Novel Photoinduced Asymmetric Synthesis of Λ-[Co(acac)$_3$] from Co(acac)$_2$(H$_2$O)$_2$ and Hacac catalysed by Racemic Complexes of Δ- and Λ-[Ru(menbpy)$_3$]$^{2+}$ {menbpy = 4,4'-Di-[(1R,2S,5R)-(−)-menthoxycarbonyl)]-2,2'-bipyridine; Hacac = Pentane-2,4-dione}

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The asymmetric synthesis of M(C_3)-Λ-[Co(acac)$_3$] has been realized by the oxidation of Co(acac)$_2$(H$_2$O)$_2$ and Hacac with the racemic photocatalysts of [Ru(menbpy)$_3$]$^{2+}$ {menbpy = 4,4'-di-[(1R,2S,5R)-(−)-menthoxycarbonyl]-2,2'-bipyridine} which predominates the helical chirality of M(C_3)-Δ-[Ru(Menbpy)$_3$]$^{2+}$; the extent of the asymmetric induction by the helical photocatalyst has been enlarged by lowering the % v/v of EtOH–H$_2$O or by raising the molar ratio of [Hacac]/[Co(acac)$_2$(H$_2$O)$_2$].

Although asymmetric photocatalysis with chiral transition-metal complexes seems of interest and significant in photochemical reactions, it has hitherto been the subject of only limited investigation, probably because of the difficulty in the molecular design of effective chiral photocatalysts possessing a long lifetime (τ) without photodecomposition or photoracemization; the only one previously reported Λ-[Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine and τ = 580 ns in H$_2$O[1]) used for the stereoselective reduction of rac-[Co(acac)$_3$] did not behave as an efficient photocatalyst,[2] because it racemized easily (the quantum yield of photoracemization Φ_{rac} = 2.88 × 10^{-4} in EtOH[3]).

In this report, we describe the efficiency of a racemic photocatalyst, Δ- and Λ-[Ru(menbpy)$_3$]$^{2+}$ (1a for Δ, 1b for Λ), for the following novel asymmetric synthesis of a chiral tris-bidentate complex Δ- or Λ-[Co(acac)$_3$] (2a for Δ, 2b for Λ) from Co(acac)$_2$(H$_2$O)$_2$ 3 and acac$^-$.

The racemic photocatalyst of 1a–b [λ_{max} (ϵ) of metal-to-ligand charge transfer = 466 nm (27 200) in EtOH] has a long lifetime (τ = 1460 ns in EtOH) and was prepared by the reaction of RuCl$_3$·6H$_2$O and the chiral bipyridine ligand (menbpy) in EtOH at 90 °C for 7 days under deaerated conditions. The EtOH–H$_2$O (50–100% v/v) solution contain-

ing 20 µmol dm^{-3} of 1a–b, 10 mmol dm^{-3} of 3 and 10–10^3 mmol dm^{-3} of Hacac was irradiated (λ > 400 nm of a 500 W xenon lamp) at 25 °C in an O$_2$ atmosphere. When the 1a–b complex catalysed the oxidation of Co^{II}(acac)$_2$(H$_2$O)(acac$^-$) formed directly from 3 and acac$^-$ through the generation of the rac-Ru^{III} complex (1'a–b) by the reaction of the photoactivated ruthenium(II) complex (1*a–b) with O$_2$, the 2a–b complexes were produced substantially with the predominant formation (*viz.*, asymmetric synthesis) of 2b† (Fig. 1), and the % e.e. value of 2b was directly influenced by the % v/v of EtOH–H$_2$O or by the molar ratio of [Hacac]/[3] (Table 1).

The energetically most stable Δ- and Λ-[Ru(menbpy)$_3$]$^{2+}$ (complexes 1a and 1b determined by the molecular mechanics calculations[4]) shown in Scheme 1, do not have symmetrical conformations to each other, as indicated by the circular dichroism (CD) spectrum ascribed to M(C_3)-1a; [M(C_3) =
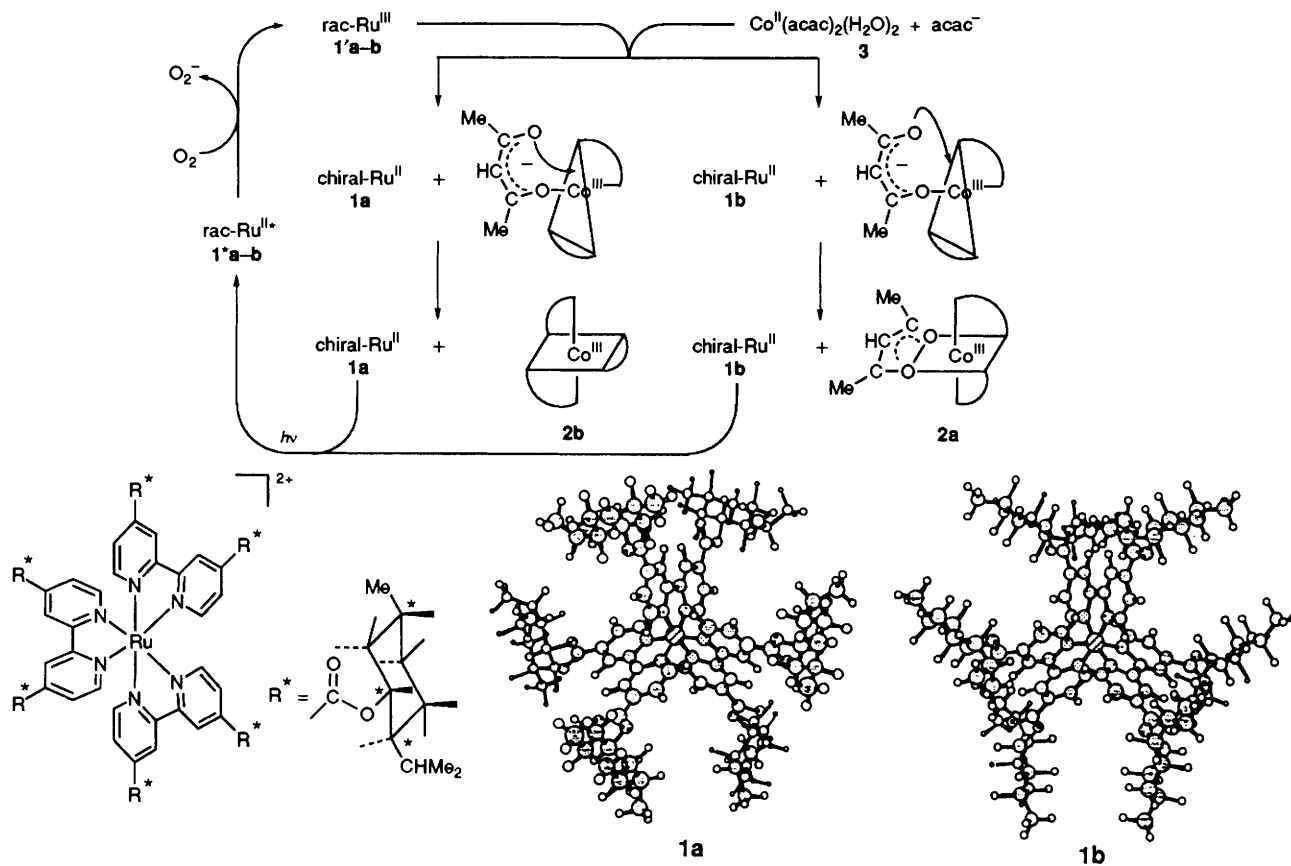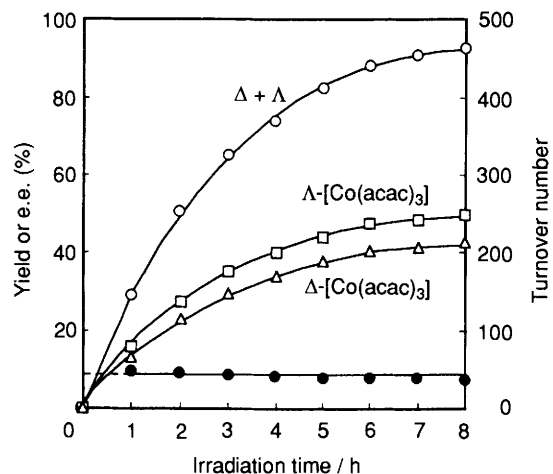

Scheme 1

Fig. 1 Enantiomeric excess (e.e.) (●) or yields of **2a** (△), **2b** (□) and **2a** + **2b** (○) synthesized by the photoinduced oxidation of **3** and Hacac with **1a–b** in 80% v/v EtOH–H₂O at 25 °C

minus or counterclockwise screw arrangement along the C_3 axis] rather than $P(C_3)$-**1b** [$P(C_3)$ = plus or clockwise screw]. The racemic **1a–b** photocatalyst with predominant chiral $M(C_3)$ molecular helicity, which oxidizes $Co^{II}(acac)_2(H_2O)$-$(acac^-)$ intermediate both catalytically and asymmetrically, results in the predominant synthesis of the same $M(C_3)$ helical Λ-[Co(acac)₃] **2b**. Probably, the molecular helicity of the photocatalyst seems to play an important role in the determi-

Table 1 Photoinduced asymmetric synthesis of **2a** or **2b** from **3** and Hacac with **1a–b**[a]

% v/v EtOH	[Hacac]/[3][b]	Yield (%)[c]	E.e. (%)[d]	E.e. (%) Enhancement[e]
100	100	79	1.9	9.5
	10	67	0.3	1.5
	1	70	0.2	1
90	100	84	2.2	22
	10	74	0.7	7.0
	1	71	0.1	1
85	100	80	6.5	
80	100	74	8.3	16
	10	79	2.3	4.4
	1	65	0.5	1
75	100	49	9.9	8.3
	10	76	4.9	4.0
	1	62	1.2	1
70	100	40	10	2.3
	50	38	10	2.3
	10	44	8.5	1.9
	1	55	4.4	1
65	100	28	10	
60	100	25	10	1.6
	50	26	9.2	1.5
	10	32	8.5	1.4
	1	34	6.3	1
50	100	21	10	1.5
	50	21	9.7	1.4
	10	19	9.1	1.3
	1	21	6.9	1

[a] Irradiation ($\lambda > 400$ nm) in O₂ at 25 °C, [**1a–b**] = 20 μmol dm⁻³. [b] [**3**] = 10 mmol dm⁻³. [c] For **2a** + **2b** after 4 h reaction. [d] Experimental error within ± 0.02% e.e. [e] Based on [Hacac]/[**3**] = 1.
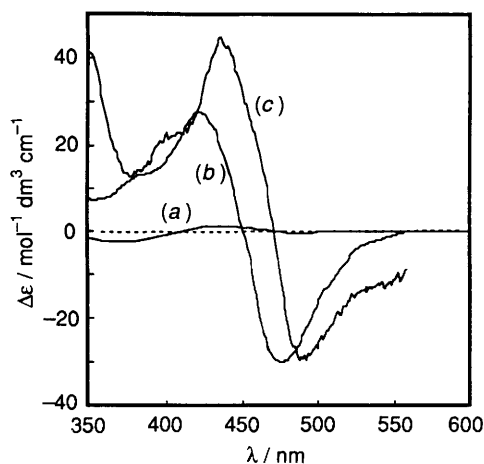
Fig. 2 CD spectra of (a) rac-[Ru(menbpy)₃]²⁺, (b) Δ-[Ru(bpy)₃]²⁺ and (c) Δ-[Ru(menbpy)₃]²⁺

sphere contact interaction of the chiral catalyst with the substrates as follows: (i) the increase of the solvent polarity (viz., low % v/v EtOH–H₂O) facilitates the hydrophobic interaction of hydrophobic reactants (1a–b and 3) so as to enhance the % e.e. value of 2b, and (ii) the increase of [acac⁻H⁺]/[3] ratio elevates the ionic strength of the solvent efficiently in the higher % v/v EtOH–H₂O so that the larger the magnitude of the hydrophobic interaction between 1a–b and 3 in the increased ionic strength of high [acac⁻H⁺]/[3] ratio, the more remarkable the extent of the % e.e. enhancement in the higher % v/v EtOH–H₂O (see Table 1).

nation of the prevailing helicity $P(C_3)$-Δ- or $M(C_3)$-Λ-[Co-(acac)₃] in the asymmetric reaction process (see Scheme 1).

The magnitude of such an asymmetric induction by the photocatalyst should be enhanced by intensifying the outer-

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