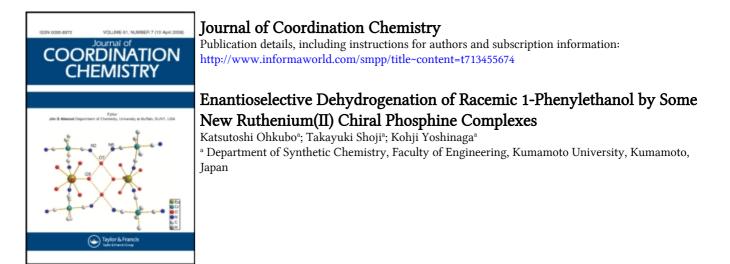
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SHORT COMMUNICATION Enantioselective Dehydrogenation of Racemic 1-Phenylethanol by Some New Ruthenium(II) Chiral Phosphine Complexes

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INTRODUCTION

Ruthenium(II) triphenylphosphine complexes are known to catalyze the transfer hydrogenation of olefins by primary or secondary carbinols:¹

RR'CHOH + C = C $RuCl_{2}(PPh_{3})_{3} \text{ or } RuH_{2}(PPh_{3})_{4}$ $RR'C = O + CHCH \qquad (1)$

When the above reaction is carried out with Ru(II) chiral phosphine complexes, an enantioselective dehydrogenation of racemic RR'CHOH could be expected.

The present authors report, here, on the enantioselective dehydrogenation of racemic 1-phenylethanol, I, by isolated crystalline Ru(II) chiral phosphine complexes² of RuCl₂((-)-o-ampp)₂(PPh₃), RuCl₂((-)-p-ampp)₂(PPh₃), RuCl₂((+)-bmpp)₃, RuCl₂((-)-pmpp)₃, and Ru₂Cl₄((-)-diop)₃ (note Table I) or by RuCl₂((+)-nmdp)₃ and RuBr₂((+)nmdp)₃ (nmdp = neomenthyldiphenylphosphine) prepared *in situ* from RuCl₂(PPh₃)₃ (and/or RuBr₂-(PPh₃)₃) and nmdp.

The enantioselective dehydrogenation of I by the above chiral Ru(II) complexes at 120–190°C in the presence of benzylideneacetone resulted in the appreciably predominant consumption of one of the enantiomers with an almost quantitative formation of acetophenone. The enantioselectivity was very low but reproducible, and the optical purity (O.P.) of I obtained by fractional distillation without any contaminants possessing the optical rotation increased with increasing conversion (Conv.), obeying a pseudo-first-order rate law reflected in almost constant $k_{\rm R}/k_{\rm S}$ ratio under Conv. 70% (see Table I):

$$\begin{array}{c} \text{R-(+)-I} & \xrightarrow{k_{\text{R}}} \\ \text{S-(-)-I} & \xrightarrow{k_{\text{S}}} \\ \end{array} \xrightarrow{\text{chiral Ru(II) complex}} \text{RR'C = 0} \quad (2) \end{array}$$

where each rate constant was evaluated by $k_{\rm R} = (\ln[{\rm R}]_0/[{\rm R}])/t = -(\ln(100\text{-Conv.})(100 - 0.{\rm P.})/10^4)/t \ k_{\rm S} = (\ln[{\rm S}]_0/[{\rm S}])/t = -(\ln(100 - 0.{\rm P.})/10^4)/t$ $Conv.)(100 + O.P.)/10^4)/t$ (t: reaction time). The results of a representative series of the experiments are shown in Table I. There was no regularity between the selection of the R or S isomer and the optical rotation (+ or -) of the complex or the chiral phosphine, and the magnitude of the enantioselectivity (defined by k_R/k_S) showed no direct correlation with the dehydrogenation rate and the molecular rotation $([\alpha]_M)$ of the complex or the phosphine.³ These facts may imply that the reaction course and the coordination distance of RR'CHOH toward a complex in Reaction(3c) are not systematically constant. However, it can be said that the unsaturated additive of benzylideneacetone substantially increases the selectivity, in comparison with the results of the dehydrogenation of I without olefins, via the induced asymmetry⁴ shown by the intermediate II in Reaction(3b). In this respect, the hydrogenation of benzylideneacetophenone by I with $RuCl_2((+)-nmdp)_3$ or that of 2-ethylhexylmethacrylate by I with $Ru_2 Cl_4((-)-diop)_3$ at 180°C under the same conditions as in Table I resulted in $k_{\rm R}/k_{\rm S}$ = 1.27 (O.P. = 2.01% at Conv. = 17.3%) and

TARIFI	Enantioselective dehydrogenation of I by Ru(II) chiral phosphine complexes in the presence of benzylideneacetone ^a
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Complex ^b	Temp.	Time	Conv.	[α] 23 ^c	0.P.	10, k _S	10 ° k S	k _R /kS	ΔH [‡] ΔH [‡]	-Δs [‡] -Δs [‡]
(^W [∞])	(c)	(hr)	(%)	(deg.)	(%)	(sec ⁻¹)	(sec ⁻¹)		(kcal/mol)	(e.u.)
	165	5.0	18.7	-0.616	1.17	12.1	10.8	1.12	21.1 ± 0.6	32.7±1.3
	(165)	(0.2)	(11.3)	(-0.035)	(0.01)	(6.73)	(6.65)	(1.01)	22.5 ± 0.7	30.6 ± 1.4
	170	5.0	27.9	-0.892	1.70	19.1	17.2	1.11	1.4	2.1
RuCl ₁ ((+)-	180	2.5	22.8	-0.910	1.73	30.7	26.9	1.14		
nmdp) ₃	180	5.0	38.2	-1.199	2.28	28.0	25.5	1.10		
	(180)	(2.0)	(19.4)	(-0.023)	(0.044)	(12.0)	(11.9)	(1.01)	(14.3)	(20.3)
	180	7.5	54.1	-1.613	3.07	30.0	27.7	1.08	(14.5)	(49.9)
	190	5.0	60.3	-1.106	2.11	52.4	50.1	1.05	(0.2)	(0.4)
RuBr ((+)-	170	5.0	23.5	-0.899	1.71	15.8	13.9	1.14	34.3 ± 0.1	3.81 ± 0.1
nmdn)	180	2.0	28.6	-0.293	0.56	47.6	46.1	1.03	36.1 ± 0.1	-0.01 ± 0.1
6/Janua	190	1.0	27.1	-0.321	0.61	89.4	86.4	1.03	1.8	3.82
RuCl ₁ ((-)-0-	160	30.0	8.56	0.088	0.17	0.85	0.88	0.96	41.6 ± 0.1	-8.88 ± 0.1
umpp),(PPh,)	170	24.0	21.29	0.170	0.32	2.69	2.76	0.97	39.8 ± 0.1	-4.97 ± 0.2
(-2600°)	180	10.0	51.58	-1.645	3.13	21.0	19.3	1.09	1.8	3.91
RuCl((-)-p-	160	7.0	36.63	0.100	0.19	18.3	18.4	0.99,	$20.69 \pm 0.0_3$	-33.31
ampp) ₁ (PPh ₃)	170	6.0	45.31	0.136	0.26	27.6	27.8	0.993	$20.67 \pm 0.0_3$	-33.34
(-26.7°)	180	5.0	63.47	0.192	0.37	55.0	55.4	0.99	0.02	0.03
RuCl. ((+)-	160	24.0	54.73	-0.335	0.64	9.25	9.10	1.02	16.5 ± 0.5	44.3±1.1
mnn).	170	17.0	61.82	-0.518	0.99	15.9	15.6	1.02	16.3 ± 0.5	44.6 ± 1.1
(-685 4°)	180	9.0	49.31	-0.469	0.89	21.3	20.7	1.03	0.2	0.3
	190	8.0	63.89	-0.726	1.38	35.9	34.9	1.03		
RuCl ₂ ((-)-	160	14.5	34.24	0.379	0.72	7.89	8.17	0.99	4.18	73.0
$pmpp_{3}(+260^{\circ})$	170	12.0	32.36	0.096	0.18	9.01	9.09	0.99	3.22	75.2
									0.96	2.2
Ru, Cl, ((-)-	120	34.0	18.51	-0.152	0.09	2.35	2.28	1.03	20.4 ± 0.1	33.1 ± 0.3
diop),	130	24.0	35.94	-0.324	0.62	5.23	5.09	1.03	20.3 ± 0.2	33.3 ± 0.4
+6938~)	150	6.0	27.10	-0.303	0.58	14.9	14.4	1.03	0.1	0.2

 b_1^{c} complex]₀ = 8.0 mM except [Ru₂Cl₄((-)-diop]₀ = 4.0 mM. ampp = anisylmethylphenylphosphine; bmpp = benzylmethylphenyl-phosphine; pmpp = propylmethylphosphine; diop = 2,2-dimethyl4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane. $c[\alpha] \hat{D}_3^3 - 52.5^\circ$ (c 2.27, CH₂Cl₂).⁶ Italic values are parameter difference between the isomers, and values in parentheses are those for the reaction without olefins.

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 $k_{\rm R}/k_{\rm S} = 1.175$ (O.P. = 6.15% at Conv. = 53.4%), respectively. At any rate, it is notable from the linear Arrhenius-dependence of each rate constant $(k_{\rm R}$ or $k_{\rm S}$) being kept constant during the reaction that the smaller enthalpy of activation (ΔH_R^{\ddagger} or ΔH_S^{\ddagger} for the R or S isomer respectively), which almost corresponds to that for the rate-limiting step of the α -carbonbound hydrogen abstraction by the complex in Reaction(3d),⁵ requires more negative entrophy of activation (ΔS_R^{\ddagger} or ΔS_S^{\ddagger}) and that the order of the difference between the ΔH_R^{\ddagger} and ΔH_S^{\ddagger} values, $\operatorname{RuCl}_2((-)\operatorname{-o-ampp})_2(\operatorname{PPh}_3) \cong \operatorname{RuBr}_2((+)\operatorname{-nmdp})_3 > RuCl_2((+)-nmdp)_3 \ge RuCl_2((-)-pmpp)_3 > RuCl_2$ $((+) \cdot bmpp)_{3} > Ru_{2}Cl_{4}((-) \cdot diop)_{3} > RuCl_{2}((-) \cdot diop)_{3$ $p-ampp)_2(PPh_3)$, is well reflected in that of the difference between the ΔS_{R}^{\pm} and ΔS_{S}^{\pm} values. Namely, an isokinetic relationship (linear relation between ΔH^{\dagger} and ΔS^{\dagger}) can be realized if one plots the parameters each other. From the latter fact mentioned above, the increase in the difference of the ΔS^{\sharp}_R and ΔS^{\sharp}_S values substantially elevates that of the ΔH_R^{\ddagger} and ΔH_S^{\ddagger} values with a linear correlation between $\Delta\Delta S^{\dagger} (= \Delta S_{R}^{\dagger} - \Delta S_{S}^{\dagger})$ and $\Delta\Delta H^{\dagger} (= \Delta H_{R}^{\dagger} - \Delta S_{S}^{\dagger})$ ΔH_{S}^{\dagger}). It is deduced, therefore, that the enantioselective process in Reaction(3c) might be controlled by steric factors (reflected in ΔS^{\dagger}) compensating electronic ones (reflected in ΔH^{+}).

$$\operatorname{RuCl}_2 L_3^* \longrightarrow \operatorname{RuCl}_2 L_2^* \operatorname{Ru} + L^*$$
 (3a)

$$Ru + R^{1}CH = CHR^{2} \xrightarrow{Ru} II$$

$$R^{1}HC - CHR^{2} II$$
(3b)

II + RR'CHOH
$$\xrightarrow{-H^{+}}$$

[RR'CHO---Ru $< \stackrel{CHR^{1}}{\underset{CHR^{2}}{\overset{I}}$] III (3c)

III
$$\xrightarrow{\text{rate-limiting step}^5}$$

[RR'C-O-- Ru-- CHR¹CH²R²] $\xrightarrow{\text{H}^{+6}}$ RR'C = O +
R¹CH₂CH₂R² + Ru (3d)

Interestingly, the enantioselectivity tends to decrease with elevating the reaction temperature except the case of the in situ prepared complexes, which, on the contrary, tend to increase the selectivity at the lower temperature. This is presumably related to the equilibrium in Reaction(3a); that is, the temperature elevation promotes an increase in the concentrations of the active complex $(RuCl_2 L_2^*)^5$ and the free phosphine which is able to make a new chiral ligand of a phosphobetain $(R'_3PCH(Ph)CH=C(Me)\overline{O})$ by the reaction with such unsaturated ketones as benzylideneacetone.⁷ In fact, the addition of (+)-nmdp into RuCl₂(PPh₃)₃ monotonically increased the selectivity until the excess phosphine $([(+)-nmdp]_0/[RuCl_2(PPh_3)_3]_0>6)$ prevents the formation of the active $RuCl_2((+)-nmdp)_2$ through the change of the equilibrium toward the formation of the less active $RuCl_2((+)-nmdp)_3$ (Table II). In the case of the reaction with $RuCl_2((+)-nmdp)_3$ (prepared from $[(+)-nmdp]_0/[RuCl_2(PPh_3)_3]_0 = 6)$, the temperature elevation promotes the accumulation of the excess free phosphine and makes the interaction of the intermediate II with I less rigid at the transition state of Reaction(3c).

TABLE II The effect of (+)-nmdp concentration on the enantioselection of I by the *in situ* prepared $\operatorname{RuCl}_2((+)-\operatorname{nmdp})_3$ with benzylideneacetone²

$\frac{[(+)-nmdp]_{0}}{[RuCl_{2}(PPh_{3})_{3}]_{0}}$	Time (hr)	Conv. (%)	$-[\alpha] D^{3}$ (deg.)	O.P. (%)	$\frac{10^{5}kR}{(sec^{-1})}$	$10^{s}k_{\rm S}$ (sec ⁻¹)	k _R /k _S
0	3.5	40.9	0	0	4.69	4.69	1.00
1.5	5.0	47.6	0.737	1.40	3.67	3.51	1.05
3.0	5.0	36.4	0.989	1.88	2.62	2.41	1.09
6.0	5.0	38.2	1.199	2.28	2.80	2.55	1.19
9.0	5.0	48.5	1.500	2.86	3.85	3.53	1.09
12.0	5.0	52.4	1.310	2.50	4.26	3.98	1.07

^aReaction temperature = 180° C and [benzylideneacetone]₀/[I]₀ = 0.84.

 $b[RuCl_2(PPh_3)_3]_0 = 8.0 \text{ mM}.$

The detailed investigation of these circumstances of the temperature effect is now in progress in connection with the enhancement of the enantioselectivity by the use of more bulky carbinols and effective Ru(II) chiral phosphine complexes.

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