CHEMISTRY LETTERS, pp. 1545-1548, 1989.

Enantioselective Electron Transfer Reaction Catalyzed by a Novel Photosensitizer, $[Ru(S(-) \text{ or } R(+)\text{-PhEt}^{*}bpy)_3]^{2+}$

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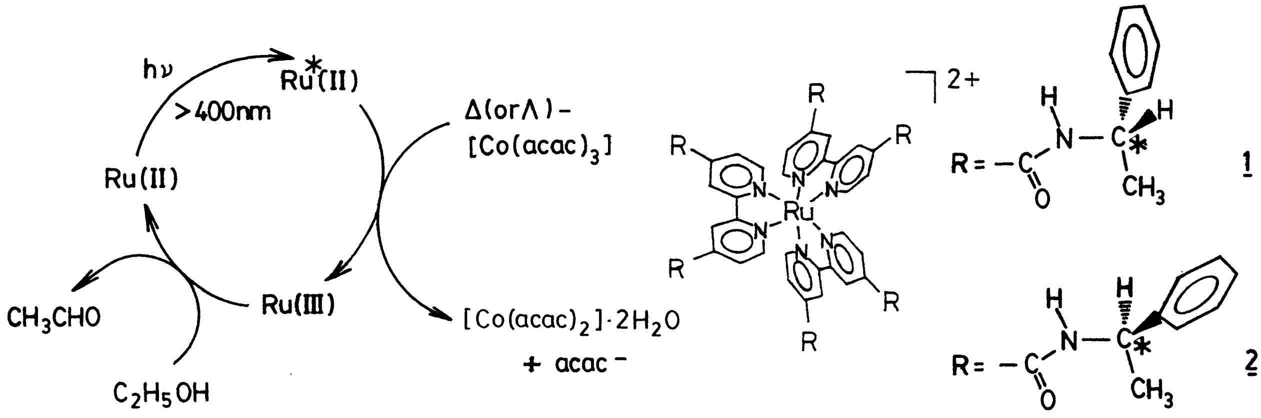
A novel ruthenium photosensitizer, $[Ru(S(-)\text{-PhEt}^{*}bpy)_3]^{2+}$, was found to have Λ-configuration predominantly and reduce $[Co(acac)_3]$ catalytically with high enantioselectivity (k_Λ/k_Δ = 1.54) under irradiation of light ($\lambda > 400$ nm) in ethanol/water (9:1 v/v).

Stereoselective electron transfer reactions between transition metal complexes which have molecular asymmetry such as Δ or Λ-configuration have been known,1) and it has been reported that the enantiomer rate ratio (k_Λ/k_Δ) for electron transfer reaction between Δ-$[Ru(bpy)_3]^{2+}$ and $[Co(acac)_3]$ (acacH = acethylacetone) is 1.08.1a) However, there are few reports concerning enantioselective electron transfer between the metal complex having chiral ligands and the metal complex having molecular asymmetry such as Δ or Λ form. We report here that a ruthenium complex, $[Ru(S(-)\text{-PhEt}^{*}bpy)_3]^{2+}$ (1) (or $[Ru(R(+)\text{-PhEt}^{*}bpy)_3]^{2+}$ (2)) reduces $[Co(acac)_3]$ catalytically with high enantioselectivity under irradiation of light ($\lambda > 400$ nm) in an aqueous ethanol (Scheme 1).

The chiral ligands, S(-) and R(+)-PhEt*bpy, were synthesized by amidation of 4,4'-dicarboxy-2,2'-bipyridine with S(-) and R(+)-1-phenylethylamine, respectively. $[Ru(S(-) \text{ or } R(+)\text{-PhEt}^{*}bpy)_3]^{2+}$ was prepared by heating an ethanol solution (3 cm^3) containing ruthenium trichloride (27 mg) and the chiral ligand (0.152 g) in a sealed tube at 90°C for 5 days, and were purified by chromatography



Scheme 1.

on Silica gel using acetone/chloroform (1:1 v/v) as an eluent; yield 45%.[2)] The absorption (λ_{max} = 464 nm, ε = 21200 in ethanol) and emission spectra (λ_{max} = 621 nm in ethanol) of the ruthenium complex are essentially the same as those of $[Ru(bpy)_3]^{2+}$.

The reduction of $[Co(acac)_3]$ was performed by irradiation for a thoroughly degassed aqueous ethanol solution of the ruthenium complex 1 (or 2) (3.2×10^{-5} mol dm^{-3}) and $[Co(acac)_3]$ (2.4×10^{-3} mol dm^{-3}). The photochemical reduction was monitored by a decrease in the absorption band (λ_{max} = 595 nm) of $[Co(acac)_3]$, and was found to proceed catalytically with obeying pseudo-first-order kinetics. The turnover number was 40 for 1 hour in the photoreduction catalyzed by 1 in ethanol/water (1:1 v/v). The electron donor is ethanol since acetaldehyde

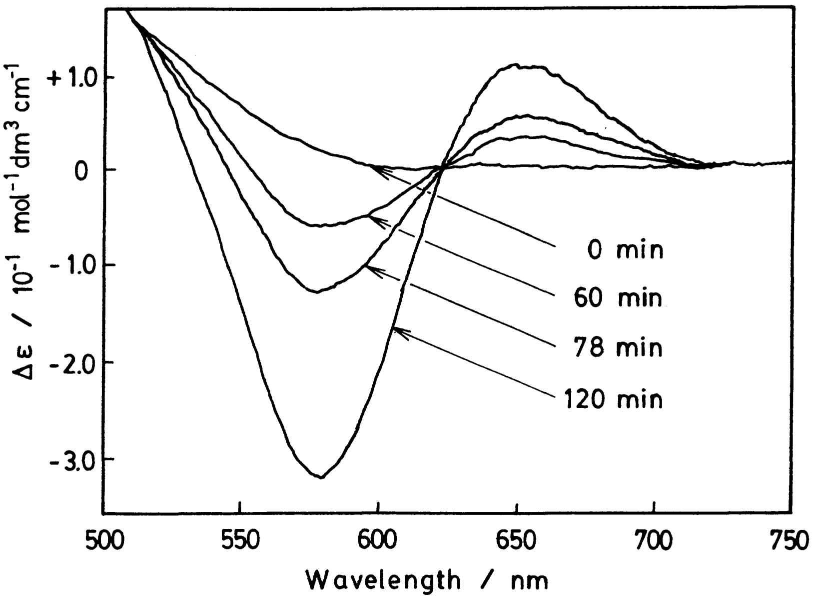


Fig. 1. CD spectral changes of the reaction solution (ethanol/water 9:1 v/v) containing 1 and $[Co(acac)_3]$.

was detected by colorimetric analysis. At the same time, the CD spectra of the reaction solution drastically changed as shown in Fig. 1. The changes by the reaction with 1 are attributable to relative increase of Δ-[Co(acac)$_3$] by more consumption of Λ-[Co(acac)$_3$]. The k_{obsd} values and the selectivities (enantiomer rate ratio)$^{3)}$ are listed in Table 1, and are largely dependent on the solvent. As the ethanol content in the solvents increased, k_{obsd} values decreased, while the selectivities increased. The maximum enantioselectivity of 1 was 1.54 (Λ/Δ) in ethanol/water (9:1 v/v). The catalyst 2 reacted to Δ-[Co(acac)$_3$] predominantly with the opposite selection (Δ/Λ = 1.54) to the case of 1.

Table 1. Photoreduction of [Co(acac)$_3$] catalyzed by the chiral ruthenium complexes

Cat.	Ethanol content / %	$10^2 k_{obsd}$ / min^{-1}	Selectivity
1	90	0.23 ± 0.01	Λ / Δ 1.54
	70	1.79 ± 0.01	1.05
	50	2.25 ± 0.01	1.03
2	97	0.04 ± 0.01	Δ / Λ 1.54

The CD spectra of the ruthenium complexes, 1, 2, and Δ-[Ru(bpy)$_3$]$^{2+}$, are shown in Fig. 2. The catalysts 1, 2 show CD bands around 300 nm which are

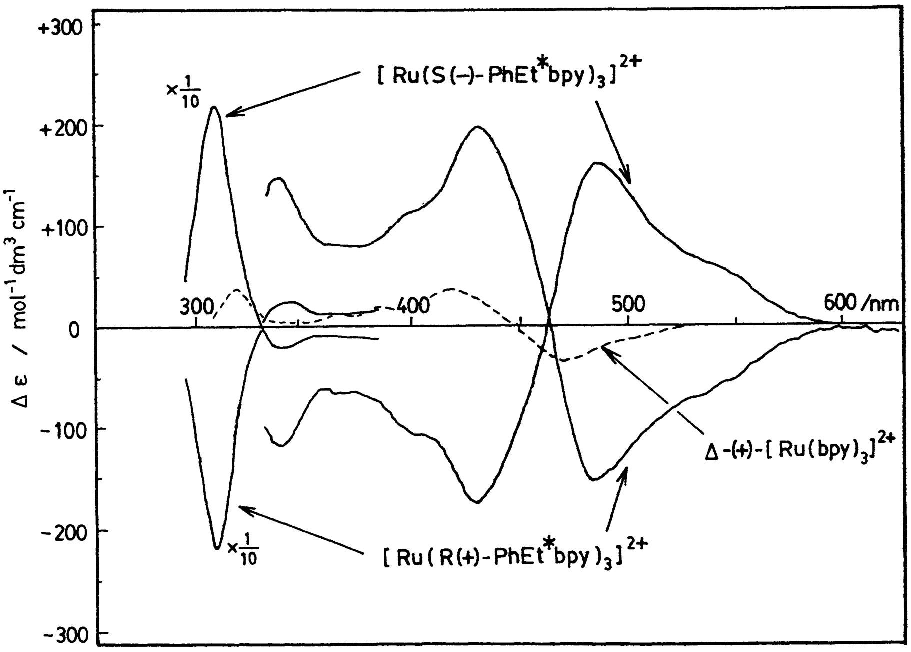


Fig. 2. The CD spectra of the ruthenium complexes.

assigned to the chiral ligands and the bands around 400 - 500 nm which are assigned to the molecular asymmetry. The fact that the CD bands of 1 around 400 - 500 nm are reverse to those of Δ-[Ru(bpy)$_3$]$^{2+}$ strongly suggests that 1 shows predominantly generated molecular asymmetry of the Λ-form. On the other hand, 2 gives the fully reverse CD spectrum toward that of 1, that is, R(+)-PhEt*bpy induces Δ-configuration predominantly for the ruthenium complex. The stereoselective electron transfer reaction from Δ-[Ru(bpy)$_3$]$^{2+}$ to Λ-[Co(acac)$_3$] has been already reported.[1a] Therefore, the present stereoselection may be induced by chirality (S(-) or R(+)) in the ligands of the ruthenium complexes not the molecular asymmetry (Δ or Λ), because 2 having the same configuration as Δ-[Ru(bpy)$_3$]$^{2+}$ reduces Δ-[Co(acac)$_3$] predominantly.

References

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2) Elemental analysis of [Ru(S(-)-PhEt*bpy)$_3$]Cl$_2$·6H$_2$O: Anal Found: C, 62.18; H, 5.39; N, 9.95%. Calcd for RuC$_{84}$H$_{90}$N$_{12}$O$_{12}$Cl$_2$: C, 61.83; H, 5.56; N, 10.30%.

3) The enantiomer rate ratio for the reaction catalyzed by 1 calculated from the equation, $\ln[\Lambda_0/(\Lambda_0-\Lambda)]/\ln[\Delta_0/(\Delta_0-\Delta)]$ (Δ_0, Λ_0: initial concentrations of Δ or Λ-isomer; Δ, Λ : reacted concentrations of Δ or Λ-isomer evaluated from CD spectra). On the other hand, the value by 2 evaluated from the equation, $\ln[\Delta_0/(\Delta_0-\Delta)]/\ln[\Lambda_0/(\Lambda_0-\Lambda)]$. The enantiomer rate ratio evaluated from CD spectra was constant until the reaction conversion attained to 40%; Ref. 1j. The standard $\Delta\varepsilon$ value of Δ-[Co(acac)$_3$] as -8.11 at 574 nm was used; A. F. Drake, J. M. Gould, S. F. Mason, C. Rosini, and F. J. Woodley, Polyhedron, 2, 537 (1983).

(Received June 5, 1989)