Novel Enantioselective Photocatalysis by Chiral, Helical Ruthenium(II) Complexes

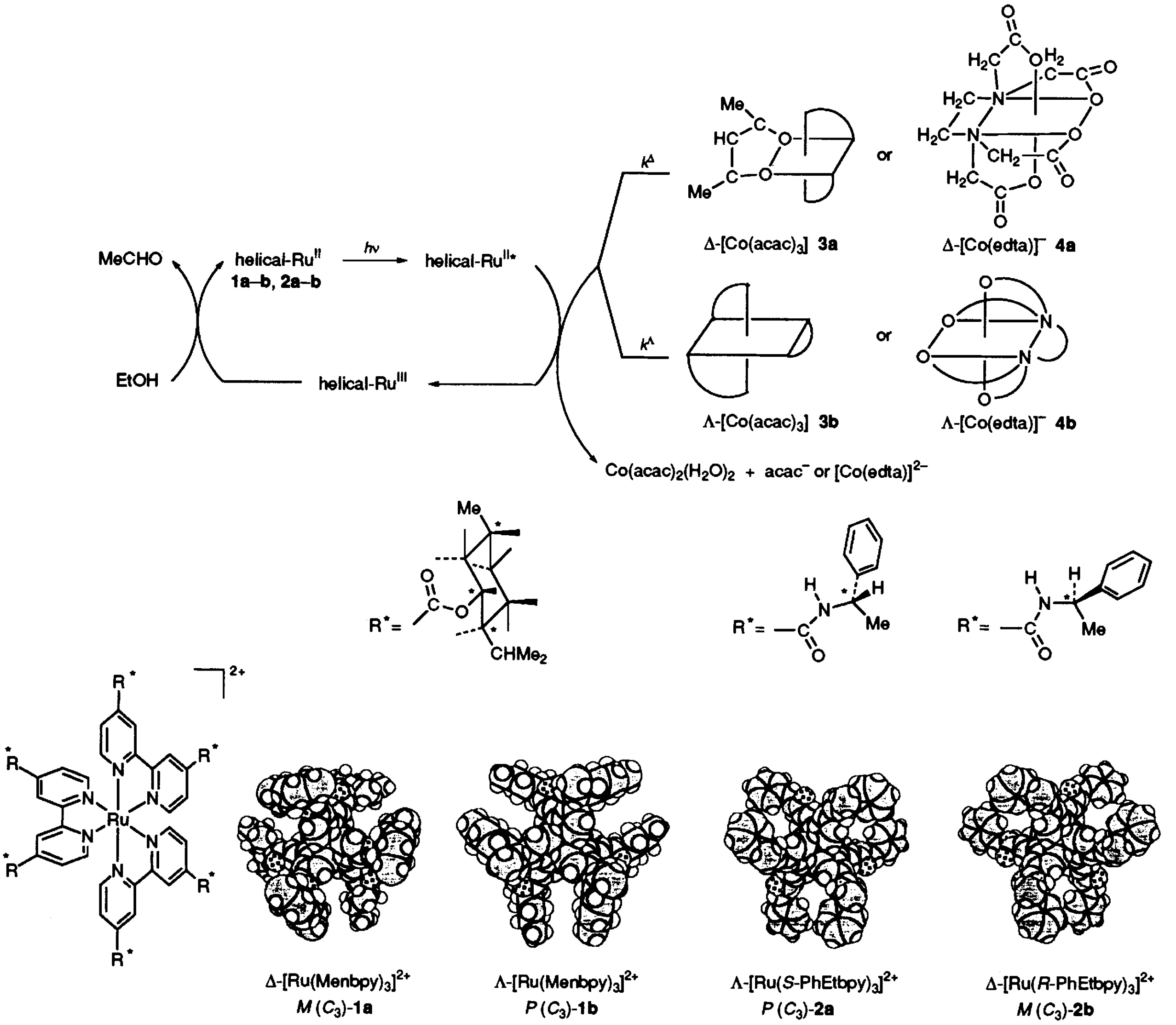
Katsutoshi Ohkubo,* Taisuke Hamada and Hitoshi Ishida

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

The enantioselective photoreduction of the helical substrates of *rac*-[Co(acac)$_3$] (acac$^-$ = acetylacetonato) and *rac*-[Co(edta)]$^-$ (edta^{4-} = ethylenediaminetetraacetato) with the newly synthesized helical photocatalysts Δ- (or *rac*)-[Ru[Menbpy)$_3$]$^{2+}$ {Menbpy = 4,4′-bis[(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl]-2,2′-bipyridine}, and Λ- (or Δ)-[Ru{(*S* or *R*)-PhEtbpy}$_3$]$^{2+}$ {(*S* or *R*)-PhEtbpy = 4,4′-bis[(*S*)-(−) or (*R*)-(+)-1-phenylethylaminocarbonyl]-2,2′-bipyridine} was realized in the helical-shape recognition reaction with a maximum enantiomer rate ratio (k^Δ/k^Λ) of 14.7 in 90% *v/v* EtOH–H$_2$O at 25 °C.

The chemistry of molecular recognition has recently received considerable attention; molecular recognition in catalytic reactions is usually expected to occur as a result of efficient interaction (especially multipoint interactions) between chiral catalysts and enantiomeric (or prochiral) substrates. Thus, non-bonding long-range interactions between chiral photocatalysts and substrates would not result in efficient enantioselectivity or asymmetric induction. Porter *et al.*[1,2] studied the enantioselective reduction of *rac*-[Co(acac)$_3$] (acac$^-$ = acetylacetonato) catalysed by the photoactivated Δ-[Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2′-bipyridine). This investigation, however, did not result in efficient photocatalysis by Δ-[Ru(bpy)$_3$]$^{2+}$, because Δ-[Ru(bpy)$_3$]$^{2+}$ racemizes easily, leading to low enantioselectivity (enantiomer rate ratio k^Λ/k^Δ = 1.08). We report here novel enantioselective photocatalysis by helical ruthenium(II) complexes, Δ-[Ru(Menbpy)$_3$]$^{2+}$ **1a** or *rac*-[Ru(Menbpy)$_3$]$^{2+}$ **1a–b** {Menbpy = 4,4′-bis[(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl]-2,2′-bipyridine}, Λ-[Ru(*S*-PhEtbpy)$_3$]$^{2+}$ **2a** or Δ-[Ru(*R*-PhEtbpy)$_3$]$^{2+}$ **2b** {(*S*) or *R*)-PhEtbpy = 4,4′-bis[(*S*)-(−) or (*R*)-(+)-1-phenylethylaminocarbonyl]-2,2′-bipyridine}, in the reduction of *rac*-[Co(acac)$_3$] **3** (**3a** = Δ, **3b** = Λ; acac$^-$ = acetylacetonato) or *rac*-[Co(edta)]$^-$ **4** (**4a** = Δ, **4b** = Λ; edta^{4-} = ethylenediaminetetraacetato).

The ruthenium(II) photocatalysts were prepared by the



Scheme 1

method described in our previous reports,[3,4] and the helical catalysts **1a**, **2a** and **2b**) were obtained by resolution of their racemates using silica gel column chromatography (eluent: $CHCl_3$–MeOH).

The characteristic molecular symmetries of **1a–b** and **2a–b** are reflected in their CD spectra (in EtOH) shown in Fig. 1; **1a** and **2b** have the same Δ-symmetry as Δ-$[Ru(bpy)_3]^{2+}$, while **2a** shows Λ-symmetry, and **1a–b** {racemate of **1a** and Λ-$[Ru(Menbpy)_3]^{2+}$ **1b**} indicates the predominance of the Δ-symmetry of **1a** rather than the Λ-symmetry of **1b**. From the energy minimized conformations [determined by molecular mechanics (MM2) calculations] of their chiral ligands,[5] **1a** and **2b** were found to adopt $M(C_3)$ helicity while **1b** and **2a** have $P(C_3)$ helicity, where $P(C_3)$ or $M(C_3)$ indicates a plus (clockwise) or minus (counterclockwise) helical arrangement along the C_3 axis, respectively.

The helical complexes of **1a–b** and **2a–b**, which have the metal to ligand charge transfer absorption at λ_{max} (ε) = 466 nm (27200 mol^{-1} dm^{-3} cm^{-1}) and 464 nm (21200 mol^{-1} dm^3 cm^{-1}) in EtOH, respectively, were more stable to light and had longer lifetimes (τ) than Δ-$[Ru(bpy)_3]^{2+}$; the observed values of τ (1550 ns for **1a–b** and 1800 ns for **2a–b** in EtOH at 25 °C) and quantum yield of photoracemization ($\phi_{rac} = 4.0 \times 10^{-6}$ for **1a** and 7.6×10^{-6} for **2a** or **b** in EtOH at 25 °C) were respectively much larger and smaller than those (τ = 790 ns in H_2O at 25 °C[6] and $\phi_{rac} = 2.88 \times 10^{-4}$ in EtOH at 25 °C[2]) for Δ-$[Ru(bpy)_3]^{2+}$. The excited-state oxidation potentials ($E^{3+/2+*}$ in Table 1) determined for **1a–b** and **2a–b** by using the Rehm–Weller relation[7] were lower than that of Δ-$[Ru(bpy)_3]^{2+}$ because of the esterification or amidation of the bipyridine ligands.[8]

The photoreduction of 2.4 mmol dm^{-3} racemic **3** or **4** ($E^{3+/2+} = -0.34$[9] or 0.13[10] V *vs.* SCE for **3** or **4**, respectively) by 32 μmol dm^{-3} **1a–b** or **2a–b** under photoirradiation (λ > 400 nm, 500 W xenon lamp) in deaerated aqueous EtOH solution at 25 °C produced only $Co(acac)_2(H_2O)_2$–acac$^-$ or $[Co(edta)]^{2-}$ as reduction product and proceeded catalytically and enantioselectively (Fig. 2); in this reaction, the EtOH solvent contributes to the photocatalysis of **1a–b** or **2a–b** as a reductant, as shown in Scheme 1.

The reaction rates were followed by monitoring spectrophotometrically the amounts of **3a–b** or **4a–b** consumed,† and were found to obey a pseudo-first-order rate law with different pseudo-first-order rate constants (k^{Δ} and k^{Λ}) during the initial

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† The total concentration {[**3a** (or **4a**)] + [**3b** (or **4b**)]} and the concentration difference {[**3a** (or **4a**)] − [**3b** (or **4b**)]} were determined respectively by using ε = 133 (347) mol^{-1} dm^3 cm^{-1} at λ_{max} = 595 (533) nm for **3a–b** (**4a–b**) and $\Delta\varepsilon$ = −8.11 (**3a**) and +8.11 (**3b**) mol^{-1} dm^3 cm^{-1} at λ_{CD} = 574 nm and +1.73 (**4a**) and −1.73 (**4b**) at λ_{CD} = 585 nm.

Table 1 Photoreduction of the helical **3** or **4** racemates with the helical photocatalysts **1a–b** and **2a–b**[a]

			Reaction					Quenching			
Photocatalyst	Substrate	$E^{3/2+*}$/ V vs. SCE[b]	$10^2\phi_{react}$	k^{Δ}/ $10^{-6}\,s^{-1}$	k^{Λ}/ $10^{-6}\,s^{-1}$	k^{Δ}/k^{Λ}	Prevailed helicity	k_q^{Δ}/ $10^8\,s^{-1}$	k_q^{Λ}/ $10^8\,s^{-1}$	$k_q^{\Delta}/k_q^{\Lambda}$	Prevailed helicity
$M(C_3)$-**1a**	**3**	−0.45	1.3	74.0	5.0	14.7	$P(C_3)$	1.98	1.49	1.28	$P(C_3)$
				239[c]	28.0[c]	8.65[c]	$P(C_3)$				
1a–b [= $M(C_3)$-**1a**	**3**	−0.45	1.8	117	67	1.67	$P(C_3)$	1.57	1.41	1.14	$P(C_3)$
+$P(C_3)$-**1b**]	**4**	−0.45	0.02[d]	0.55[d]	0.29[d]	1.90[d]	$P(C_3)$	156[d]	110[d]	1.42[d]	$P(C_3)$
$P(C_3)$-**2a**	**3**	−0.60	0.84	31.5	48	1/1.51	$M(C_3)$	1.44	1.67	1/1.16	$M(C_3)$
$M(C_3)$-**2b**	**3**	−0.60	0.15[e]	4.13[e]	2.66[e]	1.54[e]	$P(C_3)$	1.69	1.57	1.08	$P(C_3)$
$P(C_3)$-Δ-$[Ru(bpy)_3]^{2+}$	**3**	−0.81[f]	4[g]			1/1.08[h]	$M(C_3)$			1/1.03[g]	$M(C_3)$

[a] The photoreactions were carried out with [**1a–b** or **2a–b**] = 32 μmol dm^{-3} and [**3** or **4**] = 2.4 mmol dm^{-3} in deaerated 90% *v/v* EtOH–H_2O at 25 °C. [b] In MeCN at 25 °C. SCE = standard calomel electrode. [c] In 80% *v/v* EtOH–H_2O. [d] In 50% *v/v* EtOH–H_2O. [e] In 97% *v/v* EtOH–H_2O. [f] Ref. 7. [g] In H_2O, see ref. 2. [h] Ref. 1.

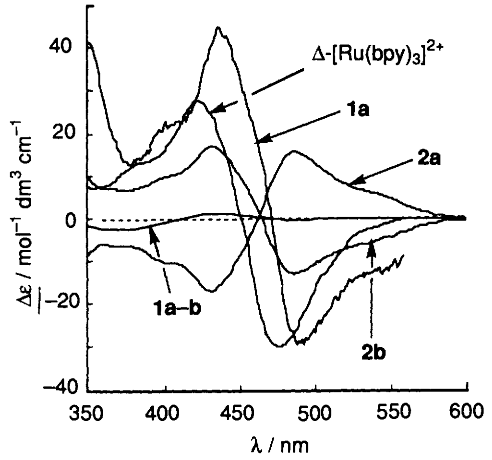

Fig. 1 CD spectra of **1a–b**, **2a–b**, and Δ-$[Ru(bpy)_3]^{2+}$ in EtOH

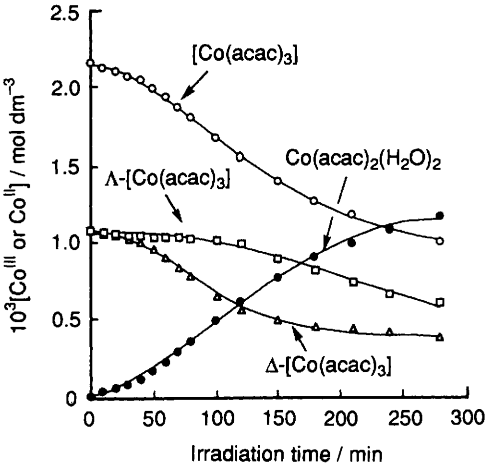

Fig. 2 The concentration change of **3** (○), **3a** (△), **3b** (□), and $Co(acac)_2(H_2O)_2$ (●), in the photoreduction of racemate **3** by **1a** in 90% *v/v* EtOH–H_2O at 25 °C

stage of the reaction (up to *ca.* 30% conversion); the accumulation of the unreacted enantiomer after *ca.* 30% conversion facilitated the reaction of the photocatalyst with the accumulated enantiomeric substrate so that pseudo-first-order kinetics were no longer observed. Among the helical photocatalysts tested (**1a–b** and **2a–b**), **1a** resulted in a maximum and reproducible enantiomer rate ratio (k^{Δ}/k^{Λ}) of 14.7 in 90% *v/v* EtOH–H_2O solvent, a value which decreased to 8.65 in 80% *v/v* EtOH–H_2O (Table 1).

It is also noteworthy from Table 1 that $M(C_3)$-**1a** (or **2b**) and *rac*-**1a–b** [*viz.*, $M(C_3)$-**1a** + $P(C_3)$-**1b**] are oxidized or quenched predominantly by **3a** (or **4a**) possessing $P(C_3)$ helicity while $P(C_3)$-**2a** reacts more easily with **3b** having $M(C_3)$ helicity; in the case of $P(C_3)$-Δ-$[Ru(bpy)_3]^{2+}$, $M(C_3)$-**3b** is selected as the prevailing substrate. Thus, the molecular helicities of the present photocatalysts recognized those of the substrates in their preferential reactions between the different $P(C_3)$ and $M(C_3)$ configurations without any direct bonding interaction. In this novel 'photocatalytic shape recognition' reaction, the change in the molecular structures of the photocatalysts on photoactivation compared with those of their ground-states is negligible.‡ The k^{Δ}/k^{Λ} values, which reflect the extent of the shape recognition reaction between the helical photocatalysts and substrates are much higher than those ($k_q^{\Delta}/k_q^{\Lambda}$) obtained from the quenching experiments, especially in the reduction of **3** by **1a**. This is ascribed to the asymmetric formation of $[Co(acac)_3]$ possessing the same helicity as that of the photocatalyst *via* oxidation of the photoreduction products $[Co(acac)_2(H_2O)_2\text{–}acac^-]$ by the Ru^{III} complexes generated from the Ru^{II} photocatalysts;[12] the predominant formation of $M(C_3)$-**3b** from $Co(acac)_2(H_2O)_2\text{–}acac^-$ by the $M(C_3)$-**1a** catalyst which reduces $P(C_3)$-**3a** preferentially resulted in the accumulation of $M(C_3)$-**3b** (Λ) and enhanced the k^{Δ}/k^{Λ} ratio up to 14.7 in 90% *v/v* EtOH–H_2O at 25 °C.

Received, 29th March 1993; Com. 3/01774E

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‡ *E.g.* the maximum difference in the bond lengths between the photoactivated state (MLCT) and ground state (GS) ($r_{MLCT} - r_{GS}$) is 0.070 Å (C^2–C^3) and −0.04 Å (C^2–$C^{2'}$) in the case of $[Ru(bpy)_3]^{2+}$.[11]