

A Novel Photocatalytic Asymmetric Synthesis of (*R*)-(+)-1,1'-Bi-2-naphthol Derivatives by Oxidative Coupling of 3-Substituted-2-naphthol with Δ -[Ru(menbpy)₃]²⁺ [menbpy = 4,4'-di(1*R*,2*S*,5*R*)-(-)-menthoxy-carbonyl-2,2'-bipyridine], which possesses Molecular Helicity

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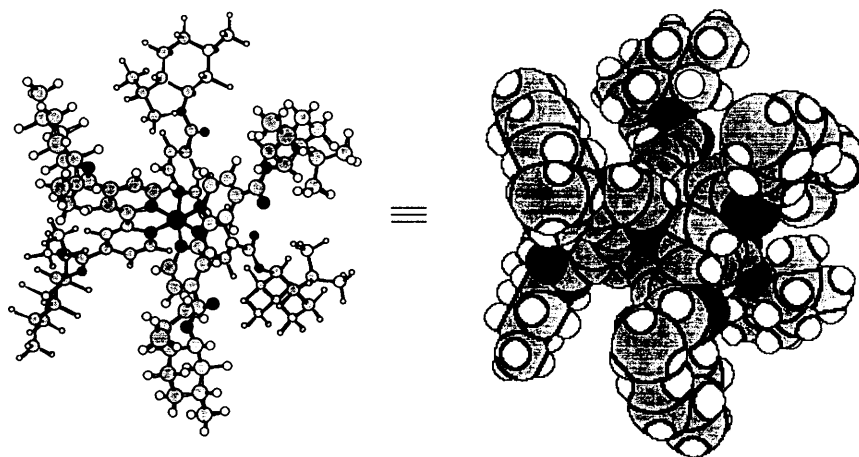
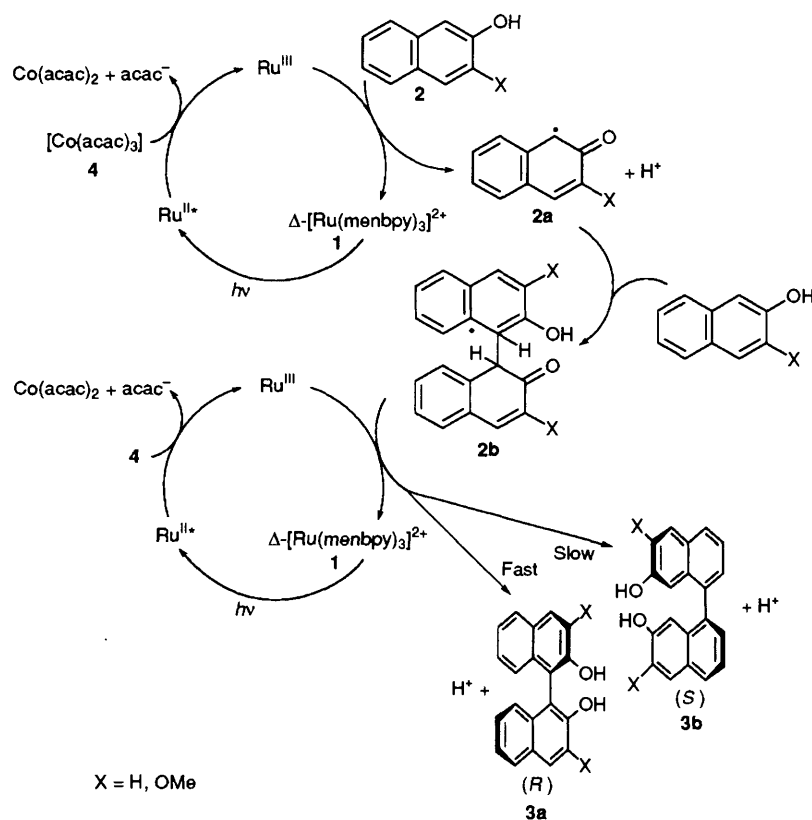
The asymmetric synthesis of (*R*)-(+)-1,1'-bi-2-naphthol [or (*R*)-(+)-1,1'-bi-3-methoxy-2-naphthol] from 2-naphthol (or 3-methoxy-2-naphthol) is performed photocatalytically by using the chiral ruthenium complex, $M(C_3)$ - Δ -[Ru(menbpy)₃]²⁺ [$M(C_3)$ = counterclockwise molecular helicity along the C₃ axis, menbpy = 4,4'-di(1*R*,2*S*,5*R*)-(-)-menthoxy-carbonyl-2,2'-bipyridine] as a photosensitizer and [Co(acac)₃] (acac⁻ = acetylacetonato) as an oxidant.

Although asymmetric synthesis with transition metal complex catalysts has received considerable attention, photocatalytic synthesis of chiral organic compounds has only been subjected to limited investigation, because of the lack of photocatalytically efficient metal complexes with high asymmetric-induction ability.¹ We have designed a photostable chiral ruthenium trisbipyridine-type complex, Δ -[Ru(menbpy)₃]²⁺ as a photocatalyst, which possesses a high redox ability; Δ -[Ru(menbpy)₃]²⁺ synthesized by the introducing of (1*R*,2*S*,5*R*)-(-)-menthoxy-carbonyl groups into the 4,4'-positions of 2,2'-bipyridine (bpy) ligands in Δ -[Ru(bpy)₃]²⁺ has a counterclockwise $M(C_3)$ molecular helicity along the C₃ axis² as described below (Fig. 1).

The chiral ruthenium photocatalyst of Δ -[Ru(menbpy)₃]²⁺, which was prepared by optical resolution of racemic [Ru(menbpy)₃]²⁺ with silica gel column chromatography

(eluent: chloroform/MeOH 95:5 v/v)³ has a long excited state lifetime (τ = 1940 ns in MeCN) and extremely low quantum yield of photoracemization ($\Phi_{\text{rac}} = 4 \times 10^{-6}$ in MeCN) and decomposition ($\Phi_{\text{decomp.}} = 4 \times 10^{-6}$ in MeCN) compared with those (τ = 850 ns in MeCN, $\Phi_{\text{rac}} = 3 \times 10^{-4}$ in EtOH at 25 °C,⁴ and $\Phi_{\text{decomp.}} = 1 \times 10^{-5}$ in H₂O at 70 °C⁵) of Δ -[Ru(bpy)₃]²⁺, and the redox potential of Δ -[Ru(menbpy)₃]²⁺ ($E^{3+/2+} = +1.55$ V vs. SCE in MeCN[†]) is more positive than that (+1.29 V in MeCN)⁶ of Δ -[Ru(bpy)₃]²⁺.

[†] The reduction potential was estimated by using the E_{0-0} energy of 2.00 V and the excited-state oxidation potential [$E(3+/2+^*) = -0.45$ V vs. SCE in MeCN] which was obtained by means of the Rehm-Weller relation between some reduction potentials of quenchers and its quenching rate constants for [Ru(menbpy)₃]²⁺. See ref. 6.

M (C₃)-Δ-[Ru(menbpy)₃]²⁺Fig. 1 The conformation of Δ-[Ru(menbpy)₃]²⁺ determined by molecular mechanics calculations²

Scheme 1

We report here a novel photoaccelerated asymmetric synthesis of an axially symmetrical (*R*)-(+)-1,1'-bi-2-naphthol derivative **3a** catalysed by Δ-[Ru(menbpy)₃]²⁺ **1** with an oxidant of [Co(acac)₃] **4** (Scheme 1). Because the one-electron oxidation potential of the 2-naphthol derivative (X = H or OMe) **2** is +1.34 (X = H) or +1.32 (X = OMe) V vs. SCE in MeCN, ‡ Δ-[Ru(menbpy)₃]³⁺ formed by an oxidative quenching of Δ-[Ru(menbpy)₃]²⁺ with **4**, can oxidize **2** efficiently so as to generate the radical **2a**⁷ which produce a precursor of the 1,1'-bi-2-naphthol derivative **2b**. The oxidation of **2b** by **1**

might produce **3a-b** with the prevailing formation of **3a** (or **3b**).

An acetonitrile solution containing **1** (50 μmol dm⁻³), **2** (10 mmol dm⁻³) and **4** (12 mmol dm⁻³) was prepared and deaerated by freeze-pump-thaw cycles. Then the solution placed in a Pyrex cell at 25 °C was irradiated with visible light (λ > 400 nm) from a 500 W xenon lamp with a Toshiba L-42 glass filter. The photocatalytic reaction was monitored from the decrease of the **2** and the increase of **3a-b** by HPLC [Merck RP-18; MeOH/H₂O (7:3 v/v) for **2** (X = H) or MeOH/H₂O (7:3-10:0 v/v linear gradient) for **2** (X = OMe)] and from the decrease of **4** oxidant by a Hitachi model U3210 spectrophotometer. The enantiomeric excess (e.e.) of **3a** or **3b** was calculated from the amounts of **3a**, **b**, which were observed by means of HPLC with a chiral column [YMC K03; n-hexane/CH₂Cl₂/EtOH (80:20:2 v/v/v) for **2** (X = H) or

‡ The oxidation potentials of the 2-naphthol derivative and the 1,1'-bi-2-naphthol derivative were determined by cyclic voltammetry. See S. Fukuzumi, K. Hironaka, N. Nishizawa and T. Tanaka, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2220.

Sumichiral OA-2500I; n-hexane/CH₂Cl₂/EtOH (83:15:2 v/v/v) for **2** (X = OMe)].

The chiral complex **1** substantially generated **3a** predominantly under photoirradiation with the formation of byproducts such as 1-(2-naphthoxy)-2-naphthol, and the equivalent consumption of **2** and **4** by the catalyst **1** resulted in a turnover number *ca.* 66 after a 16 h reaction; **3a** was produced in excess rather than **3b**, with 16.2% e.e. (X = H) or 3.95% e.e. (X = OMe).

In the present reaction the enantioselective reduction of the *rac*-[Co(acac)₃] oxidant by the photoactivated Δ-[Ru(menbpy)₃]^{2+*} complex was included. § When the coupling reaction of **2** (X = H) by *rac*-[Ru(bpy)₃]²⁺ was carried out in the presence of Δ(or Λ)-[Co(acac)₃], **3a** (or **3b**) (X = H) was produced in its 1.53% e.e. (or 1.33% e.e.). Therefore, the contribution of Δ(or Λ)-[Co(acac)₃] *per se* to the e.e. for the chiral product was found to be negligible. Anyway, the chiral Δ-[Ru(menbpy)₃]²⁺ catalyst **1** which possesses the M(C₃) molecular helicity yields (*R*)-(+)-isomer of **3a** as the prevailing configuration of the product. When the molecular helicities of **3a**, **b** [P(C₂) for **3a** and M(C₂) for **3b**] are taken

into consideration, the M(C₃) helicity of **1** plays an important role in the predominant molecular recognition of the P(C₂) helical **3a** generated in the oxidation of **2b** by **1**.

In conclusion, the chiral M(C₃)-ruthenium(II) catalyst **1** yields P(C₂)-**3a** preferentially *via* the molecular recognition at the transition state of the **2b** oxidation reaction, and the present asymmetric reaction was accelerated photocatalytically with 'shape recognition' of the molecular helicities of the reacting species.

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References

- 1 A. G. Lappin and R. A. Marusak, *Coord. Chem. Rev.*, 1991, **109**, 125.
- 2 H. Ishida, T. Hamada, Y. Fujishita, Y. Saito and K. Ohkubo, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 714.
- 3 K. Ohkubo, T. Hamada and T. Inaoka, *Inorg. Chem.*, 1989, **28**, 2021.
- 4 G. B. Porter and R. H. Sparks, *J. Photochem.*, 1980, **13**, 123.
- 5 J. Van Houten and R. J. Watts, *Inorg. Chem.*, 1978, **17**, 3381.
- 6 C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan and J. K. Nagle, *J. Am. Chem. Soc.*, 1979, **101**, 4815.
- 7 M. J. S. Dewar and T. Nakaya, *J. Am. Chem. Soc.*, 1968, **90**, 7134.
- 8 K. Ohkubo, T. Hamada, S. Usui and H. Ishida, *J. Am. Chem. Soc.*, submitted for publication.

§ In regard to the prevailing consumption of Δ-[Co(acac)₃] during the photoreduction of *rac*-[Co(acac)₃] by Δ-[Ru(menbpy)₃]²⁺. See ref. 8.