# Photoinduced Deracemization of $[Co(acac)_3]$ (acac$^-$ = acetylacetonate) with Chiral *Δ*-$[Ru(menbpy)_3]^{2+}$ (menbpy = 4,4'-bis{(1*R*,2*S*,5*R*)-(–)-menthoxycarbonyl}-2,2'-bipyridine)

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Deracemization of a racemic mixture of Δ- and Λ-$[Co(acac)_3]$ (acac$^-$ = acetylacetonate) was successfully carried out with a chiral ruthenium(II) complex, Δ-$[Ru(menbpy)_3]^{2+}$ [menbpy = 4,4'-bis{(1*R*,2*S*,5*R*)-(–)-menthoxycarbonyl}-2,2'-bipyridine], in acetnitrile-$H_2O$ (7:3 v/v), in the presence of either triethylamine or NaOH under visible light irradiation ($420 < \lambda < 470$ nm). The Λ-isomer was obtained preferentially with the enantiomeric excess of 38%.

Deracemization of a racemic mixture is an interesting reaction to obtain optically active compounds, where the deracemization means that one enantiomer in a racemic mixture isomerizes to the other. Thermal deracemization of $[Fe(4,4'\text{-}Me_2bpy)_3]^{2+}$ (4,4'-$Me_2$bpy = 4,4'-dimethyl-2,2'-bipyridine) was recently carried out with a chiral anion, (*P*)-tris{tetrachlorobenzene-1,2-bis(olate)}phosphate ((*P*)-TRIPHAT), and a very high enantiomeric excess (ee) value over 96% was reported.[1] However, application of this deracemization technique seems to be limited to labile transition metal complexes with positive charge. On the other hand, photoderacemization is expected to be applied to inert transition metal complexes. However, only a few reports of photoderacemization have been presented. For instance, photoderacemizations of tris(oxalato)chromium(III),[2] tris(acetylacetonato)chromium(III),[3] and 1,1'-binaphthyl[4] with circular polarized light and that of *p*-tolylsulfoxide with chiral aromatic amines[5] were reported and the ee values of these reactions were very small; the best value was 12% reported in photoderacemization of *p*-tolylsulfoxide with (+)-*N*-(trifluoroacetyl)-1-naphthylamine.[5f]

Previously, stereoselective photoreduction of $[Co(acac)_3]$[6] and photoasymmetric synthesis of $[Co(acac)_3]$ from $Co(acac)_2$[7] were performed with Δ-$[Ru(menbpy)_3]^{2+}$ [menbpy = 4,4'-bis-{(1*R*,2*S*,5*R*)-(–)-menthoxycarbonyl}-2,2'-bipyridine] in EtOH-$H_2O$ mixed solvent. Recently, we unexpectedly observed that photoderacemization of $[Co(acac)_3]$ by Δ-$[Ru(menbpy)_3]^{2+}$ occurred in acetnitrile-$H_2O$ mixed solvent under visible light irradiation. This is the first example of photoinduced deracemization by a transition metal photosensitizer. In this paper, we wish to report this outstanding photoderacemization, dependence of enantiomeric excess on reaction conditions, and its reaction mechanism.

Δ-$[Ru(menbpy)_3]^{2+}$ was prepared[8] according to the method previously reported.[6] Its optical purity was checked by comparing its Δε value with the reported one.[9] A racemic mixture of Δ- and Λ-$[Co(acac)_3]$ (*rac*-$[Co(acac)_3]$) was purchased from Nakarai chemical Co. Ltd. and used after recrystalyzation from EtOH-hexane.[10] In a typical reaction, an acetonitrile-$H_2O$ (7:3 v/v) solution containing Δ-$[Ru(menbpy)_3]^{2+}$ (32 μmol dm$^{-3}$), *rac*-$[Co(acac)_3]$ (5.0 mmol dm$^{-3}$), and triethylamine (TEA; 0.50 mmol dm$^{-3}$) was irradiated in a pyrex cuvette at 25 °C by using a 500W xenon lamp (USHIO UXL-500D) with cut-off filters (Toshiba L-42 + KL-46). This light ($420 < \lambda < 470$ nm) corresponds to the metal to ligand charge transfer (MLCT) absorption band of Δ-$[Ru(menbpy)_3]^{2+}$. The concentrations of Δ- and Λ-$[Co(acac)_3]$ were evaluated from absorption and circular dichroism (CD) spectra which were measured with Hitachi 150-20 spectrophotometer and JASCO J-500 spectropolarimeter, respectively.

The absorption spectrum of the reaction solution changed a little by the irradiation in the presence of TEA (0.50 mmol dm$^{-3}$), but the CD spectrum considerably changed, as follows; a positive peak and a negative one appeared at 580 and 660 nm, respectively. The observed CD spectrum corresponds to that of Λ-$[Co(acac)_3]$ which exhibits a positive peak at 575 nm ($\Delta\varepsilon$ = 6.1 mol$^{-1}$ dm$^3$ cm$^{-1}$) and a negative one at 650 nm ($\Delta\varepsilon$ = –2.3 mol$^{-1}$ dm$^3$ cm$^{-1}$) in isopentane-diethyl ether.[11] These results clearly show that Λ-$[Co(acac)_3]$ exists in excess after the reaction. Though the concentration of Δ-$[Co(acac)_3]$ decreased by the photoirradiation, that of Λ-$[Co(acac)_3]$ increased after a few hours of induction period, as shown in Figure 1. After 50 h, concentrations of Δ- and Λ-$[Co(acac)_3]$ changed quite a little, and the reaction reached a stationary state. The ee value was 28% and $[Co(acac)_3]$ was decomposed by 10% after 50 h (Table 1). From the above results, it should be clearly concluded that deracemization of $[Co(acac)_3]$ photochemically occurs.

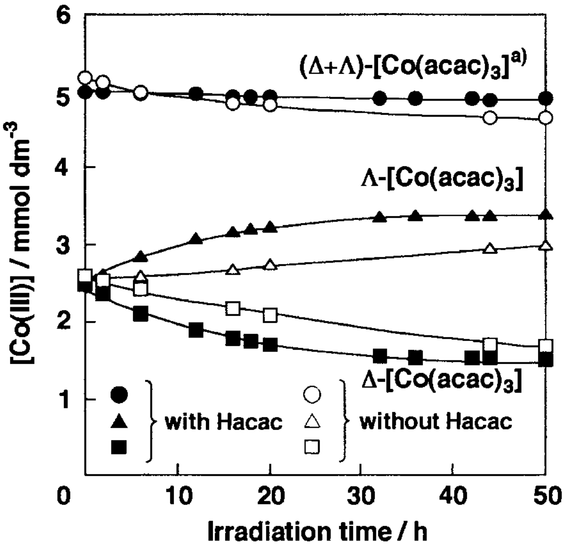


**Figure 1.** Concentration changes of Δ, Λ, and (Δ+Λ)-$[Co(acac)_3]$.$^{a)}$ Δ-$[Ru(menbpy)_3]^{2+}$ = 32 μmol dm$^{-3}$, $[Co(acac)_3]$ = 5 mmol dm$^{-3}$, [TEA] = 0.5 mmol dm$^{-3}$, [Hacac] = 50 mmol dm$^{-3}$ in acetnitrile-$H_2O$ = 7:3 (v/v) at 25 °C. a) The term "Δ+Λ" represents the sum of Δ-$[Co(acac)_3]$ and Λ-$[Co(acac)_3]$.

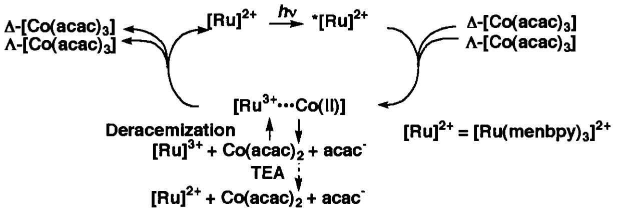
**Table 1.** The enantiomeric excess of Λ-$[Co(acac)_3]$ in the photoderacemization of $[Co(acac)_3]$ by Δ-$[Ru(menbpy)_3]^{2+}$ [a]

| [TEA] mmol $dm^{-3}$ | [Hacac] mmol $dm^{-3}$ | time[b] h | e.e.[c] % | decomp.[d] % |
|---|---|---|---|---|
| 0 | 0 | 68 | 3.5 | 3.0 |
| 0.5 | 0 | 50 | 28 | 10 |
| 1.0 | 0 | 26 | 32 | 19 |
| 5.0 | 0 | 1.8 | 31 | 47 |
| 0.5 | 50 | 32 | 38 | 1.7 |
| 0 | 50 | 24 | 5.7 | 3.0 |
| 0[e] | 50 | 24 | 38 | 5.5 |

[a] $[Ru(menbpy)_3]^{2+}$ = 32 μmol $dm^{-3}$, $[Co(acac)_3]$ = 5.0 mmol $dm^{-3}$ in acetnitrile-$H_2O$ (7:3 v/v) at 25 °C. [b] Time to reach the stationary state. [c] The e.e. value at photo-stationary state. [d] Decomposition of $[Co(acac)_3]$. [e] In the presence of [NaOH] (1.5 x $10^{-1}$ mol $dm^{-3}$).

Without TEA, the deracemization hardly occurred; the ee value observed was only 3.5%, and $[Co(acac)_3]$ was decomposed by only 3% even after 68 h (Table 1). When TEA concentration increased to 1.0 and 5.0 mmol $dm^{-3}$, the ee value somewhat increased, but the considerable amount of $[Co(acac)_3]$ was reduced to $Co(acac)_2$, because the photoreduction of $[Co(acac)_3]$ occured in this case, as reported previously.[6]

When acetylacetone (50 mmol $dm^{-3}$) was added to the reaction solution with TEA (0.5 mmol $dm^{-3}$), the concentration of Λ-$[Co(acac)_3]$ increased immediately without any induction period, and the reaction reached the stationary state earlier (Figure 1). Furthermore, the ee value increased from 28% to 38%, and the decomposition of $[Co(acac)_3]$ decreased to only 1.7%. When NaOH (1.5 x $10^{-1}$ mol $dm^{-3}$) was added to this solution instead of TEA, the deracemization proceeded too and the ee value observed (38%) was the same as that of the reaction carried out with TEA. This concentration of NaOH is enough to convert Hacac into $acac^-$. These results suggest that TEA plays a role of a base to convert Hacac into $acac^-$.



**Scheme 1.**

The reaction mechanism shown in Scheme 1 is considered plausible; the photoexcited $*[Ru(menbpy)_3]^{2+}$ is oxidatively quenched by $[Co(acac)_3]$, in which $*[Ru(menbpy)_3]^{2+}$ forms an exciplex with $[Co(acac)_3]$, followed by electron transfer to afford a successor complex, $[Ru^{III}(menbpy)_3{}^{3+}\bullet\bullet\bullet Co^{II}(acac)_3]$. The successor complex would dissociate into $[Ru^{III}(menbpy)_3]^{3+}$, $Co(acac)_2$, and $acac^-$. Part of $[Ru^{III}(menbpy)_3]^{3+}$ is reduced to $[Ru^{II}(menbpy)_3]^{2+}$ by TEA, and remaining $[Ru^{III}(menbpy)_3]^{3+}$ undergoes the reverse reaction with $Co(acac)_2$ and $acac^-$ to form the encounter complex, $[Ru^{III}(menbpy)_3{}^{3+}\bullet\bullet\bullet Co^{II}(acac)_3]$. In the encounter complex, electron transfer occurs from $[Co^{II}(acac)_3]$ to $[Ru^{III}(menbpy)_3]^{3+}$ to yield $[Co(acac)_3]$ and $[Ru(menbpy)_3]^{2+}$. In this reaction cycle, the oxidative quenching of Δ-$*[Ru(menbpy)_3]^{2+}$ by Δ- and Λ-$[Co(acac)_3]$ and the regeneration of Δ- and Λ-$[Co(acac)_3]$ from $Co(acac)_2$ and $acac^-$ would occur enantioselectively, which leads to the deracemization. Actually, our previous work showed that Δ-$[Co(acac)_3]$ was more rapidly photoreduced by Δ-$[Ru(menbpy)_3]^{2+}$ than Λ-$[Co(acac)_3]$ in EtOH-$H_2O$ under visible light irradiation,[6] and that Λ-$[Co(acac)_3]$ was photochemically synthesized from $Co(acac)_2$ with $[Ru(menbpy)_3]^{2+}$ to a great extent than Δ-$[Co(acac)_3]$.[7]

The other possible reaction mechanism is mentioned here, in which Δ-$*[Ru(menbpy)_3]^{2+}$ is reductively quenched by TEA, $acac^-$, and/or $Co(acac)_2$,[12] to afford one electron reduced Δ-$[Ru(menbpy)_3]^+$. Δ-$[Ru(menbpy)_3]^+$ would enantioselectively reduce $[Co(acac)_3]$ to yield $Co(acac)_2$ and $acac^-$ with regeneration of $[Ru(menbpy)_3]^{2+}$. In this case, the reduction of Δ- and Λ-$[Co(acac)_3]$ by Δ-$[Ru(menbpy)_3]^+$ and the oxidation of $Co(acac)_2$ to $[Co(acac)_3]$ by Δ-$*[Ru(menbpy)_3]^{2+}$ would enantioselectively occur, which leads to the deracemization. Actually, previous pulse radiolysis of Δ-$[Ru(menbpy)_3]^{2+}$ revealed that Δ-$[Ru(menbpy)_3]^+$ enantioselectively reduced $[Co(acac)_3]$ with the selectivity of 2.7 (Δ-$[Co(acac)_3]$/Λ-$[Co(acac)_3]$) in 85% EtOH-$H_2O$.[9,13] However, $[Co(acac)_3]$ was not produced at all by irradiating the solution involving Δ-$[Ru(menbpy)_3]^{2+}$ (32 μmol $dm^{-3}$), $Co(acac)_2$ (5.0 mmol $dm^{-3}$), Hacac (50 mmol $dm^{-3}$), and TEA (0.5 mmol $dm^{-3}$) with the visible light. From this, it is reasonably suggested that this reaction mechanism might be excluded and the deracemization occurs through the mechanism shown in Scheme 1.

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## References and Notes

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8 Purity was confirmed by elemental analysis. Anal. Found: H, 7.81; C, 63.79; N, 4.38%. Calc. for $[Ru(menbpy)_3]Cl_2 \cdot 5H_2O$ = $C_{96}H_{142}N_6O_{17}Cl_2Ru$: H, 7.85; C, 63.21: N, 4.61%. Δε (λ) / $mol^{-1}$ $dm^3$ $cm^{-1}$ (nm) = –31.9 (485) and +37.3 (432).
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