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Asymmetric Dehydrogenation of Secondary Carbinols by Ruthenium(II) Chiral Phosphine Complexes

KATSUTOSHI OHKUBO, TAKAYUKI SHOJI, AND KOHJI YOSHINAGA

Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860, Japan

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The magnitude of enantioselectivity in the dehydrogenation of racemic secondary carbinols catalyzed by Ru(II) chiral phosphine complexes with or without unsaturated hydrogen acceptors was shown to be substantially dependent on the equilibrium of the complex in the reaction system, the molecular asymmetry induced by unsaturated species, and on the reaction temperature. A completely linear isokinetic relationship was established between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values obtained for each enantiomer, and there was also a linear correlation between the differences of the above activation parameters for the enantiomers. Such kinetic relationships led to an assumption that the enantioselective process was controlled by the different coordination distance of each enantiomer to the chiral complex.

INTRODUCTION

Enantio-differentiating reactions with chiral transition-metal complexes have recently 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 Rh(I) chiral phosphine complexes, in the hydrogenation of prochiral olefins has been extensively investigated by taking notice of the structural effect of chiral phosphine ligands or of prochiral olefins on the optical yields of chiral products (*3–5*). In this regard, there are some reports dealing directly with the interaction between chiral metal complexes (*viz.*, platinum(II) complexes) and enantiomers (*6*, *7*).

More recently, asymmetric induction by chiral metal complexes has been studied in detail (*8–14*) with enantiomeric excesses of 95 to 96% in the hydrogenation of α-acylaminoacrylic acids (*8*, *13*).

However, the catalytic enantioselection of racemates with chiral metal complexes is also interesting in connection with the asymmetric synthesis of chiral compounds with the metal complexes. In our laboratory, Ru(II) chiral phosphine complexes were found to be catalytically active for the enantioselective dehydrogenation of racemic carbinols. The present paper describes an attempt to discuss how the enantioselective ability of chiral Ru(II) complexes for the asymmetric dehydrogenation of secondary carbinols depends on the equilibrium of the complex in the reaction system, the structures of unsaturated hydrogen acceptors (including molecular asymmetry induced by their coordination to the chiral complex), and the reaction temperature (involving thermodynamics of the reaction).

EXPERIMENTAL

Materials

Chiral phosphines of (−)-*o*-anisylmethylphenylphosphine (*o*-AMPP) (*15*), (−)-*p*-anisylmethylphenylphosphine (*p*-AMPP) (*15*), (−)-propylmethylphenylphosphine

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(PMPP) (*15*), (+)-benzylmethylphenylphosphine (BMPP) (*15*), (+)-neomenthyldiphenylphosphine (NMDP) (*16*), and (−)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane (DIOP) (*5*) were prepared according to the methods described previously. Ru(II) chiral phosphine complexes (except $Ru_2Cl_4(DIOP)_3$ (*17*) and $RuCl_3(NMDP)_3$ prepared *in situ* from NMDP and $RuCl_2(PPh_3)_3$) were obtained by refluxing the above chiral phosphine and $RuCl_2(PPh_3)_4$ (in their molar ratio of 4:1) in hexane for 1 to 10 hr under N_2 atmosphere until a change in the solution color was observed. The analytical results are shown below.

$RuCl_2(o\text{-AMPP})_2(PPh_3)$: ^1H NMR ($CDCl_3$) δ 1.54 (*d*, 6*H*, J = 4 Hz), 3.75 (*s*, 6*H*), 7.25 (*m*, 33*H*). Anal. Calcd: C, 61.74; H, 5.03; Cl, 7.94. Found: C, 61.80; H, 5.14; Cl, 7.82.

$RuCl_2(p\text{-AMPP})_2(PPh_3)$: ^1H NMR ($CDCl_3$) δ 1.65 (*d*, 6*H*, J = 3 Hz), 3.75 (*s*, 6*H*), 7.25 (*m*, 33*H*). Anal. Calcd: C, 61.74; H, 5.03; Cl, 7.94. Found: C, 61.17; H, 5.38; Cl, 7.71.

$RuCl_2(PMPP)_3$: ^1H NMR ($CDCl_3$) δ 0.80 (broad *m*, 3*H*), 1.77 (broad *m*, 7*H*), 7.23 (*m*, 5*H*). Anal. Calcd: C, 53.74; H, 6.77; Cl, 10.58. Found: C, 53.82; H, 6.57; Cl, 10.35.

$RuCl_2(BMPP)_3$: ^1H NMR ($CDCl_3$) δ 1.60 (broad, 3*H*), 3.45 (broad, 2*H*), 7.02 (*m*, 5*H*), 7.32 (*m*, 5*H*). Anal. Calcd: C, 61.92; H, 5.57; Cl, 8.70. Found: C, 62.01; H, 5.64; Cl, 8.61.

Reaction Procedure and Analysis

The dehydrogenation of freshly distilled secondary carbinols (1-phenylethanol, 1-phenyl-1-propanol, and 1-phenyl-2-propanol) by the Ru(II) chiral phosphine complex was carried out at 160 to 195°C under N_2 atmosphere with and without unsaturated hydrogen acceptors such as benzalacetone. After the desired conversion of the reaction was obtained, the unreacted carbinol was fractionally distilled under reduced pressure and was subjected to optical rotation measurements. In the dehydrogenation of achiral carbinols such as benzyl alcohol with the Ru(II) chiral phosphine complexes, it was confirmed that the distilled carbinols 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 carbinol enriched in one of the enantiomers, we used the average value of the optical rotation measured four times.

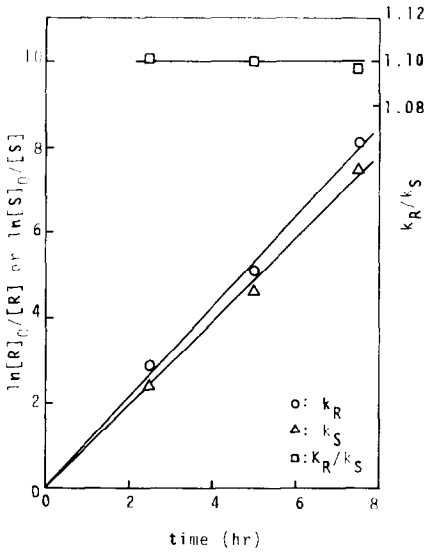


FIG. 1. A typical example of the present pseudo-first-order reaction (the dehydrogenation of 1-phenylethanol by 8 m*M* $RuCl_2(NMDP)_3$ prepared *in situ* from $[NMDP]_0/[RuCl_2(PPh_3)_3]_0 = 6$ in the presence of benzalacetone).

The product distribution was followed by gas chromatographic analyses, and some side reaction products such as racemic or *meso*-bis(1-phenylethyl) ether were analyzed by 60 MHz ^1H NMR after their fractional collection by the use of gas chromatography. A highly sensitive UNION PM-101 polarimeter (error within ±0.0004°) was used for the rotation measurements.

TABLE 1

Enantioselective Abilities of Some Ru(II) Chiral Phosphine Complexes in the Dehydrogenation of Racemic 1-Phenylethanol with Benzalacetone at 180°C[a]

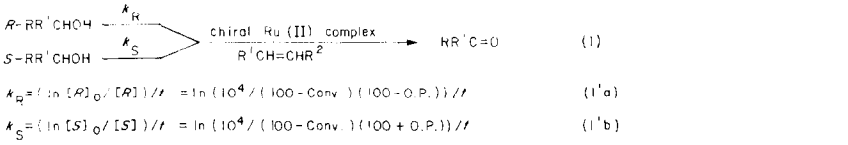
Complex	Concentration (mM)	Time (hr)	Conversion (%)	$[\alpha]_D^{23}$ [b] (deg)	O.P. (%)	$10^5 k_R$ (sec^{-1})	$10^5 k_S$ (sec^{-1})	k_R/k_S (sec^{-1})
$RuCl_2(NMDP)_3$[c]	8.0	5.0	38.2	−1.199	2.28	2.80	2.55	1.10
$RuCl_2$(*o*-AMPP)$_2(PPh_3)$	8.0	14.0	38.1	−0.684	1.30	0.974	0.923	1.06
$Ru_2Cl_4(DIOP)_3$	4.0	4.0	57.9	−0.923	1.76	6.13	5.89	1.04
$RuCl_2(BMPP)_3$	8.0	9.0	49.3	−0.469	0.90	2.13	2.07	1.03
$RuCl_2(PMPP)_3$	4.0	3.0	40.5	−0.124	0.24	4.83	4.76	1.01
$RuCl_2$(*p*-AMPP)$_2(PPh_3)$	8.0	5.0	63.5	+0.192	0.37	5.50	5.54	0.993

[a] $[\text{benzalacetone}]_0/[\text{1-phenylethanol}]_0 = 0.84$.
[b] $[\alpha]_D^{23}$ −52.5° (c 2.27, CH_2Cl_2) from (*21*).
[c] $[NMDP]_0/[RuCl_2(PPh_3)_3]_0 = 6$ and $[RuCl_2(PPh_3)_3]_0 = 8.0$ mM.

RESULTS AND DISCUSSION

Enantioselective Abilities of Chiral Ru(II) Complexes

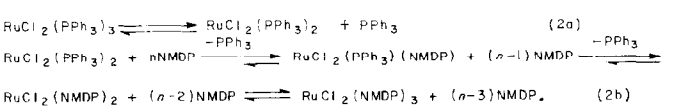
When the dehydrogenation of 1-phenylethanol, **I**, by the chiral Ru(II) complexes was carried out at 180°C with benzalacetone as a hydrogen acceptor, the optical purity (O.P.) of unreacted **I** enriched in *R*-(+)- or *S*-(−)-enantiomer increased monotonically with increasing conversion (Conv.), obeying a pseudo-first-order rate law, as reflected in the constant k_R/k_S ratio during the reaction (Fig. 1):



where the square brackets signify the concentration; the subscript zero = the initial state; t = reaction time; Conv./100 = $1 - ([R] + [S])/([R]_0 + [S]_0)$; O.P./100 = $([R] - [S])/([R] + [S])$.

In the case of the dehydrogenation of **I** (PhMeCHOH), the products consisted of acetophenone (AP) at more than 95 mol% in the products with small amounts of racemic or *meso*-bis(1-phenylethyl) ether (PEE), styrene, and ethylbenzene. The enantioselectivity (defined by k_R/k_S), which was very low but reproducible, was substantially dependent on the structure of the chiral phosphine ligand (Table 1). The chiral ligand possessing different and bulky substituents seems more effective, and the enantioselective ability follows the order: *in situ* prepared $RuCl_2(NMDP)_3$ > $RuCl_2$(*o*-AMPP)$_2(PPh_3)$ > (Ru_2Cl_4(DIOP)$_3$) > $RuCl_2(BMPP)_3$ > $RuCl_2$(PMPP)$_3$ > $RuCl_2$(*p*-AMPP)$_2(PPh_3)$, where $RuCl_2(NMDP)_3$ is not the sole complex (see later), and the bridged dimer complex of $Ru_2Cl_4(DIOP)_3$ is shown for the sake of comparison.

The enantioselective ability of the most effective $RuCl_2(NMDP)_3$, however, considerably suffered the concentration effect of the NMDP thereof, and the selective ability was the greatest around $[NMDP]_0/[RuCl_2(PPh_3)_3]_0 = 6$ (Fig. 2). This phenomenon is presumably relevant to the following equilibrium of $RuCl_2(NMDP)_3$ in the reaction system:



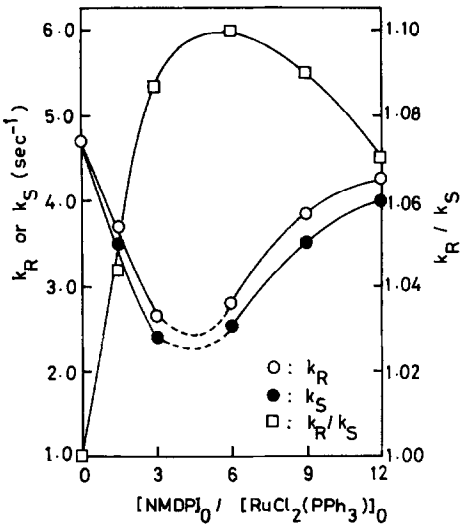


FIG. 2. Concentration effect of NMDP on the reaction rate and the enantioselectivity in the dehydrogenation of I by $RuCl_2(NMDP)_3$ (8.0 mM) with benzalacetone ([benzalacetone]$_0$/[I]$_0$ = 0.84) at 180°C.

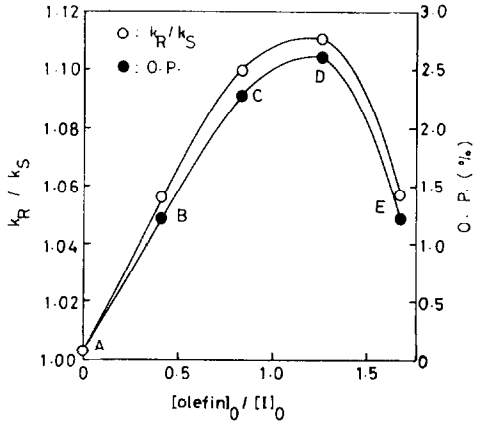


FIG. 3. Olefin concentration effect on the enantioselectivity in the dehydrogenation of I by $RuCl_2(NMDP)_3$ (8.0 mM) with benzalacetone at 180°C for 5 hr ([NMDP]$_0$/[$RuCl_2(PPh_3)_3$]$_0$ = 6). [Conv. (%), AP (mol%), PEE (mol%)] = A (19.4, 42.0, 47.3); B (36.7, 85.6, 10.2); C (38.2, 95.7, trace); D (38.5, 96.4, trace); E (37.0, 93.2, trace.)

In the case of

$$n = [NMDP]_0/[RuCl_2(PPh_3)_3]_0 < 6,$$

the presence of NMDP in the coordination sphere of $RuCl_2(PPh)_3$ decreases the dehydrolyzing ability of $RuCl_2(PPh_3)_3$ with diminution of the reaction rate, and the ligand exchange between PPh_3 and NMDP, which resulted in the formation of $RuCl_2(PPh_3)(NMDP)$, $RuCl_2(NMDP)_2$, and/or $RuCl_2(NMDP)_3$, also gives rise to a retardation of the reaction because the above Ru(II) complexes possessing the chiral NMDP ligand are catalytically less active than $RuCl_2(PPh_3)_3$. On the contrary, the formation of Ru(II) complexes involving the chiral NMDP ligand elevates the enantioselectivity with a monotonic decrease of the reaction rate up to $n \simeq 6$, and, at $n \simeq 6$, the amount of $RuCl_2(NMDP)_3$ seems to become largest among the chiral Ru(II) complexes.

At excess concentration of NMDP ($n > 6$), the selectivity was lowered by increasing the NMDP concentration; the excess free phosphine (NMDP) changes the above equilibria presumably through the promotion of the reverse reaction or the retardation of $RuCl_2(NMDP)_3$ formation and decreases the amount of $RuCl_2(NMDP)_3$ in comparison with $RuCl_2(NMDP)_2$. The result is that the selectivity becomes lowered by decreasing the $RuCl_2(NMDP)_3$ concentration with respect to the amounts of the other chiral Ru(II) complexes, [$RuCl_2(NMDP)_2$ and/or $RuCl_2(PPh_3)(NMDP)$]. In such a situation, the reaction rate per se starts to increase again, probably owing to the increase of the active $RuCl_2(NMDP)_2$ in comparison with $RuCl_2(NMDP)_3$. Increase in the basicity of the reaction system by the free phosphine also contributes to raising the reaction rate. In this respect, basic additives such as 2,5-xylidine markedly the reaction rate without any considerable change in the selectivity (an excess amount of the basic additive made the selectivity lower, possibly because of the shielding of the active sites of the complex through the coordination of the additive or the ligand exchange of the additive with the chiral phosphine). This basicity effect on the rate enhancement is directly related to the contribution of bases to the dissociation of the oxygen-bound proton from the

carbinol in the Reactions (3a) or (4b) below (*18*, *19*).

In the present reaction, the selectivity was also affected by the concentration of hydrogen acceptor with respect to the carbinol (Fig. 3).

$$RR'CHOH + (Ru) \xrightarrow{-H^+} [RR'CHO{-}(Ru)] \quad (3a)$$

$$RR'CHOH + H^+ \longrightarrow RR'CHOH_2^+ \xrightarrow{[RR'CHO{-}(Ru)]} (RR'CH)_2O \quad (3b)$$

((Ru) = chiral Ru(II) complex)

The low olefin concentration presumably prevents the intermediate [RR'CHO—(Ru)] from converting into RR'C=O and the hydride complex (Ru–H) because of the lack of the hydrogen acceptor, and it promotes the PEE formation via Reaction (3b). In Reaction (3b), the intermediate [RR'CHO—(Ru)] may also take part in the PEE formation, because the selectivity (k_R/k_S) cannot be kept constant during the reaction without the enantioselection in the PEE formation process expressed by Reactions (3a) and (3b). As Fig. 3 also indicates, the gradual increase in the olefin concentration makes the [PEE]/[AP] ratio smaller through the hydrogen transfer

TABLE 2

Enantioselectivity Change in the Dehydrogenation of 1-Phenylethanol by Molecular Asymmetry Induced by Hydrogen Acceptors[a]

No.	Hydrogen acceptor[b]	Temperature (°C)	Time (hr)	Conversion (%)	$-[\alpha]_D^{23}$ (deg)	O.P. (%)	$10^5 k_R$ (sec^{-1})	$10^5 k_S$ (sec^{-1})	k_R/k_S
		180	8	17.3	1.055	2.01	0.728	0.589	1.24
1	Benzalacetophenone	190	8	46.4	2.264	4.31	2.32	2.02	1.15
		195	8	81.2	2.514	4.79	5.98	5.65	1.06
		165	5	18.7	0.616	1.17	12.1	10.8	1.12
2	Benzalacetone	170	5	27.9	0.892	1.70	19.1	17.2	1.11
		180	5	38.2	1.199	2.28	28.0	25.5	1.10
		190	5	60.3	1.106	2.11	52.4	50.1	1.05
		180	8	26.2	0.053	0.10	1.09	1.05	1.04
3	*trans*-Stilbene	195	8	41.8	0.026	0.05	1.88	1.87	1.00_2
		165	8	7.6	0.046	0.09	0.278	0.272	1.02
4	Ethyl cinnamate	180	8	36.1	0.050	0.10	1.56	1.55	1.01
5	*n*-Dodecyl methacrylate	180	5	34.2	0.065	0.12	2.33	2.32	1.00_4
		170	9	14.0	0.145	0.28	0.475	0.458	1.04
6	2-Ethylhexyl methacrylate	190	7	36.7	0.855	1.63	1.88	1.75	1.07
7	*n*-Hexyl methacrylate	180	8	13.7	0.073	0.138	0.516	0.506	1.02
8	Secobarbital[c]	180	5	18.9	0.376	0.715	1.46	1.39	1.06
		165	5	11.3	0.035	0.07	0.673	0.665	1.01
9	None	180	5	19.4	0.023	0.04	1.20	1.19	1.01

[a] Catalyst: $RuCl_2(NMDP)_3$ (8 m*M*) prepared from $[NMDP]_0/[RuCl_2(PPH_3)_3]_0 = 6$.

[b] $[\text{hydrogen acceptor}]_0/[\text{carbinol}]_0 = 0.84$.

[c] Enantiomeric excesses of the chiral saturated species were not determined in order to simplify the table.

TABLE 3

Enantioselection of Secondary Carbinols by $RuCl_2(NMDP)_3$ with Benzalacetone[a]

No.	RR'CHOH		Temperature (°C)	Time (hr)	Conversion (%)	$-[\alpha]_D$[b] (deg)	O.P. (%)	$10^5 k_R$ (sec^{-1})	$10^5 k_S$ (sec^{-1})	k_R/k_S
	R	R'								
			160	7	26.2	0.840	1.60	1.27	1.14	1.11
10	Ph	Me	170	6	34.3	0.829	1.58	2.02	1.87	1.08
			180	5	47.3	0.912	1.74	3.66	3.47	1.05
			190	2	41.5	0.719	1.37	7.63	7.25	1.05
			170	7	26.3	0.549	1.37	1.26	1.16	1.09
11	Ph	Et	180	5	38.7	0.328	0.82	2.77	2.68	1.03
			190	3	36.4	0.401	1.00	4.29	4.10	1.05
			170	12	31.1	0.018	0.09	0.861	0.865	0.995
12	$PhCH_2$	Me	180	6	27.4	0.015	0.07	1.48	1.49	0.993
			190	4	39.9	0.018	0.09	3.53	3.55	0.994

[a] $[NMDP]_0/[RuCl_2(PPh_3)_3]_0 = 3$ and $[RuCl_2(PPh_3)_3]_0 = 8$ mM; $[benzalacetonel]_0/[carbinol]_0 = 1$.
[b] Ph(Et)CHOH: $[\alpha]_D^{17-20}$ +40.0° (c 5, C_6H_6) from (*22*); $PhCH_2$(Me)CHOH: $[\alpha]_D^{25}$ −20.2° (c 5, $C_2H_5OC_2H_5$) from (*23*).

from the carbinol to olefin via Reaction (3a) (see later) and results in the higher selectivity. However, the excess concentration of olefin suspends the selectivity, probably through a blocking of the active sites of the complex by the olefin thereof. In fact, the reaction rate increased monotonically up to $[olefin]_0/[I]_0 = 1.26$, but it decreased in excess olefin concentration: ($[olefin]/[I]$; k_R, k_S) = (0.0; 1.21, 1.19), (0.42; 2.61, 2.47), (0.84; 2.80, 2.55), (1.26; 2.85, 1.56), and (1.68; 2.64, 2.50) under the conditions shown in Fig. 3.

Molecular Asymmetry Induced by Unsaturated Hydrogen Acceptors

The enantioselectivity was also found to vary from olefin to olefin, and representative results are shown in Table 2 by taking the dehydrogenation of **I** by the *in situ* prepared $RuCl_2(NMDP)_3$. There are

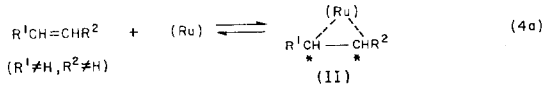
TABLE 4

Activation Parameters[a]

Experiment	$\Delta H_R^{\ddagger}$	$\Delta H_S^{\ddagger}$ (kcal/mol)	$\Delta\Delta H^{\ddagger}$	$-\Delta S_R^{\ddagger}$	$-\Delta S_S^{\ddagger}$ (e.u.)	$\Delta\Delta S^{\ddagger}$
1	29.3	31.5	2.2	18.2	13.8	4.4
2	23.0	23.8	0.8	28.7	27.2	1.5
3	14.5	15.4	0.9	50.2	48.2	2.0
4	44.5	45.0	0.5	−16.8	−17.8	1.0
6	27.2	26.5	0.7	22.4	24.1	1.7
9	14.3	14.5	0.2	50.3	49.9	0.4
10	23.0	23.8	0.8	28.7	27.2	1.5
11	23.9	24.9	1.0	27.6	25.7	1.9
12	27.9_7	27.9_9	0.02	19.6	19.5	0.1

[a] The experimental errors of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are within ±0.09 kcal/mol and ±0.08 e.u., r espectively. Th experiment numbers are the same as in Tables 2 and 3.

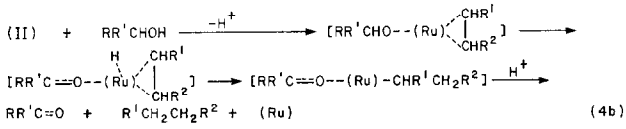
two possible explanations concerning the structural effect of the hydrogen acceptors on the selectivity: (a) The change in the type of the hydrogen acceptor affects the equilibrium of the complex (for example, the distribution of $RuCl_2(PPh_3)(NMDP)$, $RuCl_2(NMDP)_2$, and $RuCl_2(NMDP)_3$ in Reactions (2a) and (2b) and brings about the different selectivity and (b) the coordination of the unsaturated hydrogen acceptor to the chiral Ru(II) complex gives rise to a new chiral field.



(4a)

Such a structural effect of the hydrogen acceptor on the selectivity can be recognized in the cases of the dehydrogenation of the carbinols catalyzed by other complexes. For example, k_R/k_S (olefin) = 1.11 (benzalacetophenone), 1.06 (2-ethylhexyl methacrylate), and 1.03 (none) in the dehydrogenation of **I** by $Ru_2Cl_4(DIOP)_3$ at 190°C. In this sense, explanation (b) seems more reasonable, even though the induced molecular asymmetry of olefins coordinated with platinum(II) amine complexes is confirmed only at temperatures much lower than 160 to 195°C in the present experiments (*6*, *7*); that is, the newly formed asymmetric centers in the intermediate (**II**) might not be completely diminished via the epimerization (*6*) at the temperature range 160 to 195°C.

Among the hydrogen acceptors tested, two unsaturated ketones of PhCH=CHR (R = acetyl and benzoyl) were the most effective in terms of the enhancement of the selectivity, though PhCH=CHPh was markedly less effective than the above ketones. Hence, one could suppose that, with the particular hydrogen acceptors (the unsaturated ketones) chosen, the formation of phosphobetaine can be expected from the reaction of the above ketone with the chiral ligand (*20*), especially in the case of the *in situ* prepared complex, and the phosphobetaine ($R_3'\overset{+}{P}CH(Ph)CH=C(R)\bar{O}$) is then bound in the metal complex as a new chiral ligand. The unsaturated esters such as methacrylate ones (except 2-ethylhexyl methacrylate possessing an asymmetric carbon center) were found to be relatively less effective, probably because the negatively charged oxygen binds the ester to the metal complex and disturbs the coordination of the chiral ligand in the case of the *in situ* prepared complex. At any rate, the structural effect of the hydrogen acceptors was substantially recognized in terms of the change of the selectivity, probably via Reaction (4a), which is followed by the following subsequent reactions:



(4b)

The participation of the free proton in Reaction (4b) has already been confirmed in the transfer hydrogenation of benzalacetophenone by the deuterated 1-phenylethanol with $RuCl_2(PPh_3)_3$ (*19*). Through Reactions (4a) and (4b), the abstraction of the α-carbon-bound hydrogen by the Ru metal is the rate-determining step (*19*), and the change in the structures of RR'CHOH (viz., (R, R') = (Ph, Me), (Ph, Et), and ($PhCH_2$, Me)) showed different reaction rates and enantioselectivities

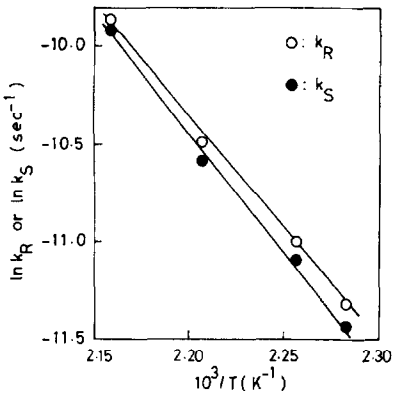


FIG. 4. Arrhenius plots of rate constant vs $1/T$ in the dehydrogenation of **I** by $RuCl_2(NMDP)_3$ with benzalacetone (rate constants are specified in Table 2).

(Table 3). The selectivity order was not simply reflected in the bulkiness of the substituents (R and R′).

Activation Parameter Relationships

The enantioselectivity was also dependent on the reaction temperature and was raised by lowering the temperature (Tables 2 and 3). Presumably, the lower temperature makes the interactions among

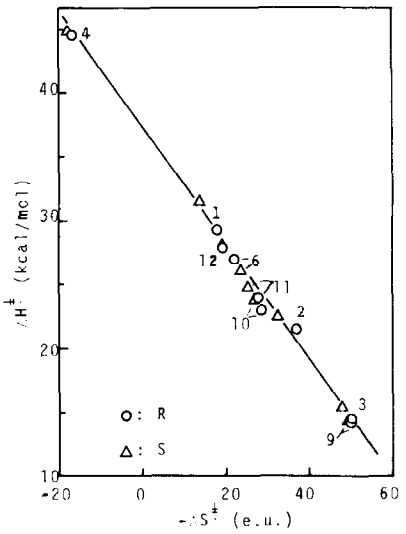


FIG. 5. Isokinetic relationship (numbers are the same as in Tables 2 and 3).

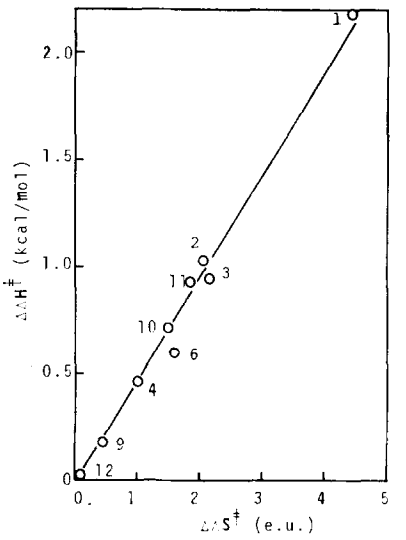
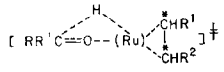


FIG. 6. Linear correlation between $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values.

the species in Reactions (4a) and (4b) more rigid. The temperature dependence of the reaction rate in the present reaction was expressed by the linear Arrhenius dependence of the rate constant for each enantiomer, and a typical example is shown in Fig. 4. The activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) are summarized in Table 4. Notably, the activation parameters which reflect those for the rate-determining hydrogen-abstraction process in Reaction (4b) well established an isokinetic relationship; that is, the smaller $\Delta H^{\ddagger}$ values for one of enantiomers always require negatively larger $\Delta S^{\ddagger}$ values (Fig. 5). Such an isokinetic relationship is obtainable from the reaction steps common to the present reaction, especially from the following transition state of the reaction:



In view of the fact that the $\Delta H_R^{\ddagger}$ (for *R*-enantiomer) and $\Delta H_S^{\ddagger}$ (for *S*-enantiomer) values are substantially different from each other and require different $\Delta S^{\ddagger}$ ($\Delta S_R^{\ddagger}$ and $\Delta S_S^{\ddagger}$ for respective *R*- and *S*-enantiomers) values in the isokinetic rela-

tion, the coordination distance between the carbonyl oxygen and the Ru metal in the above transition state might be different between the enantiomers. The shorter coordination distance probably makes the $\Delta H\ddagger$ value smaller, requiring the negatively larger $\Delta S\ddagger$ value. If this is true, the difference ($\Delta\Delta H\ddagger$) between the $\Delta H_R\ddagger$ and $\Delta H_S\ddagger$ values might have a correlation with the ($\Delta\Delta S\ddagger$) between the $\Delta S_R\ddagger$ and $\Delta S_S\ddagger$ values. In this regard, there is a linear correlation between the $\Delta\Delta H\ddagger$ and $\Delta\Delta S\ddagger$ values with intercept zero (Fig. 6). Presumably, such a correlation emphasizes the enantioselective process controlled by steric factors (reflected by $\Delta S\ddagger$) which compensate electronic ones (reflected by $\Delta H\ddagger$); The hydrogen migration from RR'CHOH to the Ru(II) complex and the enantioselective coordination of RR'CHOH to the complex might simultaneously occur in the different coordination distance between the enantiomers.

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