

Stereoselective Photocatalysis of Helical Ruthenium(II) Complexes in the Reduction of Racemic Tris(acetylacetonato)cobalt(III)

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The stereoselective photoreduction of *rac*-[Co(acac)₃] (Hacac = acetylacetonato) possessing molecular helicities [*P*(C₃) for Δ and *M*(C₃) for Λ] by several ruthenium(II) photocatalysts having either *P*(C₃) or *M*(C₃) helical symmetry was successfully performed with a maximum enantiomeric excess of 38.7% at 40% conversion {to [Co(acac)₂(H₂O)₂] in EtOH–H₂O (7:3) at 25 °C with an enantiomer rate ratio *k*^Δ/*k*^Λ of 5.2:1.

While molecular recognition in catalytic reactions is usually expected if there is an efficient interaction between the chiral catalyst and enantiomeric (or prochiral) substrate, the extent of molecular recognition in non-bonding long-range photocatalytic reactions would be expected to be small. Thus Porter and Sparks^{1,2} have reported that the stereoselective reduction of *rac*-[Co(acac)₃] (Hacac = acetylacetonato) by photoactivated Δ-[Ru(bipy)₃]²⁺ (bipy = 2,2'-bipyridine) shows very low stereoselectivity (with an enantiomer rate ratio *k*^Δ/*k*^Λ of 1.08:1). Here we describe the first efficient stereoselective photoreduction of *rac*-[Co(acac)₃] (Δ **1a**, Λ **1b**) with a series of diastereomeric ruthenium(II) complex photocatalysts of *rac*-[Ru(L¹)₃]²⁺ **2** or Δ-[Ru(L¹)₃]²⁺ **2a** {L¹ = 4,4'-di[(1*R*,2*S*,5*R*)-(–)-menthoxyacetyl]-2,2'-bipyridine} and *rac*-[Ru(L²)₃]²⁺ **3**, Δ-[Ru(L²)₃]²⁺ **3a** or Λ-[Ru(L²)₃]²⁺ **3b** {L² = 4,4'-di[(*R*)-(+) or (*S*)-(–)]-1-phenylethylaminocarbonyl]-2,2'-bipyridine}, Schemes 1 and 2.

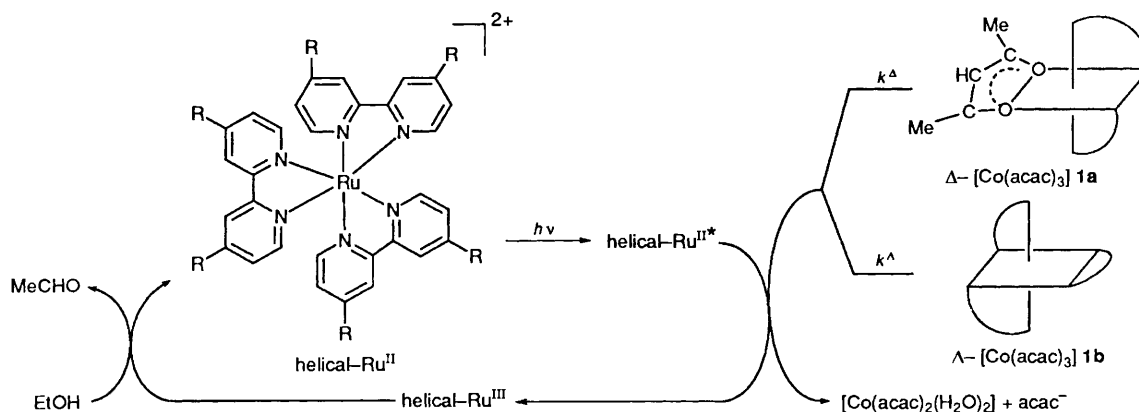
The ruthenium(II) chloride complexes were prepared according to the method described previously.^{3,4} Among the chiral ruthenium(II) complexes (their conformations viewed from the C₃ axis are shown in Scheme 2), **2a**, **R-3a** and **S-3b** were obtained by optical resolution of their Δ,Λ-diastereomates **2** or *R* (or *S*)-**3**, by silica gel column chromatography (eluent: chloroform–MeOH).

The molecular symmetries (Δ or Λ) of the present photo-

catalysts were determined by their CD spectra (in EtOH) on the basis of that of Δ-[Ru(bipy)₃]²⁺ **4a** (bipy = 2,2'-bipyridine) (Fig. 1). Molecular mechanics (MM2) calculations to establish the conformations adopted by the complexes indicated a helical *P*(C₃) symmetry for **S-3b** (or **R-3b**) and **4a** and a helical *M*(C₃) symmetry for **2a** and **R-3a** (or **S-3a**), where *P*(C₃) or *M*(C₃) indicates a plus (clockwise) or minus (counter-clockwise) helical arrangement along the C₃ axis, respectively. In this respect, the Δ- or Λ-[Co(acac)₃] enantiomers (**1a** or **1b**) possess helical *P*(C₃) or *M*(C₃) symmetry, respectively.

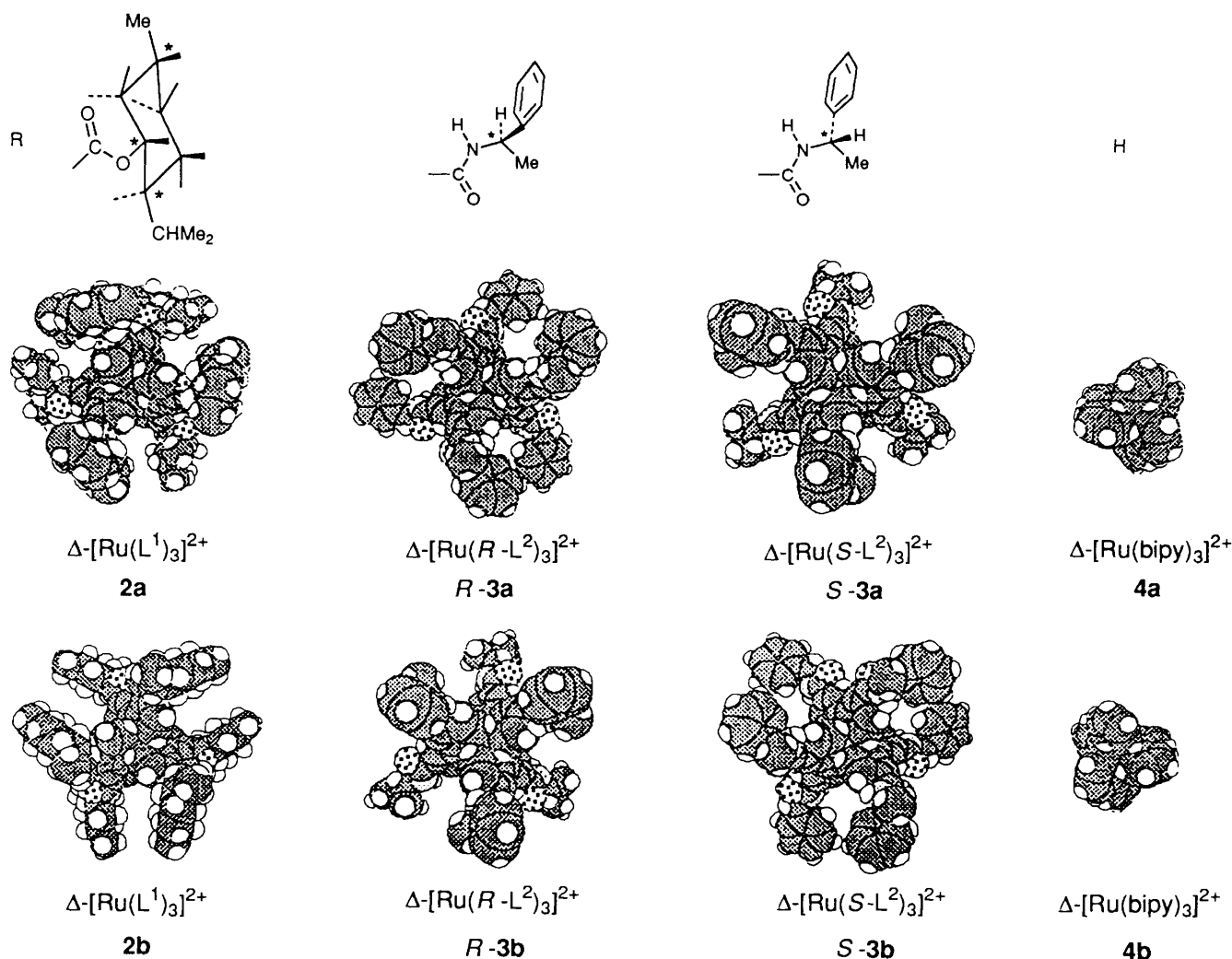
When the photoreduction of racemic **1** (2.4 mmol dm⁻³) by the photocatalyst (32 μmol dm⁻³) at λ > 400 nm (500 W xenon lamp) in deaerated EtOH–H₂O (7:3) at 25 °C was followed by monitoring unreacted **1a**, **1b** spectrophotometrically,[†] it was found to proceed catalytically and stereoselectively with the production of only [Co(acac)₂(H₂O)₂] and acac⁻ as the photoreduction products (Fig. 2).

It is noteworthy that the quantum yields (Φ) for the photoreduction of *rac*-[Co(acac)₃] and the enantiomeric excess



Scheme 1 Proposed mechanism for photocatalysis by helical ruthenium(II) complexes with [Co(acac)₃] (for definition of R see Scheme 2)

[†] The total concentration ([**1a**] + [**1b**]) and the concentration difference ([**1a**] – [**1b**]) were determined respectively using ε = 133 dm³ mol⁻¹ cm⁻¹ at λ_{UV} = 595 nm for **1** and Δε = –8.11 (**1a**) and +8.11 (**1b**) dm³ mol⁻¹ cm⁻¹ at λ_{CD} = 574 nm



Scheme 2 Structures of helical ruthenium(II) complexes as generated from molecular mechanics calculations

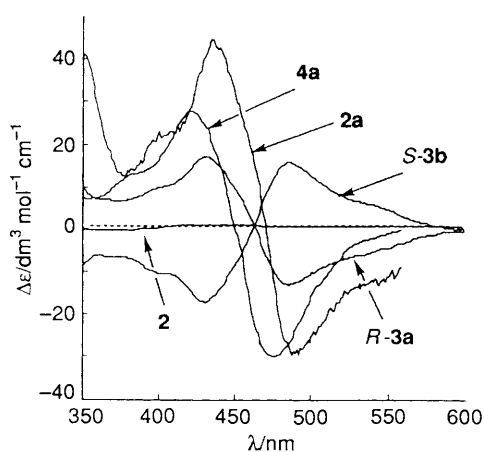


Fig. 1 CD spectra of the chiral photocatalysts

(% e.e.) values in Table 1 were similar in the photoreactions with *R*-**3** or *R*-**3a** and in the reactions with *S*-**3** or *S*-**3b**. This suggests that *R*-**3** and *S*-**3** are mainly composed of *R*-**3a** and *S*-**3b**, respectively. In fact, Δ -[Ru(*S*-L²)₃]²⁺ *S*-**3a** and Δ -[Ru(*R*-L²)₃]²⁺ *R*-**3b** were not detected in the optical resolution of *rac*-[Ru(*rac*-L²)₃]²⁺ *RS*-**3** or *rac*-[Ru{*R* (or *S*)-L²]₃]²⁺ *R* (or *S*)-**3**,⁴ and the CD spectra of the above series of the photocatalysts were found to be almost identical; probably, the formation of the *S*-**3a** (or *R*-**3b**) structure is not allowed owing to steric

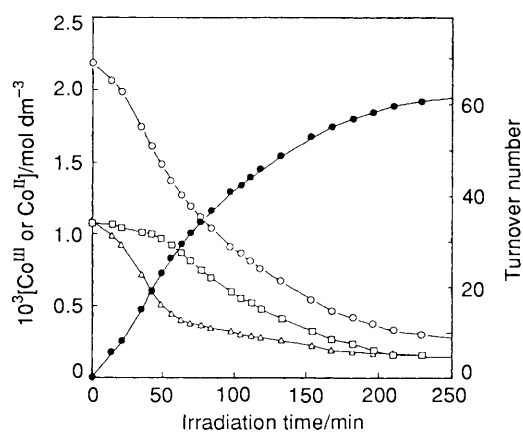


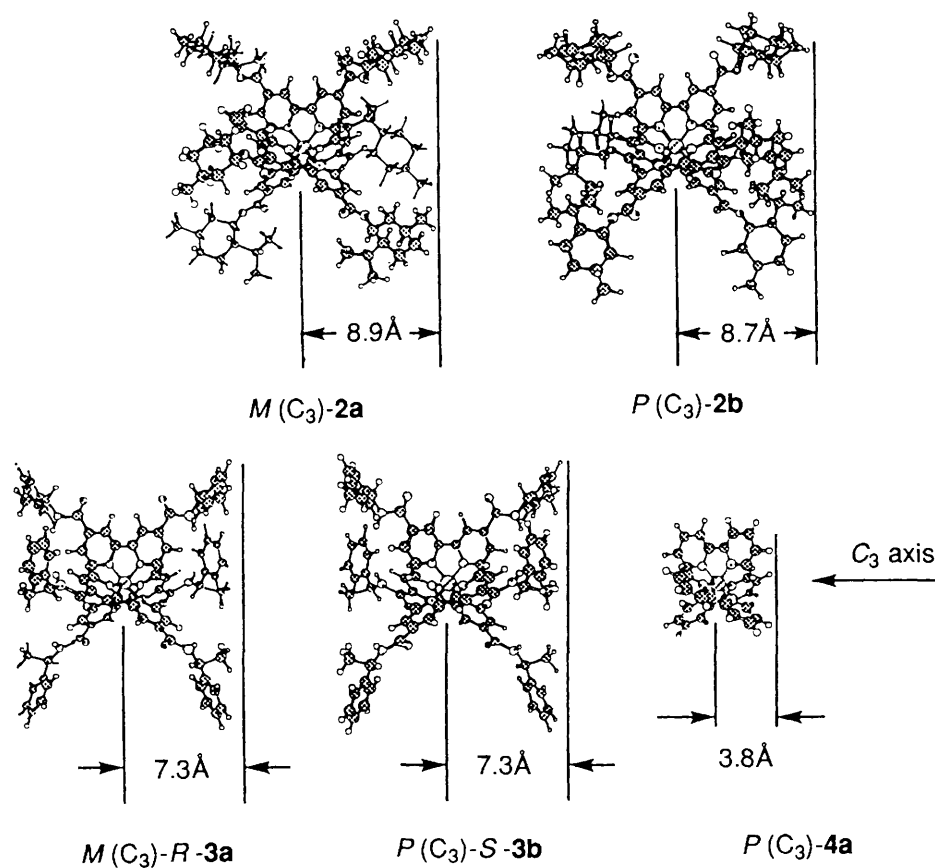
Fig. 2 Variation of concentration of the substrate [**1** (○), **1a** (△) or **1b** (□)] and [Co(acac)₂(H₂O)₂] (●) with irradiation time with **2a** photocatalyst

hindrance between the phenyl rings between the ligands. On the other hand, *rac*-[Ru(L¹)₃]²⁺ **2** contains both Δ - and Λ -[Ru(L¹)₃]²⁺ **2a**, **2b**, with the former showing the most predominant molecular helicity (Fig. 3). Significantly the order of molecular recognition abilities of the photocatalysts in the present long-range electron transfer reactions, **2a** > **2** > *S*-**3b** \approx *R*-**3a** \gg **4a**, seems to be reflected in the extent of their molecular helicities in the direction of the C₃ symmetry axis (Fig. 3) along which the reactions seem to proceed.

Table 1 Stereoselective photocatalytic reduction of *rac*-[Co(acac)₃] **1**^a

Ruthenium(II) complex	Helicity ^b	10 ⁵ Φ _{decomp.} ^c	10 ⁶ Φ _{rac} ^d	10 ² Φ ^e	Conversion/%	E.e./%	Prevailing helicity
2 <i>rac</i> -[Ru(L ¹) ₃] ²⁺	[M(C ₃)]	1.9	—	2.4	41.7	14.7	P(C ₃)
2a Δ-[Ru(L ¹) ₃] ²⁺	M(C ₃)	1.9 (1.6)	4.0 (1.7) ^f	2.8	40.3	38.7	P(C ₃)
RS- 3 <i>rac</i> -[Ru(<i>rac</i> -L ²) ₃] ²⁺	—	1.8	—	3.0	47.7	0	—
R- 3 <i>rac</i> -[Ru(R-L ²) ₃] ²⁺	[M(C ₃)]	1.8	7.6	4.7	56.3	2.1	P(C ₃)
S- 3 <i>rac</i> -[Ru(S-L ²) ₃] ²⁺	[P(C ₃)]	1.8	7.6	4.8	57.9	2.2	M(C ₃)
R- 3a Δ-[Ru(R-L ²) ₃] ²⁺	M(C ₃)	1.8	7.6	4.6	56.1	2.0	P(C ₃)
S- 3b Λ-[Ru(S-L ²) ₃] ²⁺	P(C ₃)	1.8	7.6	4.9	57.9	2.2	M(C ₃)
4 <i>rac</i> -[Ru(bipy) ₃] ²⁺	—	1.0	—	0.03	1.1	0	—
4a Δ-[Ru(bipy) ₃] ²⁺	P(C ₃)	1.0	288	0.03	1.3	<0.1	M(C ₃)

^a [Ru^{II}] = 32 μmol dm⁻³, [Co(acac)₃] = 2.4 mmol dm⁻³, EtOH-H₂O (7:3), 25 °C. ^b Square brackets indicate the helicity of the major component of the mixture. ^c Quantum yields for decomposition in EtOH. ^d Quantum yields for photoracemization in EtOH. ^e Quantum yields. ^f In EtOH-H₂O (7:3) after 50 min.

**Fig. 3** Molecular extents of M(C₃)-**2a**, P(C₃)-**2b**, M(C₃)-R-**3a**, P(C₃)-S-**3b** and P(C₃)-**4a** in the direction of C₃ symmetry axis

It is also notable from Table 1 that the M(C₃) helical photocatalysts (**2**, **2a**, R-**3** and R-**3a**) predominantly reduced the P(C₃) helical substrate **1a** (with a maximum e.e. value of 38.7% in the reduction of **1** by **2a**), while the P(C₃) helical catalysts (S-**3**, S-**3b** and **4a**) facilitated the reduction of the M(C₃) helical substrate **1b**. Thus, there appears to be a 'shape recognition' in these reactions with enhanced reactivity between opposite helical pairs P(C₃) and M(C₃).

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