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Journal of Photochemistry and Photobiology A: Chemistry 95 (1996) 231–233

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

Novel photocatalytic asymmetrical synthesis of Δ(or Λ)-[Co(acac)$_3$] (acac, pentane-2,4-dione) from [Co(acac)$_2$(H$_2$O)$_2$] and Hacac with helical ruthenium(II) complexes

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Received 8 August 1995; accepted 20 October 1995

Abstract

The photocatalytic asymmetrical synthesis of Δ(or Λ)-[Co(acac)$_3$] (acac, pentane-2,4-dione) from [Co(acac)$_2$(H$_2$O)$_2$] and Hacac was successfully performed with novel helical ruthenium(II) complexes of Δ-[Ru(Menbpy)$_3$]$^{2+}$ (**1**; Menbpy, 4,4′-bis{(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl}-2,2′-bipyridine), Δ-[Ru(*R*-PhEtbpy)$_3$]$^{2+}$ (**2a**), Λ-[Ru(*S*-PhEtbpy)$_3$]$^{2+}$ (**2b**) (*R*- or *S*-PhEtbpy, 4,4′-bis[(*R*)-(+)- or (*S*)-(−)-1-phenylethylaminocarbonyl]-2,2′-bipyridine) and Δ-[Ru(bpy)$_3$]$^{2+}$ (**3**; bpy, 2,2′-bipyridine); photocatalyst **1** possesses the most efficient extent of minus (counterclockwise) M(C_3) helicity along the C_3 symmetry axis, resulting in a maximum enantiomeric excess (37% e.e.) of Λ-[Co(acac)$_3$] in 50% v/v EtOH–H$_2$O at 298 K.

Keywords: Photocatalytic asymmetrical synthesis; Δ (or Λ)-[Co(acac)$_3$]; Helical ruthenium(II) complexes

1. Introduction

Although photocatalytic asymmetrical synthesis with chiral (and/or helical) transition metal complexes is interesting and significant in photochemical reactions, it has hitherto been the subject of only limited investigation. Only one report exists on the asymmetrical synthesis of (*R*)-(+)-1,1′-bi-2-naphthol derivatives from 3-substituted 2-naphthol with Δ-[Ru(Menbpy)$_3$]$^{2+}$ (Menbpy, 4,4′-bis{(1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl}-2,2′-bipyridine) [1]. In this work, we deal with the photocatalytic efficiencies of some helical ruthenium(II) complexes for the asymmetrical synthesis of Δ (or Λ)-[Co(acac)$_3$] (acac, pentane-2,4-dione) from [Co(acac)$_2$(H$_2$O)$_2$] and Hacac (Scheme 1). The helical ruthenium(II) complexes examined in the present photoinduced asymmetrical synthesis reactions are Δ-[Ru(Menbpy)$_3$]$^{2+}$ (**1**), Δ-[Ru(*R*-PhEtbpy)$_3$]$^{2+}$ (**2a**), Λ-[Ru(*S*-PhEtbpy)$_3$]$^{2+}$ (**2b**) (*R*- or *S*-PhEtbpy, 4,4′-bis[(*R*)-(+)- or (*S*)-(−)-1-phenylethylaminocarbonyl]-2,2′-bip yridine) and Δ-[Ru(bpy)$_3$]$^{2+}$ (**3**; bpy, 2,2′-bipyridine).

2. Preparation of the complexes

Complexes **1**, **2a** and **2b** were obtained by optical resolution of diastereomeric Δ,Λ-[Ru(L)$_3$]$^{2+}$ 2Cl$^-$ (L ≡ Menbpy or *R*- (or *S*)-PhEtbpy complexes) (prepared by the reaction of RuCl$_3$ and L in EtOH at 363 K for 5–6 days) with silica gel column chromatography (eluent, CHCl$_3$–MeOH), and Δ-[Ru(bpy)$_3$]$^{2+}$ was obtained in the usual way [2].

3. Results and discussion

Molecular mechanics (MM2) calculations of these complexes with the energetically minimized conformations of the ligands [3] gave M(C_3) helicity for **1** and **2a** and P(C_3) helicity for **2b** and **3**, where M(C_3) and P(C_3) denote minus (counterclockwise) and plus (clockwise) helical arrangement along the C_3 symmetry axis respectively. (This notation was used for tris-bidentate chelate complexes [4].) When 50% v/v EtOH–H$_2$O solutions containing [Co(acac)$_2$(H$_2$O)$_2$] (10 mmol dm^{-3}) and Hacac (100 mmol dm^{-3}) were irradiated by a 500 W xenon lamp in O$_2$ with or without photocatalyst (20 μmol dm^{-3}) under conditions of $\lambda > 400$ nm at 298 K, the formation of [Co(acac)$_3$] (**4a** for Δ and **4b** for Λ enantiomer) was obtained only in the reaction with

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SSDI 1010-6030(95)04263-6

the photocatalyst. A typical result obtained for complex **1** is shown in Fig. 1. As can be seen in Fig. 1, the asymmetrical photocatalysis of **1** caused the accumulation of **4a** and **4b** in different concentrations with a constant enantiomeric excess (e.e.) of 37% of **4b** during the photoreaction; the product concentrations of [**4a** + **4b**] and [**4b** − **4a**] were determined by UV and CD spectroscopic measurements respectively with $\epsilon = 133$ mol^{-1} dm^3 cm^{-1} at λ(UV) = 595 nm for **4a** + **4b**, $\Delta\epsilon = -8.11$ mol^{-1} dm^3 cm^{-1} (**4a**) and $\Delta\epsilon = +8.11$ mol^{-1} dm^3 cm^{-1} (**4b**) at λ(CD) = 574 nm and $\Delta\epsilon = +2.88$ mol^{-1} dm^3 cm^{-1} (**4a**) and $\Delta\epsilon = -2.88$ mol^{-1} dm^3 cm^{-1} (**4b**) at λ(CD) = 647 nm; the turnover number was evaluated on the basis of [**4a** + **4b**] with respect to [**1**]. (The extinction coefficients ϵ for UV and $\Delta\epsilon$ for CD were determined using Δ- and Λ-$[\mathrm{Co(acac)_3}]$ (**4a** and **4b** respectively) which were obtained by the optical resolution of racemic $[\mathrm{Co(acac)_3}]$ with (2*R*,3*S*)-(−)-dibenzoyl-tartaric acid monohydrate in benzene and cyclohexane. The enantiomeric excess (e.e.) of **4b** was evaluated from the equation e.e.(%) = 10^2[**4b** − **4a**]/[**4a** + **4b**].) It is notable from the e.e. values of **4b** summarized in Table 1 that the magnitude of the asymmetrical induction of the present photocatalysts follows the order of **1** ≫ **2a** = **2b** > **3** with the prevailing conformation of M(C_3)-**4b** in the case of M(C_3)-**1**(or **2a**) and of P(C_3)-**4a** in the case of P(C_3)-**2b**(or **3**). The different molecular extents of the helical photocatalysts (**1**–**3**) probably change the magnitude of asymmetrical induction; the formation of $[\mathrm{Co(acac)_3}]$ (**4a** + **4b**) from $[\mathrm{Co(acac)_2(H_2O)_2}]$ and Hacac, after oxidation of $[\mathrm{Co(acac)_2(H_2O)_2}]$ by the helical ruthenium(III) complexes (generated by the reaction of **1**–**3** with O_2), suffers from the asymmetrical induction of **1**–**3**; the extent of asymmetrical induction by M(C_3)-**1** was most remarkable in the present reactions.

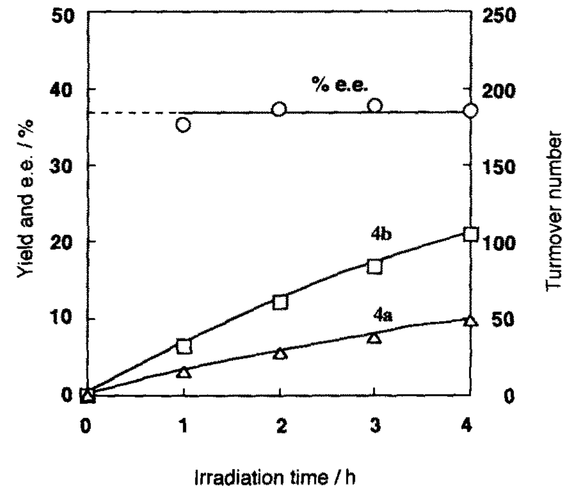
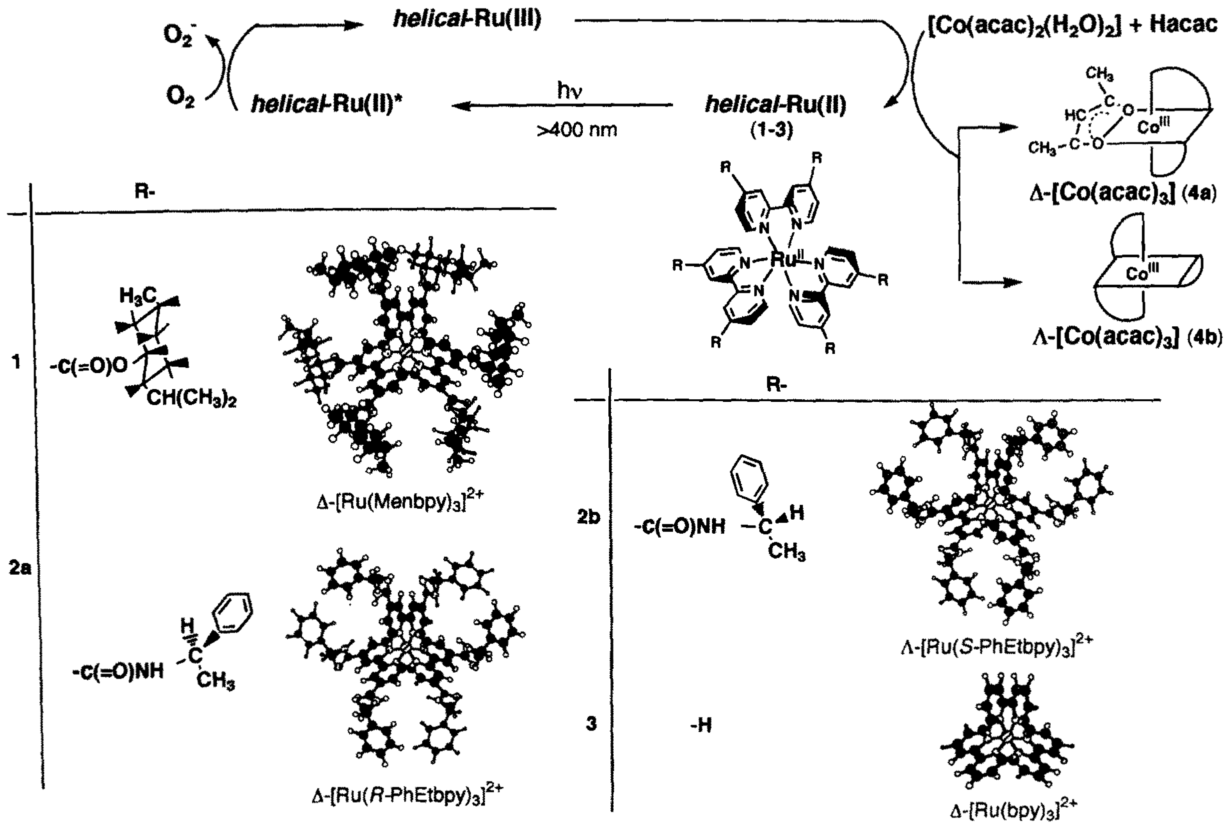


Fig. 1. Asymmetrical synthesis of Δ- and Λ-$[\mathrm{Co(acac)_3}]$ (**4a** and **4b** respectively) from $[\mathrm{Co(acac)_2(H_2O)_2}]$ (10 mmol dm^{-3}) and Hacac (1.0 mol dm^{-3}) with the photocatalyst **1** (20 μmol dm^{-3}) in 50% v/v EtOH–H_2O in O_2 at 298 K.

Detailed investigation of the photocatalysed asymmetrical synthesis reaction is now in progress.



Scheme 1.

Table 1

Asymmetrical synthesis of Δ (or Λ)-[Co(acac)$_3$] (**4a** (or **4b**)) from [Co(acac)$_2$(H$_2$O)$_2$] and Hacac with the helical photocatalysts **1–3** [a]

Photocatalyst	Molecular helicity	λ(MLCT)$_{max}$ (ε) (nm)	Yield (%)			E.e. (%)	Prevailing configuration
			4a	**4b**	Total		
Δ-[Ru(Menbpy)$_3$]$^{2+}$ (**1**)	M(C_3)	466 (27200)	9.7	21.1	30.8	37	M(C_3)
Δ-[Ru(*R*-PhEtbpy)$_3$]$^{2+}$ (**2a**)	M(C_3)	464 (21200)	21.2	21.4	42.6	0.5	M(C_3)
Λ-[Ru(*S*-PhEtbpy)$_3$]$^{2+}$ (**2b**)	P(C_3)	464 (21200)	22.6	22.4	45.0	0.5	P(C_3)
Δ-[Ru(bpy)$_3$]$^{2+}$ (**3**)	P(C_3)	452 (14600)	1.0$_5$	1.0$_5$	2.1	<0.1	P(C_3)

[a] [Photocatalyst] = 20 μmol dm^{-3}; [Co(acac)$_2$(H$_2$O)$_2$] = 10 mmol dm^{-3}; [Hacac] = 1.0 mol dm^{-3}; in 50% v.v EtOH–H$_2$O in O$_2$ at 298 K.

References

[1] T. Hamada, H. Ishida, S. Usui, Y. Watanabe, K. Tsumura and K. Ohkubo, *J. Chem. Soc., Chem. Commun.*, (1993) 909.

[2] G.B. Porter and R.H. Sparks, *J. Photochem.*, *13* (1980) 123.

[3] H. Ishida, T. Hamada, Y. Fujishita, Y. Saito and K. Ohkubo, *Bull. Chem. Soc. Jpn.*, *66* (1993) 714.

[4] A.G. Lappin and R.A. Marusak, *Coord. Chem. Rev.*, *109* (1991) 125.