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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: ${ }^{1}$

$$
\begin{align*}
& \mathrm{RR}^{\prime} \mathrm{CHOH}+\grave{\mathrm{C}}=\mathrm{C}^{\prime} \\
& \mathrm{RR}^{\prime} \mathrm{C}=\mathrm{O}+\underset{\mathrm{C}}{ } \mathrm{CHCH}^{\prime}
\end{align*}
$$

When the above reaction is carried out with $\mathrm{Ru}(\mathrm{II})$ chiral phosphine complexes, an enantioselective dehydrogenation of racemic $\mathrm{RR}^{\prime} \mathrm{CHOH}$ could be expected.

The present authors report, here, on the enantioselective dehydrogenation of racemic 1 -phenylethanol, I , by isolated crystalline $\mathrm{Ru}($ II $)$ chiral phosphine complexes ${ }^{2}$ of $\mathrm{RuCl}_{2}((-) \text {-o-ampp })_{2}\left(\mathrm{PPh}_{3}\right)$, $\mathrm{RuCl}_{2}((-) \text {-p-ampp })_{2}\left(\mathrm{PPh}_{3}\right), \mathrm{RuCl}_{2}((+) \text {-bmpp })_{3}$, $\mathrm{RuCl}_{2}\left((-)\right.$-pmpp) ${ }_{3}$, and $\mathrm{Ru}_{2} \mathrm{Cl}_{4}((-) \text {-diop) })_{3}$ (note Table I) or by $\mathrm{RuCl}_{2}((+) \text {-nmdp })_{3}$ and $\mathrm{RuBr}_{2}((+)$ $n m d p)_{3}(\mathrm{nmdp}=$ neomenthyldiphenylphosphine $)$ prepared in situ from $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}$ (and/or $\mathrm{RuBr}_{2}$ $\left.\left(\mathrm{PPh}_{3}\right)_{3}\right)$ and nmdp .

The enantioselective dehydrogenation of I by the above chiral $\mathrm{Ru}($ II $)$ complexes at $120-190^{\circ} \mathrm{C}$ 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 $k_{\mathrm{R}} / k_{\mathrm{S}}$ ratio under Conv. $70 \%$ (see Table I):

where each rate constant was evaluated by $k_{\mathrm{R}}=\left(\ln [\mathrm{R}]_{0} /[\mathrm{R}]\right) / \mathrm{t}=-(\ln (100-\mathrm{Conv}).(100-$ O.P. $\left.) / 10^{4}\right) / \mathrm{t} k_{\mathrm{S}}=\left(\ln [\mathrm{S}]_{0} /[\mathrm{S}]\right) / \mathrm{t}=-(\ln (100-$ Conv.) $\left.(100+0 . \mathrm{P}.) / 10^{4}\right) / \mathrm{t}$ ( 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 $k_{\mathrm{R}} / k_{\mathrm{S}}$ ) showed no direct correlation with the dehydrogenation rate and the molecular rotation $\left([\alpha]_{M}\right)$ of the complex or the phosphine. ${ }^{3}$ These facts may imply that the reaction course and the coordination distance of RR' $^{\prime} \mathrm{CHOH}$ 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 asymmetry ${ }^{4}$ shown by the intermediate II in Reaction(3b). In this respect, the hydrogenation of benzylideneacetophenone by I with $\mathrm{RuCl}_{2}((+) \text {-nmdp })_{3}$ or that of 2-ethylhexylmethacrylate by I with $\mathrm{Ru}_{2} \mathrm{Cl}_{4}((-) \text {-diop })_{3}$ at $180^{\circ} \mathrm{C}$ under the same conditions as in Table I resulted in $k_{\mathrm{R}} / k_{\mathrm{S}}=1.27$ (O.P. $=2.01 \%$ at Conv. $\left.=17.3 \%\right)$ and

| $\begin{aligned} & \text { Complex }^{\text {b }} \\ & \left([\alpha]_{M}\right) \end{aligned}$ | Temp. $\left({ }^{\circ} \mathrm{C}\right)$ | Time (hr) | Conv. (\%) | $\begin{aligned} & [\alpha]]^{\mathbf{b}^{\mathrm{c}}} \\ & \text { (deg.) } \end{aligned}$ | $\begin{aligned} & \text { O.P. } \\ & (\%) \end{aligned}$ | $\begin{aligned} & 10^{6} k_{\mathrm{S}} \\ & \left(\sec ^{-1}\right) \end{aligned}$ | $\begin{aligned} & 10^{6} k_{\mathrm{S}} \\ & \left(\sec ^{-1}\right) \end{aligned}$ | $k_{\mathrm{R}} / k_{S}$ | $\Delta H_{R}^{\prime}$ $\Delta H_{S}$ ( $\mathrm{kcal} / \mathrm{mol}$ ) | $\begin{aligned} & -\Delta S_{R}^{\#} \\ & -\Delta S_{S}^{\neq} \\ & \text {(e.u.) } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 165 | 5.0 | 18.7 | -0.616 | 1.17 | 12.1 | 10.8 | 1.12 | $21.1 \pm 0.6$ | $32.7 \pm 1.3$ |
|  | (165) | (5.0) | (11.3) | (-0.035) | (0.07) | (6.73) | (6.65) | (1.01) | $22.5 \pm 0.7$ | $30.6 \pm 1.4$ |
|  | 170 | 5.0 | 27.9 | -0.892 | 1.70 | 19.1 | 17.2 | 1.11 | 1.4 | 2.1 |
| $\mathrm{RuCl}_{2}(\mathbf{(}+$ - | 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) | (5.0) | (19.4) | (-0.023) | (0.044) | (12.0) | (11.9) | (1.01) | (14.3) | (50.3) |
|  | 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) |
| $\mathrm{RuBr}_{3}(\mathbf{+})-$ | 170 | 5.0 | 23.5 | $-0.899$ | 1.71 | 15.8 | 13.9 | 1.14 | $34.3 \pm 0.1$ | $3.81 \pm 0.1$ |
| nmdp), | 180 | 2.0 | 28.6 | -0.293 | 0.56 | 47.6 | 46.1 | 1.03 | $36.1 \pm 0.1$ | $-0.01 \pm 0.1$ |
|  | 190 | 1.0 | 27.1 | -0.321 | 0.61 | 89.4 | 86.4 | 1.03 | 1.8 | 3.82 |
| $\mathrm{RuCl}_{2}((-)-\mathrm{o}-$ | 160 | 30.0 | 8.56 | 0.088 | 0.17 | 0.858 | 0.88 , | 0.96 s | $41.6 \pm 0.1$ | $-8.88 \pm 0.1$ |
| ampp) ${ }_{2}\left(\mathrm{PPh}_{3}\right)$ | 170 | 24.0 | 21.29 | 0.170 | 0.32 | 2.69 | 2.76 | $0.97{ }_{3}$ | $39.8 \pm 0.1$ | $-4.97 \pm 0.2$ |
| $\left(-2600^{\circ}\right.$ ) | 180 | 10.0 | 51.58 | -1.645 | 3.13 | 21.0 | 19.3 | 1.09 | 1.8 | 3.91 |
| $\mathrm{RuCl}((-)$-p- | 160 | 7.0 | 36.63 | 0.100 | 0.19 | 18.3 | 18.4 | 0.99 5 | $20.69 \pm 0.0_{3}$ | -33.31 |
| $\mathrm{ampp}_{2}\left(\mathrm{PPh}_{3}\right)$ | 170 | 6.0 | 45.31 | 0.136 | 0.26 | 27.6 | 27.8 | 0.993 | $20.67 \pm 0.03$ | -33.34 |
| ( $-26.7^{\text {b }}$ ) | 180 | 5.0 | 63.47 | 0.192 | 0.37 | 55.0 | 55.4 | $0.99{ }^{3}$ | 0.02 | 0.03 |
| $\mathrm{RuCl}_{2}\left({ }^{(+)}\right.$- | 160 | 24.0 | 54.73 | $-0.335$ | 0.64 | 9.25 | 9.10 | 1.02 | $16.5 \pm 0.5$ | $44.3 \pm 1.1$ |
| bmpp) ${ }_{3}$ | 170 | 17.0 | 61.82 | -0.518 | 0.99 | 15.9 | 15.6 | 1.02 | $16.3 \pm 0.5$ | $44.6 \pm 1.1$ |
| $\left(-685.4{ }^{\circ}\right.$ ) | 180 | 9.0 | 49.31 6389 | -0.469 -0.726 | 0.89 1.38 | 21.3 | 20.7 | 1.03 | 0.2 | 0.3 |
|  | 190 160 | 8.0 14.5 | 63.89 34.24 | -0.726 0.379 | 1.38 0.72 | 35.9 7.89 | 34.9 | 1.03 |  |  |
| $\text { pmpp })_{3}\left(+260^{\circ}\right)$ | 170 | 14.5 12.0 | 34.24 32.36 | 0.379 0.096 | 0.72 0.18 | 7.89 9.01 | 8.17 9.09 | $0.99^{6}$ $0.99_{1}$ | 4.18 3.22 | 73.0 75.2 |
|  |  |  |  |  |  |  |  |  | 0.96 | 2.2 |
| $\mathrm{Ru}_{2} \mathrm{Cl}_{4}((-)-$ | 120 | 34.0 | 18.51 | -0.152 | 0.09 | 2.35 | 2.28 | 1.03 | $20.4 \pm 0.1$ | $33.1 \pm 0.3$ |
| diop) ${ }_{3}$ | 130 | 24.0 | 35.94 | -0.324 | 0.62 | 5.23 | 5.09 | 1.03 | $20.3 \pm 0.2$ | $33.3 \pm 0.4$ |
| (+6938 ${ }^{\circ}$ ) | 150 | 6.0 | 27.10 | -0.303 | 0.58 | 14.9 | 14.4 | 1.03 | 0.1 | 0.2 |

[^0]$k_{\mathrm{R}} / k_{\mathrm{S}}=1.175$ (O.P. $=6.15 \%$ at Conv. $=53.4 \%$ ), respectively. At any rate, it is notable from the linear Arrhenius-dependence of each rate constant ( $k_{\mathrm{R}}$ or $k_{S}$ ) being kept constant during the reaction that the smaller enthalpy of activation ( $\Delta \mathrm{H}_{\mathrm{R}}^{\neq}$or $\Delta \mathrm{H}_{\mathrm{S}}^{\ddagger}$ for the $R$ or $S$ isomer respectively), which almost corresponds to that for the rate-limiting step of the $\alpha$-carbonbound hydrogen abstraction by the complex in Reaction(3d), ${ }^{5}$ requires more negative entrophy of activation ( $\Delta \mathrm{S}_{\mathrm{R}}^{*}$ or $\Delta \mathrm{S}_{\mathrm{S}}^{\ddagger}$ ) and that the order of the difference between the $\Delta \mathrm{H}_{\mathrm{R}}^{*}$ and $\Delta \mathrm{H}_{\mathrm{S}}^{*}$ values, $\mathrm{RuCl}_{2}((-) \text {-o-ampp })_{2}\left(\mathrm{PPh}_{3}\right) \simeq \mathrm{RuBr}_{2}((+)-\mathrm{nmdp})_{3}>$. $\mathrm{RuCl}_{2}((+) \text {-nmdp })_{3} \gtrsim \mathrm{RuCl}_{2}((-)-\mathrm{pmpp})_{3}>\mathrm{RuCl}_{2}-$ $((+) \cdot \mathrm{bmpp})_{3}>\mathrm{Ru}_{2} \mathrm{Cl}_{4}((-) \text {-diop })_{3}>\mathrm{RuCl}_{2}((-)$ -p-ampp $)_{2}\left(\mathrm{PPh}_{3}\right)$, is well reflected in that of the difference between the $\Delta \mathrm{S}_{\mathrm{R}}^{\neq}$and $\Delta \mathrm{S}_{\mathrm{S}}^{\ddagger}$ values. Namely, arr isokinetic relationship (linear relation between $\Delta \mathrm{H}^{\ddagger}$ and $\Delta \mathrm{S}^{\ddagger}$ ) can be realized if one plots the parameters each other. From the latter fact mentioned above, the increase in the difference of the $\Delta S_{R}^{\ddagger}$ and $\Delta S_{S}^{\ddagger}$ values substantially elevates that of the $\Delta \mathrm{H}_{\mathrm{R}}^{\neq}$and $\Delta \mathrm{H}_{\mathrm{S}}^{\neq}$values with a linear correlation between $\Delta \Delta \mathrm{S}^{\ddagger}\left(=\Delta \mathrm{S}_{\mathrm{R}}^{\ddagger}-\Delta \mathrm{S}_{\mathrm{S}}^{\ddagger}\right)$ and $\Delta \Delta \mathrm{H}^{\ddagger}\left(=\Delta \mathrm{H}_{\mathrm{R}}^{\ddagger}\right.$ $\Delta \mathrm{H}_{\mathrm{S}}^{\ddagger}$ ). It is deduced, therefore, that the enantioselective process in Reaction(3c) might be controlled by steric factors (reflected in $\Delta S^{\ddagger}$ ) compensating electronic ones (reflected in $\Delta \mathrm{H}^{\ddagger}$ ).
$$
\mathrm{RuCl}_{2} \mathrm{~L}_{3}^{*} \rightleftharpoons \mathrm{RuCl}_{2} \mathrm{~L}_{2}^{*} \mathrm{Ru}+\mathrm{L}^{*}
$$





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 $\left(\mathrm{RuCl}_{2} \mathrm{~L}_{2}^{*}\right)^{5}$ and the free phosphine which is able to make a new chiral ligand of a phosphobetain ( $\left.\mathrm{R}_{3}^{\prime} \mathrm{PCH}(\mathrm{Ph}) \mathrm{CH}=\mathrm{C}(\mathrm{Me}) \overline{\mathrm{O}}\right)$ by the reaction with such unsaturated ketones as benzylideneacetone. ${ }^{7}$ In fact, the addition of (+)-nmdp into $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}$ monotonically increased the selectivity until the excess phosphine $\left([(+) \text {-nmdp }]_{0} /\left[\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}\right]_{0}>6\right)$ prevents the formation of the active $\mathrm{RuCl}_{2}\left({ }^{(+)} \text {-nmdp) }\right)_{2}$ through the change of the equilibrium toward the formation of the less active $\mathrm{RuCl}_{2}((+) \text {-nmdp })_{3}$ (Table II). In the case of the reaction with $\mathrm{RuCl}_{2}((+)-\mathrm{nmdp})_{3}$ (prepared from $[(+) \text {-nmdp] }]_{0} /\left[\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}\right]_{0}=6$ ), 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 $(+)-n m d p$ concentration on the enantioselection of $I$ by the in situ prepared $\mathrm{RuCl}_{2}((+)-\mathrm{nmdp})_{3}$ with benzylideneacetone ${ }^{\mathrm{a}}$

| $\frac{[(+)-n m d p]_{0} \mathrm{~b}}{\left[\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}\right]_{0}}$ | Time <br> (hr) | Conv. <br> (\%) | $\begin{aligned} & -[\alpha] \mathcal{D}^{3} \\ & (\mathrm{deg} .)^{3} \end{aligned}$ | $\begin{aligned} & \text { O.P. } \\ & \text { (\%) } \end{aligned}$ | $\begin{aligned} & 10^{5} k_{R} \\ & \left(\sec ^{-1}\right. \end{aligned}$ | $\begin{aligned} & 10^{5} k_{S} \\ & \left(\mathrm{sec}^{-1}\right) \end{aligned}$ | $k_{\mathrm{R}} / k_{\mathrm{S}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 |

[^1]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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[^0]:    ${ }^{\mathrm{a}}$ [benzylideneacetone] ${ }_{0} /[\mathrm{I}]_{0}=0.84$.
    $\mathrm{b}_{[\text {complex }]_{0}}=8.0 \mathrm{mM}$ except $\left[\mathrm{Ru}_{2} \mathrm{Cl}_{4}((-) \text {-diop }]_{0}=4.0 \mathrm{mM}\right.$. ampp $=$ anisylmethylphenylphosphine; bmpp = benzylmethylphenyl-
    phosphine; pmpp $\approx$ propylmethylphenylphosphine; diop $=2,2$-dimethyl-4,5-bis(diphenylphosphinomethyl)-1, 3-dioxolane.
    $\mathrm{C}[\alpha]_{\mathrm{D}}^{23}-52.5^{\circ}\left(\mathrm{c} 2.27, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) .{ }^{\mathrm{s}}$ Italic values are parameter difference between the isomers, and values in parentheses are those
    for the reaction without olefins.

[^1]:    ${ }^{2}$ Reaction temperature $=180^{\circ} \mathrm{C}$ and [benzylideneacetone] ${ }_{0} /[\mathrm{I}]_{0}=0.84$.
    ${ }^{\mathrm{b}}\left[\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}\right]_{0}=8.0 \mathrm{mM}$.

