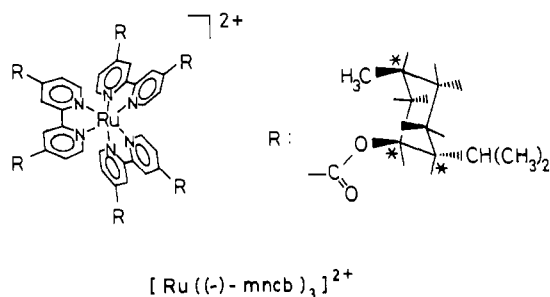


Photoinduced Enantioselective and Catalytic Reduction of $\text{Co}(\text{acac})_3$ with a Chiral Ruthenium Photosensitizer

Photoinduced enantioselective electron-transfer reactions have received considerable interest in the field of coordination chemistry, and several interesting electron-transfer reactions between transition-metal complexes¹ or transition-metal complexes and organic molecules² have been reported. However, any catalytic system of enantioselective electron-transfer reaction with chiral transition-metal complexes has not yet been reported, and the previously used catalyst, which has molecular asymmetry such as Δ - or Λ - $[\text{Ru}(\text{bpy})_3]^{2+}$, racemizes in the course of the photoreactions: the racemization quantum yield of Δ - $[\text{Ru}(\text{bpy})_3]^{2+}$ is 2.88×10^{-4} in water at 23 °C.³ Therefore, an efficient photosensitizer that does not racemize is desired for the stereoselective electron-transfer reaction, especially for the catalytic one with chiral transition-metal complexes. We wish to report here that the tris(4,4'-bis((1*R*,2*S*,5*R*)-(-)-menthylcarboxy)-2,2'-bipyridine)ruthenium(II) dication, $[\text{Ru}((-)\text{-mncb})_3]^{2+}$, which is expected not to racemize



since this complex does not have molecular asymmetry, i.e. Δ or Λ , but has optically active parts in its ligands, reduces $\text{Co}(\text{acac})_3$ ($\text{acacH} = \text{acetylaceton}$) catalytically under photoirradiation ($\lambda > 400 \text{ nm}$) with high enantioselectivities.

The chiral ligand, (-)-mncb, was prepared by refluxing a benzene solution containing (1*R*,2*S*,5*R*)-(-)-menthol, 4,4'-dicarboxy-2,2'-bipyridine,⁴ and thionyl chloride for 12 h. The chiral ruthenium complex was synthesized by heating the ethanol solution containing ruthenium trichloride (0.05 g) and (-)-mncb (0.30 g) in a sealed tube at 90 °C for 6 days. The solid obtained after evaporation was purified by means of chromatography on silica gel using acetone/chloroform as an eluent to give $[\text{Ru}((-)\text{-mncb})_3]\text{Cl}_2 \cdot 7\text{H}_2\text{O}$.⁵ The absorption ($\lambda_{\text{max}} 466 \text{ nm}$; $\epsilon 26 200$) and emission ($\lambda_{\text{max}} 622 \text{ nm}$; $\tau 1110 \text{ ns}$)⁶ spectra of the ruthenium complex in ethanol/water (7:3 v/v) are essentially the same as those of $[\text{Ru}(\text{bpy})_3]^{2+}$. Therefore, $[\text{Ru}((-)\text{-mncb})_3]^{2+}$ is proposed to be akin to $[\text{Ru}(\text{bpy})_3]^{2+}$ in terms of photoexcitation; the redox potentials of $[\text{Ru}((-)\text{-mncb})_3]^{2+}$ are similar to those of $[\text{Ru}(\text{decb})_3]^{2+}$ ($\text{decb} = 4,4'$ -bis(ethylcarboxy)-2,2'-bipyridine); $E^{3+/2+} = +1.55 \text{ V}$, $E^{2+/+} = -0.91 \text{ V}$ vs SCE in CH_3CN .⁷ The CD

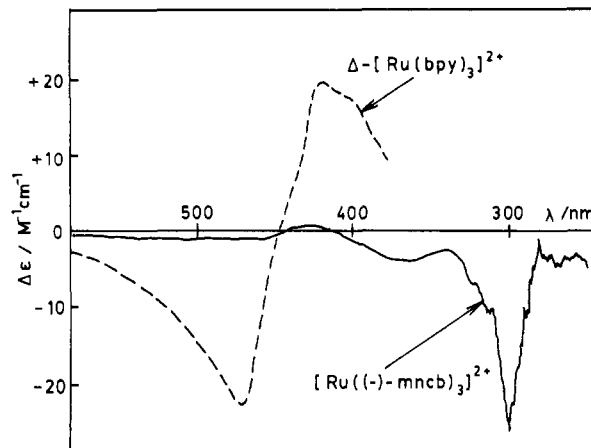


Figure 1. CD spectra of $[\text{Ru}((-)\text{-mncb})_3]^{2+}$ and Δ - $[\text{Ru}(\text{bpy})_3]^{2+}$.

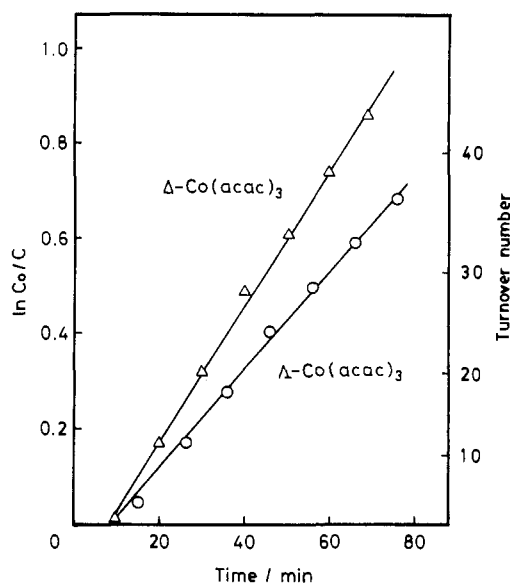


Figure 2. Pseudo-first-order plots in the reduction of $\text{Co}(\text{acac})_3$ catalyzed by $[\text{Ru}((-)\text{-mncb})_3]^{2+}$ in ethanol/water (7:3 v/v) under irradiation ($\lambda > 400 \text{ nm}$).

spectrum of $[\text{Ru}((-)\text{-mncb})_3]^{2+}$ in ethanol shows an absorption around 300 nm, which may arise from the (1*R*,2*S*,5*R*)-(-)-menthyl group; however, there is no absorption at 400–500 nm due to molecular asymmetry of Δ - or Λ - $[\text{Ru}(\text{bpy})_3]^{2+}$ ⁸ (Figure 1). The results strongly suggest that $[\text{Ru}((-)\text{-mncb})_3]^{2+}$ does not have molecular asymmetry but has optically active portions in its ligand.

A typical experiment was performed as follows. An aqueous ethanol solution of the ruthenium complex ($3.2 \times 10^{-5} \text{ mol dm}^{-3}$) and $\text{Co}(\text{acac})_3$ ($2.4 \times 10^{-3} \text{ mol dm}^{-3}$) was placed in a flask fused to a square quartz cuvette (10-mm i.d.). After thorough degassing of the solution under vacuum by five successive freeze–pump–thaw cycles, the reactants were transferred to a quartz cuvette, which was then irradiated for a few hours by the visible light of a 500-W xenon lamp with a Toshiba L-42 glass filter transmitting light of $\lambda > 400 \text{ nm}$. The photochemical reaction was monitored from the decay of the absorption band due to $\text{Co}(\text{acac})_3$, $\lambda_{\text{max}} 595 \text{ nm}$, by using an Hitachi 150-20 spectrophotometer.

The present electron-transfer reaction proceeded only under photoirradiation and did not occur thermally, and Δ - or Λ - $\text{Co}(\text{acac})_3$ quenches the luminescence of $[\text{Ru}((-)\text{-mncb})_3]^{2+}$ with rate constants of 2.24×10^8 and $1.68 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ (quenching rate ratio (Δ : Λ) 1.33) in ethanol/water (7:3 v/v), affording $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$, acac^- , and $[\text{Ru}((-)\text{-mncb})_3]^{3+}$. The ruthenium(II) complex is regenerated by oxidizing ethanol, which was confirmed

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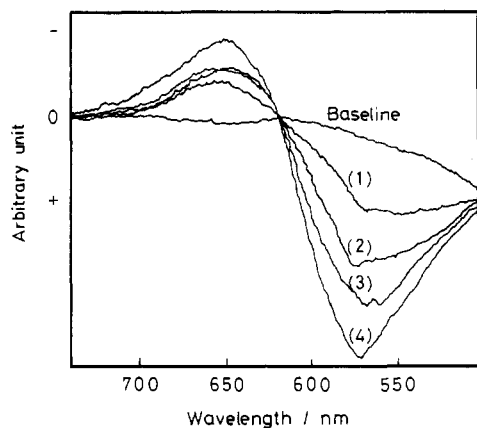


Figure 3. CD spectral changes in the course of the photoreduction of $\text{Co}(\text{acac})_3$ at various conversions: (1) 13%; (2) 23%; (3) 31%; (4) 40%.

with detection of acetaldehyde as its hydrazone derivative from the reaction mixtures by the use of (2,4-dinitrophenyl)hydrazine.⁹ Turnover numbers (converted mol of Co^{III} /mol of catalyst) achieved were 38.6 and 30.0 for Δ - and Λ - $\text{Co}(\text{acac})_3$, respectively, after 1 h, indicating also that the reaction proceeded catalytically.¹⁰

The photochemical reactions obeyed the pseudo-first-order kinetics as shown in Figure 2, which depicts the pseudo-first-order plots of Δ - and Λ - $\text{Co}(\text{acac})_3$ photoreduction catalyzed by $[\text{Ru}(-\text{mncb})_3]^{2+}$ in ethanol/water (7:3 v/v), though an induction period of ca. 10 min existed. The reaction rates ($10^2 k_{\text{obs}}$) are 1.23 ± 0.04 , 1.46 ± 0.03 , and $1.10 \pm 0.02 \text{ min}^{-1}$ for the racemic, Δ , and Λ forms of $\text{Co}(\text{acac})_3$, respectively, and the rate constants ratio ($k_{\Delta}:k_{\Lambda}$) obtained is 1.33. CD spectral changes of the reaction solution in the photoreduction of *rac*- $\text{Co}(\text{acac})_3$ determined in the same solvent system are shown in Figure 3; the absorptions at λ_{max} 574 and 647 nm increased with photoirradiation. The CD spectral changes suggest the predominant consumption of the Δ isomer of the substrate by the catalyst with accumulation of the Λ isomer. The enantioselectivities evaluated from the CD spectral changes are 1.32 ± 0.02 ,¹¹ which not only remained constant during the reaction within experimental error but also were consistent with the value from the enantiomer rate ratio ($k_{\Delta}:k_{\Lambda}$).

It is concluded that the present ruthenium complex having chiral positions in the ligands without molecular asymmetry recognizes the enantiomeric complexes of $\text{Co}(\text{acac})_3$ with a selectivity ($\Delta:\Lambda$) of 1.33 as an enantiomer rate ratio. The stereoselection of $\text{Co}(\text{acac})_3$ by chiral ruthenium complexes, which has hitherto been reported to be the enantiomer rate ratio 1.08 with Δ - $[\text{Ru}(\text{bpy})_3]^{2+}$,^{1a} was improved by $[\text{Ru}(-\text{mncb})_3]^{2+}$ possessing an efficient chiral ligand. In addition, catalytic and enantioselective reduction proceeded, suggesting that photoracemization of the chiral ligands of $[\text{Ru}(-\text{mncb})_3]^{2+}$ hardly occurred. It is also noted that the selectivity evaluated from the enantiomers' reaction rates is consistent with that from the quenching rate ratio. This experimental finding suggests that the stereoselectivity observed in the present reaction would result from the close contact between the ruthenium catalyst and the cobalt complex during the formation of the encounter complex.

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 (11) The value is calculated from the equation $\ln [\Delta_0/(\Delta_0 - \Delta)] / \ln [\Lambda_0/(\Lambda_0 - \Lambda)]$ (Δ_0, Λ_0 = initial concentrations of the Δ or Λ isomer; Δ, Λ = reacted concentrations of the Δ or Λ isomer evaluated from CD spectra).

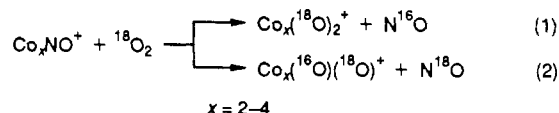
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Facile Oxygen Exchange by Cobalt Cluster Oxide Ions with Water- ^{18}O in the Gas Phase

Dissociative chemisorption (molecular activation) of small molecules such as CO , NO , N_2 , H_2 , etc. is a requisite process for heterogeneous catalysis and surface chemistry.¹ It is of interest, therefore, to understand the factors that facilitate dissociative chemisorption on transition-metal clusters. Gas phase ion techniques are particularly promising in this regard since distinct ion clusters can be selected and studied; however, distinguishing dissociative chemisorption from molecular chemisorption is quite challenging. We recently demonstrated that dissociative chemisorption of nitric oxide can be distinguished from molecular chemisorption for small bare cationic cobalt clusters by monitoring the oxygen isotopic distribution for reaction with dioxygen- $^{18}\text{O}_2$ (processes 1 and 2). This method proved useful in distinguishing



dissociative from molecular chemisorption of NO on these clusters; however, it is limited to very simple systems (i.e., systems with only one ligand). As a consequence we have investigated a number of other methods that would distinguish dissociative chemisorption of nitric oxide from molecular chemisorption for complex, multiligated clusters. These efforts led us to consider the potential of water- ^{18}O as a probe of metal cluster oxide character since oxygen exchange with water has been observed on metal oxide surfaces.³⁻⁹

All experiments were performed by using a Nicolet FTMS-1000 Fourier transform mass spectrometer equipped with a 5.08-cm cubic-trapping cell and a 3.0-T superconducting magnet.¹⁰ The theory, instrumentation, and methodology of conventional ion cyclotron resonance (ICR)¹¹ and Fourier transform mass spectrometry (FTMS)^{12,13} have been discussed at length elsewhere. The cobalt cluster oxide cations were generated by reaction of cobalt cluster carbonyl nitrosyl ions, generated from electron impact on $\text{Co}(\text{CO})_3\text{NO}$,¹⁴ with dioxygen¹⁵ followed by collisional activation (CA)^{16,17} and isolation of the desired Co_xO_y^+ ion.¹²

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