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Novel Photocatalytic Asymmetric Synthesis of Δ (or Λ)–[Co(acac)$_3$] (Hacac = pentane–2,4–dione) from [Co(acac)$_2$(H$_2$O)$_2$] and Hacac with Helical Ruthenium(II) Tris–bidentate Complexes

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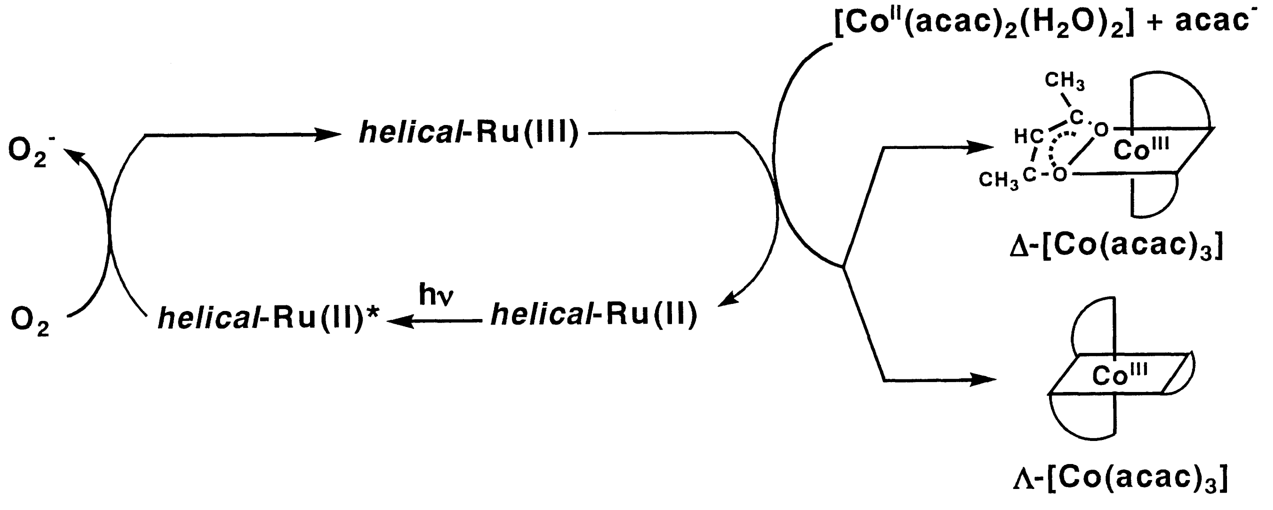
The photoinduced asymmetric synthesis of Δ (or Λ)–[Co(acac)$_3$] from [Co(acac)$_2$(H$_2$O)$_2$] and Hacac was achieved by using helical Ruthenium(II) complexes of [Ru(Menbpy)$_3$]$^{2+}$ (Menbpy = 4,4'–di((1*R*,2*S*,5*R*)–(–)–menthoxycarbonyl)–2,2'–bipyridine), and [Ru(*R*(or *S*)–PhEtbpy)$_3$]$^{2+}$ (*R*(or *S*)–PhEtbpy = 4,4'–di((*R*)–(+)(or (*S*)–(–))–1–phenylethylamino–carbonyl)–2,2'–bipyridine) with the maximum 10.0% e.e. for the Λ–[Co(acac)$_3$] formation by [Ru(Menbpy)$_3$]$^{2+}$ in 50 – 70% v/v EtOH/H$_2$O at 25 °C.

Asymmetric photosynthesis with chiral transition–metal complexes has hitherto been the subject of only limited investigation, probably because of the difficulty in the molecular design of efficient chiral photocatalysts. In this respect, there is only one report on the photocatalytic asymmetric synthesis of (*R*)–(+)–1,1'–bi–2–naphthol derivatives from 3–substituted–2–naphthol with a chiral ruthenium(II) complex.$^{1)}$ This paper first describes the asymmetric synthesis of a chiral inorganic compound, Δ (or Λ)–[Co(acac)$_3$], in the photoinduced oxidation of [Co(acac)$_2$(H$_2$O)$_2$] and Hacac with [Ru(Menbpy)$_3$]$^{2+}$ (**1**; Menbpy = 4,4'–di((1*R*,2*S*,5*R*)–(–)–menthoxycarbonyl)–2,2'–bipyridine) or [Ru(*R*(or *S*)–PhEtbpy)$_3$]$^{2+}$ (**2a** or **2b**; *R*(or *S*)–PhEtbpy = 4,4'–di((*R*)–(+)(or (*S*)–(–))–1–phenylethylaminocarbonyl)–2,2'–bipyridine):



Scheme 1.

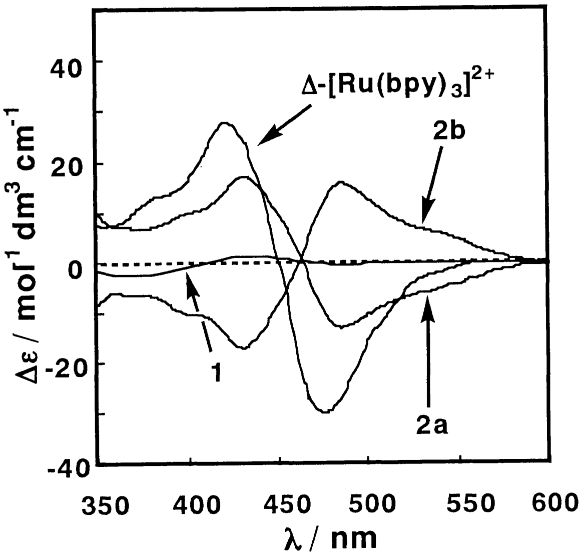


Fig. 1. CD spectra of the chiral photocatalysts.

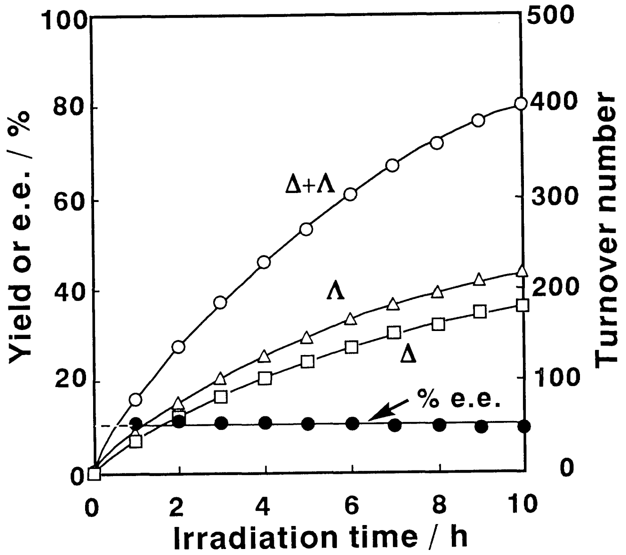


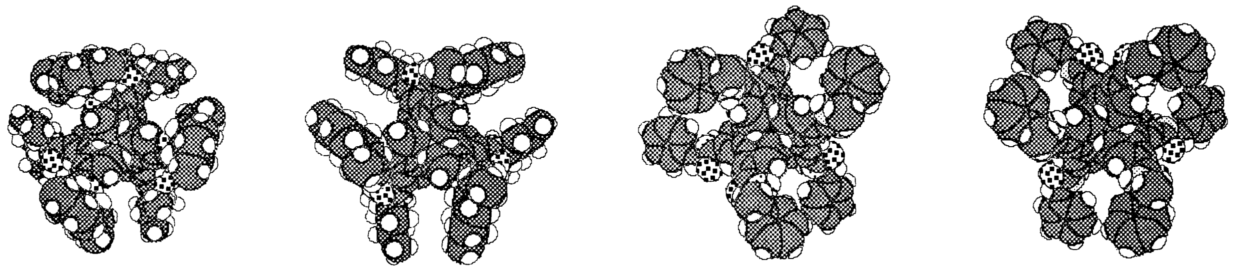
Fig. 2. Enantiomeric excess of Λ-[Co(acac)$_3$] and yield of [Co(acac)$_3$] in the oxidation of [Co(acac)$_2$(H$_2$O)$_2$] and Hacac with **1** in 70% v/v EtOH/H$_2$O at 25 °C.

The ruthenium(II) photocatalysts (**1**, **2a**, **2b**, [Ru(*rac*-PhEtbpy)$_3$]$^{2+}$ (**3**), and *rac*-[Ru(bpy)$_3$]$^{2+}$ (**4**)) were prepared in accordance to the method described previously.[2,3] The photocatalysts of **1**, **2a**, **2b**, and **3** were found stable to light and had longer excited state lifetimes (1550 ns for **1** and 1800 ns for **2a**, **2b** and **3** in EtOH at 25 °C)[4] when compared with that (790 ns in EtOH at 25 °C)[5] of **4**. In regard to the excited-state oxidation potentials ($E^{3+/2+*}$) of **1**, **2a**, **2b**, and **3**, they were determined by the Rehm–Weller plots[6] with the reduction potentials of aromatic quenchers; the $E^{3+/2+*}$ values (−0.45 for **1** or −0.60 V vs. SCE for **2a**, **2b**, and **3** in MeCN), however, became higher as compared with that (−0.81 V vs. SCE in MeCN) of **4** because of the esterification or amidation of the bipyridine ligands.[7] For the oxidation

Table 1. Asymmetric Synthesis of [Co(acac)$_3$] from [Co(acac)$_2$(H$_2$O)$_2$]/Hacac with the Helical Ru(II) Complexes[a]

Ru(II) complex	Predominant helicity	Yield/% Δ	Λ	Δ + Λ	e.e./%	Prevailing helicity
[Ru(Menbpy)$_3$]$^{2+}$ (**1**)	*M*(*C*$_3$)	9.60	11.8	21.4	10.0	*M*(*C*$_3$)
[Ru(*R*-PhEtbpy)$_3$]$^{2+}$ (**2a**)	*M*(*C*$_3$)	11.1	11.2	22.3	<0.3	*M*(*C*$_3$)
[Ru(*S*-PhEtbpy)$_3$]$^{2+}$ (**2b**)	*P*(*C*$_3$)	11.3	11.2	22.5	<0.3	*P*(*C*$_3$)
[Ru(*rac*-PhEtbpy)$_3$]$^{2+}$ (**3**)	*P*(*C*$_3$) and *M*(*C*$_3$)	9.3	9.3	18.6	0	*P*(*C*$_3$) and *M*(*C*$_3$)
rac-[Ru(bpy)$_3$]$^{2+}$ (**4**)	*P*(*C*$_3$) and *M*(*C*$_3$)	1.7	1.7	3.3	0	*P*(*C*$_3$) and *M*(*C*$_3$)
Δ-[Ru(bpy)$_3$]$^{2+}$	*P*(*C*$_3$)	1.0$_5$	1.0$_5$	2.1	<0.1	*P*(*C*$_3$)

a) [Ru(II)] = 20 μmol dm^{-3}, [Co(acac)$_2$(H$_2$O)$_2$] = 10 mmol dm^{-3}, and [Hacac] = 1.0 mol dm^{-3} in 50% v/v EtOH/H$_2$O at 25 °C for 4 h.



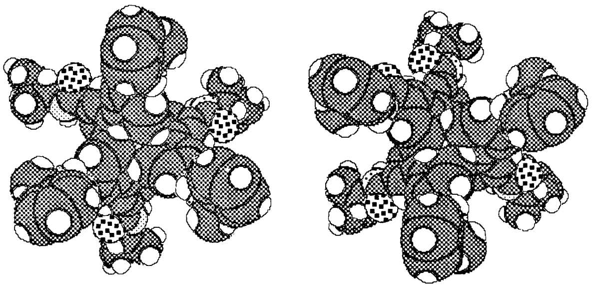
M(C_3)-Δ-1 *P*(C_3)-Λ-1 *M*(C_3)-Δ-2a *P*(C_3)-Λ-2b

Fig. 3. Molecular helicities of **1**, **2a**, and **2b**.

of [Co(acac)$_2$(H$_2$O)$_2$]/Hacac, the reduction potentials of [Ru(menbpy)$_3$]$^{3+}$ (**1'**) and [Ru(*R*(or *S*)-PhEtbpy)$_3$]$^{3+}$ (**2'a** or **2'b**) are also important, and the ruthenium(III) complexes (**1'**, **2'a**, and **2'b**) generated from the ruthenium(II) photocatalysts were determined to be $E^{3+/2+}$ = +1.55 for **1'** and +1.40 V vs. SCE for **2'a** or **2'b** in MeCN.

When the 70% v/v EtOH/H$_2$O solution containing **1** (20 μmol dm^{-3}), [Co(acac)$_2$(H$_2$O)$_2$] (10 mmol dm^{-3}), and Hacac (1.0 mol dm^{-3}) was irradiated (λ > 400 nm of a 500 W xenon lamp) in an O$_2$ atmosphere, the asymmetric synthesis of Λ-[Co(acac)$_3$] from [Co(acac)$_2$(H$_2$O)$_2$]/Hacac was realized by **1** (λ_{max} = 466 nm) with the constant value of 10.0% e.e. (Fig. 2),[8] even though [Ru(Menbpy)$_3$]$^{2+}$ (**1**) comprises Δ-[Ru(Menbpy)$_3$]$^{2+}$ and Λ-[Ru(Menbpy)$_3$]$^{2+}$. The extent of asymmetric induction was, however, found to be affected by the EtOH content in EtOH/H$_2$O and was changed from 1.9% e.e. at 100% v/v EtOH to 10.0% e.e. at 50% v/v EtOH (the lowest content for making the homogeneous solution). The asymmetric synthesis of Δ- or Λ-[Co(acac)$_3$] was then examined with the Ru(II) complexes (**2a**, **2b**, **3**, and **4**) in the 50% v/v EtOH/H$_2$O solvent, and the results were shown in Table 1. The asymmetric synthesis of Δ (or Λ)-[Co(acac)$_3$] by **2a** or **2b** was slightly observed with very low e.e. values.

Interestingly, the present photocatalysts of **2a** and **2b** indicated the molecular asymmetry in their CD spectra (Fig. 1), even though the Ru(II) complexes of **3** and **4**, which were completely inefficient for the present asymmetric synthesis, did not show any molecular asymmetry in their CD spectra. From the reproducible CD spectra of **1**, **2a**, and **2b**, the diastereomate **1** was found to include the slightly excess amount of Δ-**1**, while diastereomates **2a** and **2b** exclude Λ-**2a** and Δ-**2b**, respectively.[3] On the basis of the CD spectrum of Δ-[Ru(bpy)$_3$]$^{2+}$, **2a** or **2b** was found to show Δ or Λ-symmetry, respectively, and the conformations of **1**, Δ-**2a**, and Λ-**2b** have been characterized by the molecular mechanics (MM2) calculations as a helical symmetry (*M*(C_3)) helicity for Δ-**1** or Δ-**2a**

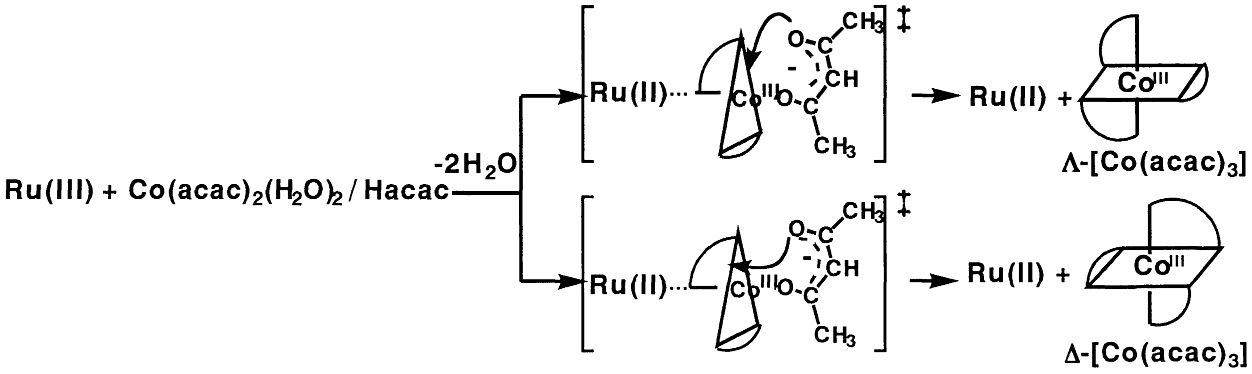


Λ-2a Δ-2b

Fig. 4. Instable Ru(II) complexes of Λ-**2a** and Δ-**2b**.

and $P(C_3)$ helicity for Λ–**1** or Λ–**2a**, where $P(C_3)$ or $M(C_3)$ indicates a plus (clockwise) or minus (counterclockwise) helical arrangement along the C_3 axis, respectively),9) as shown in Fig. 3. Therefore, the ruthenium(II) complex of **1** predominates the $M(C_3)$ helicity of Δ–**1** rather than $P(C_3)$ one of Λ–**1**, while the **2a** (or **2b**) excludes the $P(C_3)$–Λ–**2a** (or $M(C_3)$–Δ–**2b**), respectively. The difficulty of the Λ–**2a** and Δ–**2b** formations from $RuCl_3 \cdot 6H_2O$ and *R*(or *S*)–PhEtbpy was supposed to be resulted from the steric hinderance in their chiral ligands (see Fig.4).

It is also noteworthy from Table 1 that $M(C_3)$–**1** (and **2a**) resulted in Λ–[Co(acac)$_3$] possessing the $M(C_3)$ helicity, while $P(C_3)$–**2b** gave Δ–[Co(acac)$_3$] having the $P(C_3)$ one, as a prevailing configuration. Therefore, the present helical $P(C_3)$ or $M(C_3)$–Ru(II) complexes predominated the same helical $P(C_3)$ or $M(C_3)$–[Co(acac)$_3$] from [Co(acac)$_2$(H$_2$O)$_2$]/Hacac, respectively, and the extent of asymmetric induction was decreased by the higher EtOH content (in EtOH/H$_2$O) which presumably weakened the hydrophobic interaction between the Ru(III) complex and [Co(acac)$_2$–acac$^-$] at the following transition state of the asymmetric reaction.



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4) The excited state lifetimes of **1** and **2a**, **2b** were measured by means of HORIBA NAES–550 nanosecond fluorometer.

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7) C. M. Elliott, R. A. Freitag, and D. D. Blaney, *J. Am. Chem. Soc.*, **107**, 4647 (1985).

8) The present reaction produced only [Co(acac)$_3$] from [Co(acac)$_2$(H$_2$O)$_2$] and Hacac, and the total concentration of Δ– and Λ–[Co(acac)$_3$] and the concentration difference between the Δ– and Λ–enantiomer were determined respectively by using ε = 133 mol^{-1} dm^3 cm^{-1} at λ_{CD} = 595 nm for [Co(acac)$_3$] and $\Delta\varepsilon$ = –8.11 (Δ–[Co(acac)$_3$]) and +8.11 (Λ–[Co(acac)$_3$]) mol^{-1} dm^3 cm^{-1} at λ_{CD} = 574 nm.

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