with and without unsaturated hydrogen acceptors ($R^1CH=CHR^2$):

$$\begin{array}{l} R\text{-RR'CHOH} \xrightarrow{k_R} \\ S\text{-RR'CHOH} \xrightarrow{k_S} \end{array} \begin{array}{l} \xrightarrow{Ru_2Cl_4((-)\text{-diop})_3} \\ \xrightarrow{R^1CH=CHR^2} \end{array} RR'C{=}O + R^1CH_2CH_2R^2 \quad (1)$$

where k_R and k_S denote, respectively, the pseudo-first-order rate constants for *R* and *S* enantiomers.

In the present work, some isolated crystalline complexes, such as $RuCl_2((+)\text{-bmpp})_3$ (bmpp=benzylmethylphenylphosphine) and an *in situ* prepared complex of $RuCl_2((+)\text{-nmdp})_3$ (nmdp=neomenthyldiphenylphosphine), were also used in Reaction 1 instead of the dimeric $Ru_2Cl_4((-)\text{-diop})_3$ complex for the sake of comparison.

Experimental

Materials. (−)-*O*-2,3-Isopropylidene-1,4-bis(diphenylphosphino)butane (diop) was prepared by Kagan's method,[5] and the chiral phosphines of (−)-*o*-methoxyphenylmethylphenylphosphine (*o*-ampp), (−)-propylmethylphenylphosphine (pmpp), and (+)-benzylmethylphenylphosphine (bmpp) were prepared according to Mislow *et al.*[31] (+)-Neomenthyldiphenylphosphine (nmdp) was made by means of Morrison's method.[32] $Ru_2Cl_4((-)\text{-diop})_3$ was supplied by James *et al.*,[25] and $RuCl_2((+)\text{-nmdp})_3$ was prepared *in situ* from $[(+)\text{-nmdp}]_0/[RuCl_2(PPh_3)_3]_0=6$. The other complexes, $RuCl_2((-)\text{-ampp})_2(PPh_3)$, $RuCl_2((-)\text{-pmpp})_3$, and $RuCl_2((+)\text{-bmpp})_3$, were made according to the phosphine-exchange method;[33] $RuCl_2\text{-}(PPh_3)_4$ and the chiral phosphine (in their molar ratio of 1:4) were refluxed in hexane for 1—10 h in a nitrogen atmosphere until a change in the solution color was observed, and satisfactory elementary analyses were obtained for the isolated crystalline complexes, as is shown below: $Ru_2Cl_4((-)\text{-diop})_3$: ^1H NMR ($CDCl_3$) δ 0.86 (s, 6H), 1.57 (broad, 12H), 3.02 (broad, 6H), 6.98 (m, 2OH), 7.18 (m, 40H). Found: C, 60.78; H, 5.73; Cl, 7.58%. Calcd for: C, 60.72; H, 5.22; Cl, 7.72%. $RuCl_2((-)\text{-ampp})_2(PPh_3)$: ^1H NMR ($CDCl_3$) δ 1.54 (d, 6H, J=4 Hz), 3.75 (s, 6H), 7.25 (m, 33H). Found: C, 61.80; H, 5.14; Cl, 7.82%. Calcd for: C, 61.74; H, 5.03; Cl, 7.94%. $RuCl_2((-)\text{-pmpp})_3$: ^1H NMR ($CDCl_3$) δ 0.80 (broad, 3H), 1.77 (broad, 7H), 7.23 (m, 5H). Found: C, 53.82; H, 6.57; Cl, 10.35%. Calcd for: C, 53.74; H, 6.77; Cl, 10.58%. $RuCl_2((+)\text{-bmpp})_3$: ^1H NMR ($CDCl_3$) δ 1.60 (broad, 3H), 3.45 (broad, 2H), 7.02 (m, 5H), 7.32 (m, 5H). Found: C, 62.01; H, 5.64; Cl, 8.61%. Calcd for: C, 61.92; H, 5.57; Cl, 8.70%.

Reaction Procedure and Optical Analysis. The dehydrogenation of freshly distilled secondary alcohols (1-phenyl-

ethanol and 1-phenyl-1-propanol) by the Ru(II) chiral phosphine complex was carried out without solvents at 120—195 °C in a N_2 atmosphere in the absence or in the presence of unsaturated hydrogen acceptors such as benzylideneacetone. After a desired conversion of the reaction was obtained, the unreacted alcohol was fractionally distilled under reduced pressure and then subjected to optical-rotation measurements. In the dehydrogenation of achiral alcohols such as benzyl alcohol with the Ru(II) chiral phosphine complexes at 120—195 °C, it was confirmed that the distilled alcohols include no optically active contaminants, such as the chiral Ru(II) complex, chiral ligands, and their decomposed products. To determine the optical purity of the alcohol enriched in one of the enantiomers, the average value of the optical rotations measured four times with a highly sensitive UNION PM-101 polarimeter was used as the observed one. The distribution of reaction products was followed by gas-chromatographic analyses, and some side reaction products, such as the racemic or meso bis(α-methylbenzyl) ether obtained from the dehydrogenation of 1-phenylethanol, were identified by means of 60 MHz ^{1}H NMR after their fractional collection by gas chromatography.

Results and Discussion

Pseudo-first-order Enantioselective Reaction. When the asymmetric dehydrogenation of the alcohol (8.34×10^{-2} mol) by using $Ru_2Cl_4((-)\text{-diop})_3$ (2 mM) or $RuCl_2L_3^*$ (L*=chiral ligand) (4 mM) was carried out with a hydrogen acceptor (6.84×10^{-2} mol) at 120—195 °C, the optical purity (O.P.) of the unreacted alcohol (RR'CHOH), obtained by fractional distillation without any optically active contaminants, increased with an increase in the conversion (Conv.), obeying pseudo-first-order rate law up to Conv. $\simeq$65% with a constant k_R/k_S ratio, which reflects the enantioselectivity (Table 1).

$$k_R = (\ln [R]_0/[R])/t$$
$$= \ln (10^4/(100-\text{Conv.})(100-\text{O.P.}))/t \quad (2a)$$
$$k_S = (\ln [S]_0/[S])/t$$
$$= \ln (10^4/(100-\text{Conv.})(100+\text{O.P.}))/t \quad (2b)$$

where $[R]_0$ and $[S]_0$ mean, respectively, the initial concentrations of the *R* and *S* enantiomers, and where *t* is the reaction time. As is indicated in Table 1, the present chiral Ru(II) catalyst produced acetophenone as the main dehydrogenation product of 1-phenylethanol, with a quantitative saturation of the unsaturated hydrogen acceptor, but small amounts of racemic and meso bis(α-methylbenzyl) ether (^{1}H NMR($CDCl_3$) δ 1.46 (d, 6H, J=6.4 Hz), 4.53 (q, 2H, J=6.4 Hz), 7.29 (s, 10H) and δ 1.40 (d, 6H, J=6.4 Hz), 4.25 (q, 2H, J=6.4 Hz), 7.31 (s, 10H)) were also detected, together with negligible amounts of styrene and ethylbenzene. The formation of such a side product of the ether was remarkably accelerated by RhCl((−)-diop) (prepared *in situ* from $[\text{diop}]_0/[(RhCl(C_2H_4)_2)_2]_0=3$); hence, the ruthenium-diop complex is superior to the rhodium-diop complex in terms of the promotion of the hydrogen transfer from the racemic alcohols to hydrogen acceptors, with a higher enantioselection of the former.

Efficiency of diop as a Chiral Ligand. In order to confirm the actual efficiency of diop as a chiral ligand of the Ru(II) complex in comparison with other chiral phosphine ligands, we examined the asymmetric dehydrogenation of 1-phenyl-1-propanol in the presence of benzylideneacetophenone at 165 °C with $Ru_2Cl_4((-)\text{-diop})_3$, $RuCl_2((-)\text{-ampp})_2(PPh_3)$, $RuCl_2((-)\text{-pmpp})_3$, $RuCl_2((+)\text{-bmpp})_3$, and $RuCl_2((+)\text{-nmdp})_3$. Although the enantioselective ability of the dimeric $Ru_2Cl_4((-)\text{-diop})_3$ complex is not directly comparable with those of the other monomeric derivatives ($RuCl_2L_3^*$ or $RuCl_2L_2^*(PPh_3)$: L*=chiral ligand), among the complexes tested, the diop ligand substantially brought about the highest activity for the binuclear $Ru_2Cl_4((-)\text{-diop})_3$ complex in the dehydrogenation and enantioselection of racemic 1-phenyl-1-propanol (Table 2). One could suppose, here, that the low enantioselective ability of $RuCl_2L_3^*$ (or $RuCl_2L_2^*(PPh_3)$), including the Mislow phosphine ligand (L*), was the result of the incomplete racemization of L* at 165 °C, even as the metal complexes. However, this is not true, because the $RuCl_2L_3^*$ (or $RuCl_2L_2^*(PPh_3)$) complex appreciably increased its dehydrolyzing and enantioselective ability even at temperatures higher than 165 °C; for example, $RuCl_2((-)\text{-ampp})_2(PPh_3)$ resulted in O.P.(Conv.)= 0.80% (50.5%), $k_R=6.59\times10^{-6}$ s^{-1}, $k_S=8.33\times10^{-6}$ s^{-1}, and $k_R/k_S=1.023$ at 185 °C in the same reactions in Table 2. Presumably, the slightly higher temperature promotes the dissociation of the chlorine atom from the Ru(II) complex so as to make active sites and that of

Table 1. Enantioselective dehydrogenation of 1-phenylethanol (8.34×10^{-2} mol) by $Ru_2Cl_4((-)\text{-diop})_3$ (2 mM) with benzylideneacetone (6.84×10^{-2} mol) at 165 °C

Time (h)	Conv. (%)	$-[\alpha]_D^{23}$ a) (deg)	O.P. (%)	10^6k_R (s^{-1})	10^6k_S (s^{-1})	k_R/k_S	Products (mol %) b) AP	PEE	Others
2	23.0	0.46	0.88	37.5	35.1	1.07	98.89	trace	—
3	32.7	0.65	1.24	37.8	35.5	1.06	83.56	15.51	0.93
4	41.0	0.92	1.75	37.9	35.4	1.07	87.01	12.33	0.66
6	54.9	1.28	2.44	38.0	35.7	1.06	88.00	11.38	0.62
8	65.3	1.49	2.84	37.8	35.8	1.06	88.37	11.17	0.46
48 c)	39.2	0.046	0.088	2.88	2.87	1.00_3	13.85	85.07	1.08
74 c)	53.7	0.084	0.16	2.89	2.88	1.00_3	28.80	70.67	0.53

a) $[\alpha]_D^{23}$ −52.5° (*c* 2.27, CH_2Cl_2).[41] b) AP=acetophenone; PEE=racemic or meso bis(α-methylbenzyl) ether; others=styrene and ethylbenzene. c) *in situ* prepared RhCl((−)-diop) (2 mM) formed from $[\text{diop}]_0/[(RhCl(C_2H_4)_2)_2]_0=3$ was used instead of $Ru_2Cl_4((-)\text{-diop})_3$.

Table 2. Enantioselective dehydrogenation of 1-phenyl-1-propanol (8.34×10^{-2} mol) by chiral ruthenium(II) complexes with benzylideneacetophenone ($6.84\times10^{-}$ mol) at 165 °C

Complex	Concn (mM)	Time (h)	Conv. (%)	$-[\alpha]_D^{20}$ a) (deg.)	O.P. (%)	10^6k_R (s^{-1})	10^6k_S (s^{-1})	k_R/k_S
$Ru_2Cl_4((-)\text{-diop})_3$	2.0	24	56.8	4.41	11.0	11.1	8.51	1.30
$RuCl_2((-)\text{-ampp})_2(PPh_3)$	4.0	78	51.8	0.04	0.09	2.60_2	2.596	1.00_2
$RuCl_2((-)\text{-pmpp})_3$	4.0	3	40.5	0.12	0.24	48.3	47.6	1.01
$RuCl_2((+)\text{-bmpp})_3$	4.0	70	26.3	0.54	1.36	1.27	1.16	1.09
$RuCl_2((+)\text{-nmdp})_3$	4.0	72	59.1	0.21	0.51	3.47	3.43	1.01

a) $[\alpha]_D^{17-20}$ +40.0° (*c* 5, C_6H_6).[42]

the hydrogen attached to the α-carbon in the alcohol.

Structural Effect of Hydrogen Acceptors. The addition of hydrogen acceptors to the reaction system substantially enhanced the enantioselection of the racemic alcohol by the chiral Ru(II) complex in comparison with that in the same reaction without hydrogen acceptors, and a structural effect of hydrogen acceptors on the enantioselectivity defined by k_R/k_S was observed (Table 3). Such a structural effect of hydrogen acceptors has also been reported in the enantioselective dehydrogenation of 1-phenylethanol by $RhCl((+)\text{-nmdp})_3$ prepared *in situ*[34] or by $RuCl_2((+)\text{-nmdp})_3$.[35] There are two possible explanations of such a structural effect of the hydrogen acceptors on the selectivity: (a) the change in the type of hydrogen acceptor affects the equilibrium of the $Ru_2Cl_4((-)\text{-diop})_3$ complex in the solution, if there is an equilibrium of the complex, and (b) the coordination of the unsaturated hydrogen acceptor ($R^1CH{=}CHR^2$) to the chiral Ru(II) complex gives rise to newly formed asymmetric centers, as is shown below:

$$R^1CH{=}CHR^2\ (R^1\neq H \text{ and } R^2\neq H) + (Ru) \rightleftharpoons \underset{\ast\quad\ast}{\overset{(Ru)}{R^1CH\text{——}CHR^2}}\ (I) \qquad (3)$$

where (Ru) denotes a catalytically active species supplied from $Ru_2Cl_4((-)\text{-diop})_3$.

The equilibrium of the bridged dimer complex of $(diop)Cl_2Ru\text{-}P\text{-}P\text{-}RuCl_2(diop)$ (P-P=diop) in solutions has not yet been established, but one species which can be obtained from the dimeric complex is $(diop)Cl_2RuP$ (P=ligand produced by the dissociation of P-P). Even though an equilibrium between $(diop)Cl_2Ru\text{-}P\text{-}P\text{-}RuCl_2$-(diop) and $(diop)Cl_2RuP$ could be expected in solutions, it seems unreasonable to explain the effect of $R^1CH{=}CHR^2$ on the selectivity only on the basis of the (a) explanation. On the other hand, the (b) explanation seems plausible because such newly formed asymmetric centers induced by the coordination of olefins to chiral metal complexes (*viz.*, platinum amine one) have

Table 3. Structural effect of hydrogen acceptors on the enantioselectivity in the dehydrogenation of 1-phenylethanol (8.34×10^{-2} mol) by $Ru_2Cl_4((-)\text{-diop})_3$ (2 mM) with hydrogen acceptors (6.84×10^{-2} mol)

Hydrogen acceptor	Temp (°C)	Time (h)	Conv. (%)	$-[\alpha]_D^{23}$ (deg.)	O.P. (%)	10^5k_R (s^{-1})	10^5k_S (s^{-1})	k_R/k_S
Benzylideneacetophenone	150	22.0	33.5	0.183	0.34	0.520	0.511	1.02
	170	14.0	23.9	0.175	0.34	0.548	0.535	1.02
	180	8.0	37.9	0.543	1.03	1.69	1.62	1.04
	190	5.0	48.4	1.77	3.37	3.87	3.49	1.11
Benzylideneacetone	120	34.0	18.5	0.152	0.29	0.234	0.228	1.03
	130	24.0	35.9	0.324	0.62	0.522	0.509	1.03
	150	6.0	27.1	0.303	0.58	1.49	1.44	1.03
trans-Stilbene	170	10.0	12.9	0.372	0.71	0.395	0.374	1.08
	180	10.0	20.3	0.620	1.18	0.665	0.600	1.10
	190	10.0	28.3	1.45	2.76	1.25	1.06	1.18
Ethyl cinnamate	170	5.0	22.8	0.599	1.14	1.50	1.38	1.09
	180	5.0	28.8	0.674	1.28	1.96	1.82	1.08
	190	4.0	37.9	1.44	2.74	3.51	3.13	1.13
2-Ethylhexyl methacrylate	170	5.0	37.4	2.98	5.68	2.93	2.29	1.28
	180	5.0	53.4	3.23	6.15	4.59	3.91	1.17
	190	4.0	72.4	2.24	4.27	9.25	8.66	1.07
(*E*)-α-Methylcrotonic acid[a]	165	8.0	65.4	2.55	4.85	4.17	3.84	1.09
None	170	8.0	11.6	0.063	0.120	0.431	0.422	1.02
	180	7.0	15.7	0.127	0.243	0.690	0.688	1.02
	190	6.0	21.1	0.154	0.294	1.11	1.08	1.03

a) e.e. of *R*-(−)-$MeCH_2CH(Me)CO_2H$ formed=21.0%.

already been confirmed.[36-38] Although, in the case of the platinum amine complexes, Reaction 3 has been established only at temperatures much lower than 120—195 °C,[36-38] the newly formed asymmetric centers in the (I) intermediate might not be completely diminished *via* the epimerization,[36-37] even in the present temperature range. The possibility of Reaction 3 is also supported by the fact that the prochiral (*E*)-α-methylcrotonic acid used as a hydrogen acceptor instead of achiral olefins was converted into a chiral species (*R*-(−)-$MeCH_2CH(Me)CO_2H$) in an enantiomeric excess of 21.0% in the dehydrogenation of 1-phenylethanol by $Ru_2Cl_4((-)\text{-diop})_3$ at 165 °C with O.P.= 4.85%(Conv.=68.4%) of *S*-(−)-1-phenylethanol (Table 3). This double asymmetric-transfer hydrogenation with Ru(II) chiral phosphine complexes seems promising; the details of an investigation which is now in progress will be presented in a succeeding paper.

In connection with the above structural effect of hydrogen acceptors on the enantioselectivity, the change in the type of hydrogen donor(RR'CHOH) also affected the magnitude of the selection by $Ru_2Cl_4((-)\text{-diop})_3$ (Table 4); the change from 1-phenylethanol to 1-phenyl-1-propanol affected the selectivity substantially.

Reaction Mechanism. If the induced asymmetry in the (I) intermediate plays an important role in the enhancement of the enantioselectivity, the coordination of the hydrogen acceptor to the chiral metal complex is required before the coordination of the alcohol to the complex can proceed; that is, the reaction between the alcohol and the (I) intermediate should be realized. In this regard, the increase in the concentration of the hydrogen acceptor with respect to that of the alcohol resulted in a monotonous acceleration of the reaction rate up to $[R^1CH{=}CHR^2]_0/[RR'CHOH]_0 \simeq 1$, but the excess concentration of $R^1CH{=}CHR^2$ ($[R^1CH{=}CHR^2]_0/[RR'CHOH]_0 > 1$) retarded the reaction (Fig. 1). This probably implies that the increase in the $R^1CH{=}CHR^2$ concentration raises the concentration of the (I) intermediate, which reacts with the alcohol in the following way:

$$\text{(I)} + RR'CHOH \xrightarrow{-H^+} \left[RR'CHO\text{—}(Ru)\begin{matrix}{}^{*}CHR^1\\ |\\ {}^{*}CHR^2\end{matrix}\right]$$

$$\longrightarrow \left[RR'C{=}O\text{—}(Ru)\begin{matrix}H\\ \\ {}^{*}CHR^1\\ |\\ {}^{*}CHR^2\end{matrix}\right]^{*}$$

$$\longrightarrow \left[RR'C{=}O\text{—}(Ru\text{-}H)\begin{matrix}{}^{*}CHR^1\\ |\\ {}^{*}CHR^2\end{matrix}\right]$$

$$\longrightarrow [RR'C{=}O\text{—}(Ru)\text{-}{}^{*}CHR^1CH_2R^2]$$

$$\xrightarrow{H^+} RR'C{=}O + R^1CH_2CH_2R^2 + (Ru) \qquad (4)$$

In the case of the excess concentration of $R^1CH{=}CHR^2$, the shielding of active sites of the (I) intermediate by $R^1CH{=}CHR^2$ depresses the reaction between the (I) intermediate and RR'CHOH in Reaction 4. The reaction between the (I) intermediate and RR'CHOH starts *via* the deprotonation of RR'CHOH. The deprotonation process, which corresponds to the rate-determing step, can be explained by the basicity effect on the rate enhancement in the dehydrogenation of alcohols; the dehydrogenation of ethanol by $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ is enhanced by potassium hydroxide,[39] and the transfer hydrogenation of benzylideneacetophenone by $PhCH(Me)O^-Na^+$ with $RuCl_2(PPh_3)_3$ is markedly accelerated as compared with the same reaction including PhCH(Me)OH instead of $PhCH(Me)O^-Na^+$.[40]

Activation-Parameter Relationships. The rate of the dehydrogenation of RR'CHOH by the (I) intermediate is dependent on the reaction temperature between the enantiomers; hence, the enantioselectivity defined by k_R/k_S comes to be affected by the temperature (Table 3). The temperature dependence of the rate constant for each enantiomer can be expressed by the linear Arrhenius relationship (Fig. 2); the activation param-

TABLE 4. ENANTIOSELECTIVE DEHYDROGENATION OF 1-PHENYL-1-PROPANOL BY $Ru_2Cl_4((-)\text{-diop})_3$ WITH PhCH=CHCOR (R=Ph AND Me)[a]

	Hydrogen acceptor		
	PhCH=CHCOPh		PhCH=CHCOMe
Temp/°C	165	175	165
Time/h	24	11	8
Conv./%	56.8	75.7	5.63
$-[\alpha]_D^{20}$/deg.	4.41	5.63	1.01
O.P./%	11.0	14.1	2.52
$10^6 k_R/s^{-1}$	11.1	39.6	33.1
$10^6 k_S/s^{-1}$	8.51	32.4	31.3
k_R/k_S	1.30	1.22	1.03

a) The reaction conditions are the same as in Table 1.

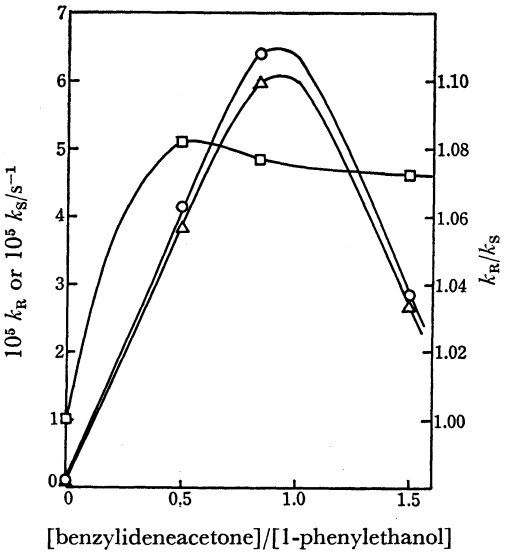

Fig. 1. Concentration effect of the hydrogen acceptor on the enantioselectivity in the dehydrogenation of 1-phenylethanol (8.34×10^{-2} mol) by $Ru_2Cl_4((-)\text{-diop})_3$ (2 mM) with benzylideneacetone at 165 °C. ((Conv. (%), AP(mol %), PEE (mol %) =A(45.7, 35.2, 64.4); B(25.0, 97.4, trace); C(28.4, 98.8, trace); D(18.2, 98.3, trace).) ○: k_R, △: k_S, □: k_R/k_S.

Table 5. Activation parameters obtained from the dehydrogenation of 1-phenyl-1-propanol by $Ru_2Cl_4((-)\text{-diop})_3$ with hydrogen acceptors[a)]

No.	Hydrogen acceptor	$\Delta H^{\ddagger}_R$	$\Delta H^{\ddagger}_S$ (kcal/mol)	$\Delta\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}_R$	$-\Delta S^{\ddagger}_S$ (e.u.)	$\Delta\Delta S^{\ddagger}$
1	Benzylideneacetone	20.36±0.11	20.30±0.15	0.06	33.11±0.26	33.31±0.36	0.20
2	Benzylideneacetophenone	38.89±0.03	37.27±0.05	1.62	−4.39±0.06	−0.72±0.06	3.67
3	*trans*-Stilbene	22.65±0.01	20.34±0.01	2.31	33.00±0.01	38.31±0.02	5.31
4	Ethyl cinnamate	16.41±0.02	15.86±0.02	0.55	44.51±0.02	45.91±0.02	1.40
5	2-Ethylhexyl methacrylate	22.64±0.03	26.26±0.03	3.62	29.10±0.02	21.41±0.02	7.69
6	None	18.42±0.00	18.32±0.00	0.10	42.33±0.00	42.61±0.00	0.28

a) The reaction conditions are the same as in Table 3, in which, also, the rate constants are specified.

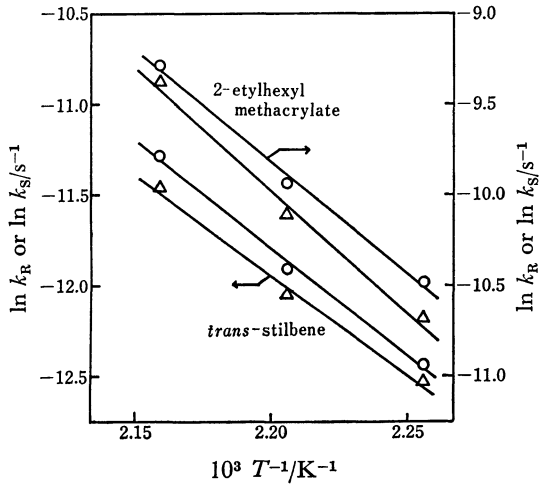

Fig. 2. Typical Arrhenius relationships of the present reaction. ○: R, △: S.

eters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) obtained for the series of experiments shown in Table 3 are summarized in Table 5. The activation parameters which reflect those for the rate-determining hydrogen-abstraction process in Reaction 4 established an isokinetic relationship well; that is, the smaller $\Delta H^{\ddagger}$ values for one of the enantiomers always require negatively larger $\Delta S^{\ddagger}$ values (Fig. 3). Such an isokinetic relationship is also obtained from the

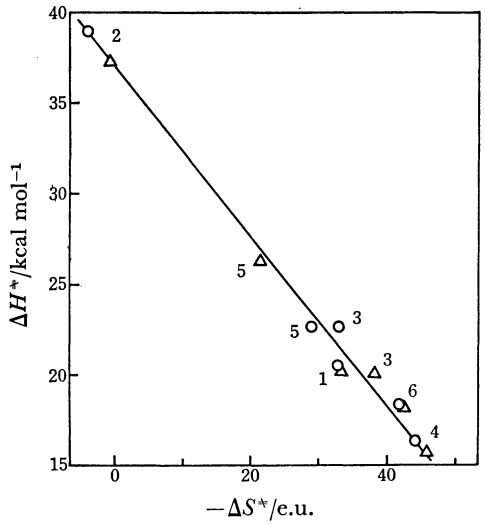

Fig. 3. An isokinetic relationship of the present reaction (numbers are the same as in Table 5). ○: R, △: S.

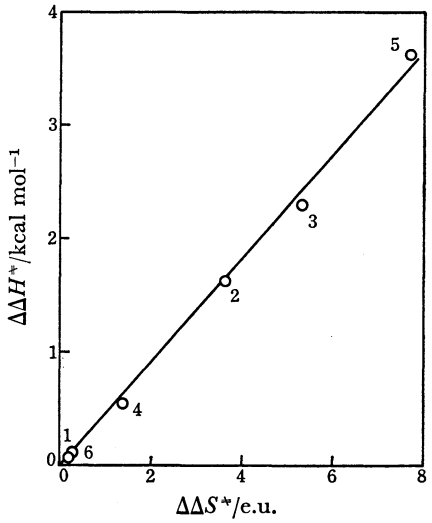

Fig. 4. Correlation between the $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values (numbers are the same as in Fig. 3).

reaction steps common to the present reaction, especially from the transition state shown in Reaction 4. The difference in the electronic factors reflected in $\Delta H^{\ddagger}$ between the *R* and *S* enantiomers ($\Delta H^{\ddagger}_R$ and $\Delta H^{\ddagger}_S$ respectively) leads to the idea that the coordination distance between the oxygen atom and the Ru metal in the transition state might be different between the enantiomers; the shorter coordination distance makes the $\Delta H^{\ddagger}$ value smaller, while requiring a negatively larger $\Delta S^{\ddagger}$ one. If this is true, the difference between the $\Delta H^{\ddagger}_R$ and $\Delta H^{\ddagger}_S$ values, $\Delta\Delta H^{\ddagger}$, will be correlated with that between the $\Delta S^{\ddagger}_R$ (for *R* enantiomer) and $\Delta S^{\ddagger}_S$ (for *S* one) values, $\Delta\Delta S^{\ddagger}$. In this respect, there is a linear correlationship between the $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values with the intersect of zero (Fig. 4). It may be deduced, therefore, that the enantioselective coordination of *R*- and *S*-RR'CHOH to the chiral complex occurs at a different coordination distance between the enantiomers under asymmetric circumstances (*viz.*, stereochemical influences of chiral ligands).

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