Formation of Optically Active $[Ru(bipy)_2Cl_2]$ (bipy = 2,2′-bipyridyl) by Photodissociation of $[Ru(bipy)_3]Cl_2$ in Dichloromethane

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An optically active bis-chelated complex, $[Ru(bipy)_2Cl_2]$ (bipy = 2,2′-bipyridyl), has been obtained when enantiomeric $[Ru(bipy)_3]Cl_2$ was illuminated by visible light in dichloromethane. From the dependence of the optical purity of the product on light intensity, it is proposed that the reaction from Δ-$[Ru(bipy)_3]Cl_2$ to Δ-$[Ru(bipy)_2Cl_2]$ (chirality retention) proceeds by way of the dissociation of a monodentate ligand, bipy*, from a photoactivated intermediate, Δ-$[Ru(bipy)_2(bipy^*)Cl]Cl$ in the dark, while the reaction to Λ-$[Ru(bipy)_2Cl_2]$ (chirality inversion) involves the further photoactivated configurational change of Δ-$[Ru(bipy)_2(bipy^*)Cl]Cl$ to Λ-$[Ru(bipy)_2(bipy^*)Cl]Cl$. Racemization is avoided under the conditions of weak light and high temperature. The synthetic value of optically active $[Ru(bipy)_2Cl_2]$ as a chiral intermediate has been exemplified by preparing a new chiral amphiphilic ruthenium(II) complex.

The complex $[Ru(bipy)_3]Cl_2$ (bipy = 2,2′-bipyridyl) is known to be converted into $[Ru(bipy)_2Cl_2]$ in dichloromethane upon illumination by visible light.[1,2] According to the proposed mechanism, an intermediate, $[Ru(bipy)_2(bipy^*)Cl]Cl$, is formed when a Ru^{II}–N bond in one of the bipy ligands is photocleaved to give a monodentate ligand, bipy*.[2] The intermediate dissociates the ligand in the dark to produce $[Ru(bipy)_2Cl_2]$. The transformation from a tris- to a bis-chelated complex is supposed to proceed with retention of the initial octahedral configuration around Ru^{II}. Thus we have attempted to obtain optically active $[Ru(bipy)_2Cl_2]$ by use of this reaction.

An enantiomer of $[Ru(bipy)_2Cl_2]$ would have synthetic potential as a chiral intermediate in the formation of chiral mixed-ligand complexes.[3,4] The complex is, however, neutral and hardly soluble in water so that it cannot be resolved with conventional ionic resolving agents. So far, resolution has been only partially successful by way of the oxidized form $[Ru(bipy)_2Cl_2]^+$.[5]

In the present work, we have established experimental conditions to obtain optically active $[Ru(bipy)_2Cl_2]$ and a new aspect of the photodissociation process of $[Ru(bipy)_3]Cl_2$ has been revealed by examining the effects of light intensity and temperature on the optical purity of the product. A new chiral amphiphilic ruthenium(II) complex is also synthesised to exemplify the synthetic value of $[Ru(bipy)_2Cl_2]$ as a chiral intermediate.

Experimental

Materials.—$[Ru(bipy)_3]Cl_2$. The complex $[Ru(bipy)_3]Cl_2$ was used as obtained from Aldrich. A 0.5 g amount of it and sodium antimony L-(+)-tartrate $Na_2[SbO(tart)]_2$ (1.5 g) were dissolved in water (10 cm^3) at 40 °C. The solution was left at 4 °C overnight to give a precipitate, Δ-$[Ru(bipy)_3][SbO(tart)]_2 \cdot nH_2O$ that was filtered off and washed with a small amount of cold water. The antimony tartrate anion in the complex was replaced with chloride anions on the chloride form of an anion-exchange resin (Dowex 1-EX2) in water. After evaporation to dryness, the complex was dissolved in dichloromethane: $\Delta\varepsilon$ at 490 nm = $-13\ dm^3\ mol^{-1}\ cm^{-1}$.

Λ-$[Ru(phen)_3]Cl_2$. The complex $[Ru(phen)_3]Cl_2$ (phen = 1,10-phenanthroline) was synthesised according to the reported method.[6] The salt Λ-$[Ru(phen)_3][SbO(tart)]_2 \cdot H_2O$ was obtained as an insoluble salt by adding potassium antimony L-(+)-tartrate $K_2[SbO(tart)]_2$ to an aqueous solution.[7] The chloride salt was obtained in the same way as for $[Ru(bipy)_3]Cl_2$: $\Delta\varepsilon$ at 470 nm = $18\ dm^3\ mol^{-1}\ cm^{-1}$.

cis-$[Ru(bipy)_2Cl_2]$. The salt $[Hbipy][Ru(bipy)Cl_4] \cdot H_2O$ (3.7 g) was dissolved in dimethylformamide (80 cm^3) and refluxed for about 3 h.[8] The solution changed from brown to violet. After being condensed to about 20 cm^3, it was mixed with acetone (50 cm^3) and cooled to 4 °C. The dark black precipitate was filtered off and dissolved in water–ethanol (1 : 1, 100 cm^3). The solution was refluxed for 2 h and filtered. After evaporating ethanol from the filtrate, LiCl (10 g) was added. The precipitate was filtered off and washed with water, yield: 1.8 g (Found: C, 51.10; H, 3.45; N, 11.90. Calc: C, 49.60; H, 3.30; N, 11.55%).

cis-$[Ru(phen)_2Cl_2]$. This complex was synthesised from $[Hphen][Ru(phen)Cl_4] \cdot H_2O$[8] in a similar way to that for *cis*-$[Ru(bipy)_2Cl_2]$ (Found: C, 56.85; H, 3.20; N, 11.05. Calc: C, 54.15; H, 3.00; N, 10.55%).

Octadecanoyldi(2-*pyridyl*)*amine* (odpa). *n*-Octadecanoyl chloride (3.5 g), di(2-pyridyl)amine (2.0 g) and triethylamine (1.2 g) were dissolved in dichloromethane (28 cm^3). After stirring the solution for 2 h at room temperature it was left overnight at 4 °C. A crystal was filtered off and washed with 0.001 mol dm^{-3} HCl, water, 0.001 mol dm^{-3} NaOH and finally water three times. The solid was recrystallized twice from acetone (yield: 2.4 g). It gave a single peak when eluted with methanol from a HPLC column of Capcel Pak C_{18} (Shiseido, Japan) (Found: C, 57.35; H, 7.95; N, 7.00. Calc: C, 59.10; H, 7.60; N, 7.40%).

cis-$[Ru(bipy)_2(odpa)][ClO_4]_2$. The complex *cis*-$[Ru(bipy)_2Cl_2]$ (2.0 g) and odpa (1.8 g) were dissolved in water–ethanol (1 : 1, 80 cm^3) and refluxed for 12 h. After cooling to room temperature, ethanol was evaporated and an excess of $NaClO_4$ was added. The precipitate was filtered off and washed with water and pentane (yield: 1.1 g) (Found: C, 53.50; H, 5.90; Cl, 6.35; N, 9.30. Calc: C, 54.90; H, 5.65; Cl, 6.75; N, 9.35%).

Dichloromethane (Wako, Japan), tetraethylammonium chloride (Wako) and other reagents were used without purification.

Instruments.—As a light source for stationary irradiation a 100 W tungsten lamp was used with a band-pass filter having a transmission maximum at 400 or 460 nm. Unless otherwise stated, a filter of 400 nm was used. Light intensity was measured with a digital lux meter, DX-100 (Takemura Electric Works, Japan). Electronic absorption spectra were measured with a UVIDEC 430A (JASCO, Japan) spectrophotometer, circular dichroism spectra on a J-250 polarimeter (JASCO).

Photodecomposition Experiments.—A dichloromethane solution (3.0 cm^3) of Δ-$[Ru(bipy)_3]Cl_2$ (1.3×10^{-5} mol dm^{-3}) or Λ-$[Ru(phen)_3]Cl_2$ (1.2×10^{-5} mol dm^{-3}) in a quartz cell [1.0 × 1.0 × 10 cm (height)] was placed in a water-bath maintained at constant temperature. The sample was illuminated with a tungsten lamp through a filter. The light intensity was calibrated with a digital lux meter at the same position as the cell. The time course of the reaction was monitored by measuring the visible spectrum of the sample at various intervals. In determining the optical purity of the photodecomposition product, the CD spectrum of the solution was measured after the reaction was complete. At one temperature the experiment was carried out three times. The effect of Cl^- was investigated at 26 °C for a solution containing 2.0×10^{-3} mol dm^{-3} NEt_4Cl.

To obtain the reaction product on a larger scale for synthetic use, the photoreaction was performed in a glass tube [30 × 5.0 cm (internal diameter)] containing a dichloromethane solution (200 cm^3) of Δ-$[Ru(bipy)_3]Cl_2$ (63 mg). After illuminating the solution at 500 lux and 43 °C for 6 h it was reduced in volume to about 30 cm^3 and washed with water to remove unreacted $[Ru(bipy)_3]Cl_2$. The solution was then evaporated to dryness and the residue rinsed with hexane and diethyl ether to remove bipyridyl ligand (yield: 27 mg). The electronic spectrum of a dichloromethane solution of the product agreed with that of $[Ru(bipy)_2Cl_2]$ synthesised as described above.

Reactions of the Photodecomposition Product.—*With 2,2′-bipyridyl.* The photodecomposition product (10 mg) from the preceding experiment was dissolved with bipy (15 mg) in ethanol (20 cm^3). After being refluxed for 30 min the solution was evaporated to dryness. The residue was rinsed with hexane and diethyl ether. Sodium perchlorate (0.1 g) was added to an aqueous solution (4 cm^3) of the residue. The precipitate was filtered off and dried (yield: 4 mg). The electronic spectrum of the water solution of the product coincided with that of $[Ru(bipy)_3]^{2+}$. From the circular dichroism spectrum, Δε was determined to be −10 dm^3 mol^{-1} cm^{-1} at 490 nm. Based on the assumption that Δε for pure Δ-$[Ru(bipy)_3]^{2+}$ is −13 dm^3 mol^{-1} cm^{-1} at 490 nm, the product was Δ-$[Ru(bipy)_3]^{2+}$ with 77% optical purity.

With odpa. The photodecomposition product (5 mg) was dissolved with odpa (6 mg) in water–ethanol (1 : 1, 5 cm^3). The solution was refluxed for 12 h, changing from violet to orange. After evaporation of ethanol, $NaClO_4$ (0.1 g) was added. The precipitate was washed with water and pentane. The electronic absorption spectrum of chloroform solution of the product coincided with that of racemic *cis*-$[Ru(bipy)_2(odpa)][ClO_4]_2$ synthesised separately.

Results and Discussion

Photoinduced Reactions of Δ-$[Ru(bipy)_3]Cl_2$.—Fig. 1 shows the change in electronic absorption spectrum with time when a dichloromethane solution of Δ-$[Ru(bipy)_3]Cl_2$ is illuminated with light of 1×10^3 lux at 26 °C. The final spectrum agrees with that reported for $[Ru(bipy)_2Cl_2]$.[1,2] By varying the intensity (I) of the incident light from 250 to 3×10^3 lux, the rate of decrease in Δ-$[Ru(bipy)_3]Cl_2$ was found to be given by equation (1) with $k_d = (2.0 \pm 0.2) \times 10^{-6}$ lux^{-1} s^{-1} at 26 °C.

$$d[Ru(bipy)_3Cl_2]/dt = -k_d I[Ru(bipy)_3Cl_2] \qquad (1)$$

Fig. 2 shows the change in the CD spectrum of the same reaction with time. A new spectrum appears with the disappearance of the initial spectrum due to Δ-$[Ru(bipy)_3]Cl_2$. The final spectrum is assigned to optically active $[Ru(bipy)_2Cl_2]$. Based on the negative and positive signs of the peaks at 278 and 300 nm, respectively, the predominant enantiomer in the solution is concluded to be Δ-$[Ru(bipy)_2Cl_2]$.[9] The presence of the isosbestic points at 265, 284 and 320 nm confirms that the racemizations of Δ-$[Ru(bipy)_3]Cl_2$ and Δ-$[Ru(bipy)_2Cl_2]$ are not negligible during the reaction.

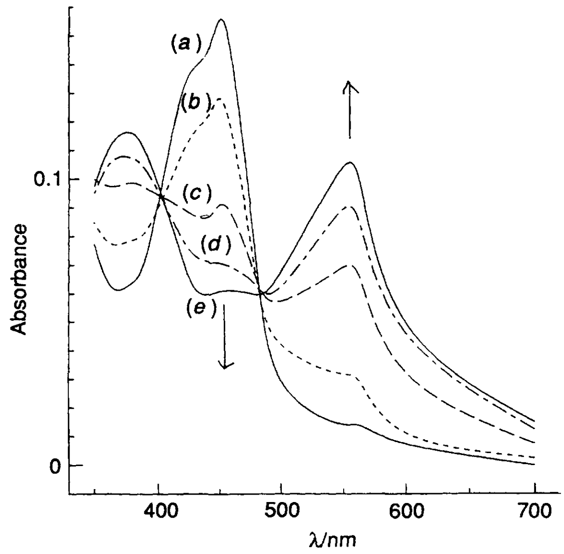


Fig. 1 Change in absorption spectrum of a dichloromethane solution of Δ-$[Ru(bipy)_3]Cl_2$ (1.3×10^{-5} mol dm^{-3}) with time under illumination with 400 nm light at 26 °C. Light intensity 1000 lux. The spectrum was recorded 0 (*a*), 60 (*b*), 180 (*c*), 300 (*d*) and 660 s (*e*) after illumination

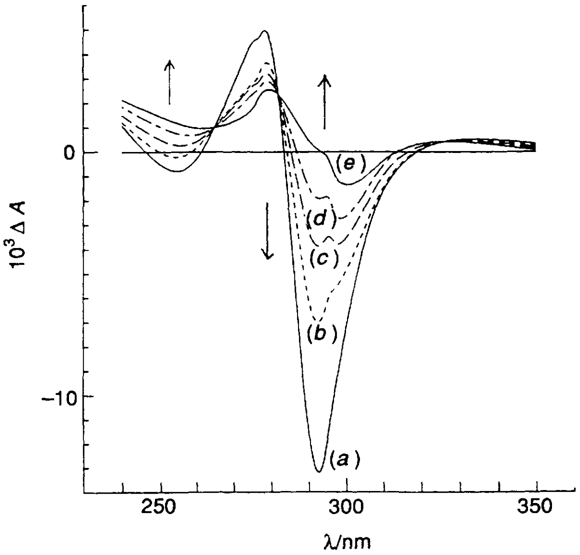


Fig. 2 Change in the CD spectrum with time under the same conditions as in Fig. 1. The spectrum was recorded 0 (*a*), 180 (*b*), 300 (*c*), 420 (*d*) and 900 s (*e*) after illumination

We examined the effects of temperature (T), wavelength (λ), intensity of incident light (I) and external Cl^- ions on the optical purity of $[Ru(bipy)_2Cl_2]$ by measuring the CD spectrum after the completion of the reaction. The relative optical purity of the complex is measured in terms of the apparent Δε at 300 nm, $\Delta\varepsilon^a_{300}$, which is calculated by dividing the amplitude of the CD spectrum (in absorbance units) at 300 nm by the concentration of $[Ru(bipy)_2Cl_2]$. Fig. 3 gives a plot of the reciprocal of $-\Delta\varepsilon^a_{300}$ as a function of I at constant T; the temperature was varied from 26 to 50 °C. In the region of $I <$ 3000 lux, the results are approximated by the linear equation (2) with

$$-\Delta\varepsilon^a_{300}{}^{-1} = a + bI \qquad (2)$$

$a = (7.0 \pm 1.0) \times 10^{-3}$ cm mol dm^{-3} and $b = (5.8 \pm 0.9) \times 10^{-6}$ cm mol dm^{-3} lux^{-1} at 26 °C; a is nearly constant but b decreases with increasing T. From the dependence of b on T the apparent activation energy is 33 ± 5 kJ mol^{-1}. The values of a and b are unaffected when the peak wavelength of the incident light is changed from 400 to 460 nm. When the reaction was investigated in the presence of 2.0×10^{-3} mol dm^{-3} NEt_4Cl at 26 °C the same rate constant, k_d, was obtained for the decrease in $[Ru(bipy)_3]Cl_2$. From Fig. 3 it is also concluded that the optical purity of the Δ-$[Ru(bipy)_2Cl_2]$ produced is unaffected by this amount of NEt_4Cl.

Fig. 3 indicates that the optical purity of the $[Ru(bipy)_2Cl_2]$ produced is high under the conditions of weak light and high temperature. Thus we conducted the synthesis of optically active $[Ru(bipy)_2Cl_2]$ by illuminating a solution of Δ-$[Ru(bipy)_3]Cl_2$ on a larger scale as described in the Experimental section. The product was identified as $[Ru(bipy)_2Cl_2]$ from the electronic spectrum. The CD spectrum of the compound is shown by the solid curve in Fig. 4. It is similar to that reported for a mixture of partially resolved $[Ru(bipy)_2Cl_2]$ and $[Ru(bipy)_2(H_2O)Cl]^+$ in water.[5] The magnitude of $-\Delta\varepsilon^a{}_{300}$, however, is 20 times larger than the literature values of analogous complexes.[5]

In interpreting the above results, we propose the reaction mechanism in Scheme 1 where Δ-A denotes an intermediate formed when a Ru^{II}–N bond in Δ-$[Ru(bipy)_3]Cl_2$ is photocleaved. A similar situation has recently been proposed for the photodissociation of bis(2,2′-bipyridyl)(3,3′-dimethyl-2,2′-bipyridyl)ruthenium(II).[10] Species **X** is an achiral intermediate formed when Δ-A undergoes further photocleavage of one of the other two bidentate ligands.

Under this scheme, the conversion of Δ-$[Ru(bipy)_3]Cl_2$ into Δ-$[Ru(bipy)_2Cl_2]$ involves a single photoactivating process, while that into Λ-$[Ru(bipy)_2Cl_2]$ involves two photoactivating processes. Applying the stationary-state approximation to Δ-A, Λ-A and X we obtain expressions (3)–(5).

$$\mathrm{d}[\Delta\text{-A}]/\mathrm{d}t = k_1I[\Delta\text{-Ru(bipy)}_3\text{Cl}_2] + k_{-2}[\text{X}] - (k_{-1} + k_2I + k_3)[\Delta\text{-A}] = 0 \quad (3)$$

$$\mathrm{d}[\text{X}]/\mathrm{d}t = k_2I([\Delta\text{-A}] + [\Lambda\text{-A}]) - 2k_{-2}\text{X} = 0 \quad (4)$$

$$\mathrm{d}[\Lambda\text{-A}]/\mathrm{d}t = k_{-2}[\text{X}] - (k_{-1} + k_2I + k_3)[\Lambda\text{-A}] = 0 \quad (5)$$

As mentioned above, the racemization of Δ-$[Ru(bipy)_3]Cl_2$ occurs to a negligible extent. This implies that the step from Λ-A to Δ-$[Ru(bipy)_3]Cl_2$ proceeds at very slow rate so that k_{-1} in equations (3) and (5) is neglected in comparison to k_2I and k_3. Under this approximation, equation (6) is obtained which is

$$\mathrm{d}[\Delta\text{-Ru(bipy)}_3\text{Cl}_2]/\mathrm{d}t = -k_1I[\Delta\text{-Ru(bipy)}_3\text{Cl}_2] \quad (6)$$

coincident with equation (1) with $k_d = k_1$.

Summing equations (3)–(5), we obtain (7) which leads to (8).

$$k_1I[\Delta\text{-Ru(bipy)}_3\text{Cl}_2] - k_3([\Delta\text{-A}] + [\Lambda\text{-A}]) = 0 \quad (7)$$

$$-\mathrm{d}[\Delta\text{-Ru(bipy)}_3\text{Cl}_2]/\mathrm{d}t = k_1I[\Delta\text{-Ru(bipy)}_3\text{Cl}_2] = k_3([\Delta\text{-A}] + [\Lambda\text{-A}]) = \mathrm{d}[\text{Ru(bipy)}_2\text{Cl}_2]/\mathrm{d}t \quad (8)$$

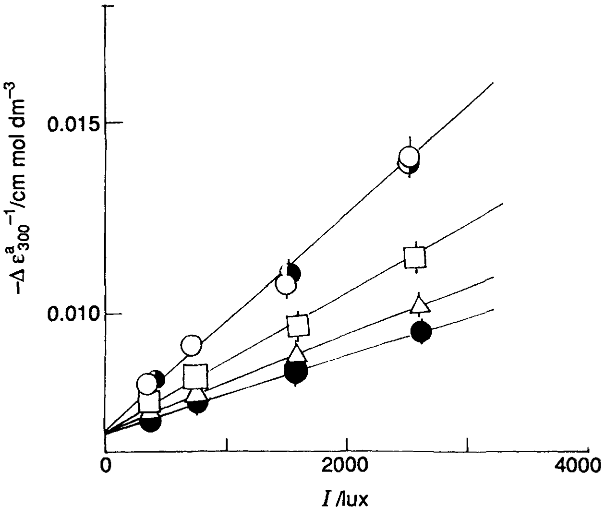


Fig. 3 Plot of the reciprocal of the apparent $-\Delta\varepsilon$ value at 300 nm against the intensity of light at 26 (○), 36 (□), 41 (△) and 50 °C (●). The results in the presence of 2×10^{-3} mol dm^{-3} tetraethylammonium chloride at 26 °C are also included (◑)

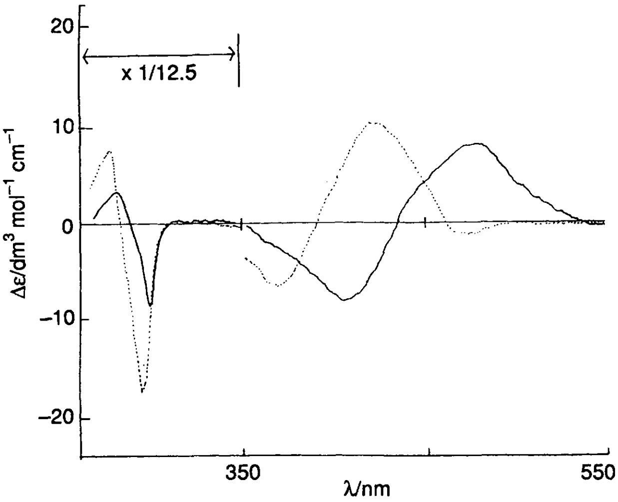
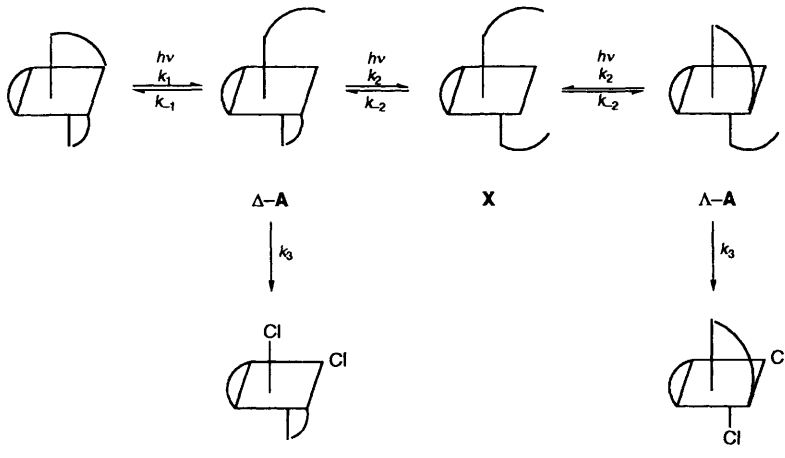


Fig. 4 The CD spectra of Δ-$[Ru(bipy)_2Cl_2]$ in dichloromethane (——) and of the product when Δ-$[Ru(bipy)_2Cl_2]$ is treated with octadecanoyldi(2-pyridyl)amine (· · · ·) (see Experimental section)



Scheme 1

This is consistent with the fact that the amounts of the intermediate species are negligible in comparison to [Ru(bipy)$_3$]Cl$_2$ and [Ru(bipy)$_2$Cl$_2$] so that the isosbestic points appear in the electronic spectra in Fig. 1.

Another consequence is that the ratio of [Δ-A] to [Λ-A] is given by equation (9). As mentioned above, the optical purity of

$$[\Delta\text{-A}]/[\Lambda\text{-A}] = (k_2I + 2k_3)/k_2I \qquad (9)$$

the [Ru(bipy)$_2$Cl$_2$] produced is kept constant during the reaction. Thus we assume that equation (10) is applicable. Using

$$[\Delta\text{-Ru(bipy)}_2\text{Cl}_2]/[\Lambda\text{-Ru(bipy)}_2\text{Cl}_2] = \text{d}[\Delta\text{-Ru(bipy)}_2\text{Cl}_2]/\text{d}[\Lambda\text{-Ru(bipy)}_2\text{Cl}_2] = [\Delta\text{-A}]/[\Lambda\text{-A}] \qquad (10)$$

this relation and (9), the reciprocal of the enantiomeric excess (e.e.) of Δ-[Ru(bipy)$_2$Cl$_2$] is given by equation (11). Equation

$$\text{e.e.}^{-1} = 1 + (Ik_2/k_3) \qquad (11)$$

(11) predicts the same dependence for the optical purity on the intensity of light as does (2). If (11) is correct, a in equation (2) corresponds to $-\Delta\varepsilon^{a}{}_{300}{}^{-1}$ for pure Δ-[Ru(bipy)$_2$Cl$_2$], or Δε at 300 nm = 143 dm^3 mol^{-1} cm^{-1}. Term b is the ratio of k_2 to k_3. Thus the apparent activation energy in b is equal to the difference in the activation energies between k_2 and k_3: $E_a(k_2) - E_a(k_3) = -33 \pm 5$ kJ mol^{-1}. The results seem to be reasonable since the activation energy for k_2 is expected to be small. This is because the photoinduced cleavage of a Ru^{II}–N bond is driven by a sufficiently large photon energy.

The fact that external Cl$^-$ ions have no effect on the reaction mechanism suggests that the present photocleavage is a unimolecular reaction or the direct attack of an external Cl$^-$ ion on Δ-A does not occur.

The complex Δ-[Ru(bipy)$_3$]Cl$_2$ is obtained by the reaction of [Ru(bipy)$_2$Cl$_2$] with bipy as described in the Experimental section. From the CD spectrum, the e.e. of the [Ru(bipy)$_3$]Cl$_2$ produced is 77%. This value provides the lower limit of the optical purity of [Ru(bipy)$_2$Cl$_2$].

Properties of Optically Active [Ru(bipy)$_2$Cl$_2$].—When a dichloromethane solution of Δ-[Ru(bipy)$_2$Cl$_2$] is placed for 5 h either in the dark or under illumination from a 400 nm light at 1000 lux and 26 °C it does not racemize at all. Neither does it racemize in ethanol under the same conditions. When a water–ethanol (1 : 4) solution of the complex is warmed for 3 h at 50 °C, $-\Delta\varepsilon^{a}{}_{300}$ decreases by 8.4%. Concomitantly the peak at 520 nm in the electronic spectrum is shifted to 500 nm. This spectral change may be ascribed to aquation of the complex. An aquated complex, [Ru(bipy)$_2$Cl(H$_2$O)]$^+$, is reported to racemize in water.[5]

The complex [Ru(bipy)$_2$Cl$_2$] is of potential utility as a chiral intermediate in the formation of optically active mixed-ligand complexes.[11,12] To exemplify this possibility, a chiral surfactant metal complex, [Ru(bipy)$_2$(odpa)][ClO$_4$]$_2$ was synthesised as described in the Experimental section. Its circular dichroism spectrum is given as the dotted curve in Fig. 4. Although the optical purity of the compound has not yet been determined, it is regarded as comparable to that of the reactant [Ru(bipy)$_2$Cl$_2$]. This is because the amplitude of the CD spectrum for the product is nearly of the same magnitude as that of the reactant in the whole wavelength range.

Photoinduced Reactions of Λ-[Ru(phen)$_3$]Cl$_2$.—To compare the photoreactivity of [Ru(bipy)$_3$]Cl$_2$ with that of [Ru(phen)$_3$]Cl$_2$, the photocleavage of enantiomeric [Ru(phen)$_3$]Cl$_2$ was studied as described in the Experimental section. Fig. 5 shows the change in the electronic spectrum with time when a dichloromethane solution of Λ-[Ru(phen)$_3$]Cl$_2$ is irradiated at 1000 lux and 26 °C. The final spectrum agrees with that of [Ru(phen)$_2$Cl$_2$] synthesised separately. The rate of the decrease in [Ru(phen)$_3$]Cl$_2$ is expressed by equation (12) with k_d = (3.0 ± 0.6) × 10^{-7} lux^{-1} s^{-1} at 26 °C. It is noted that k_d for the phen complex is about seven times smaller than that for the bipy complex.

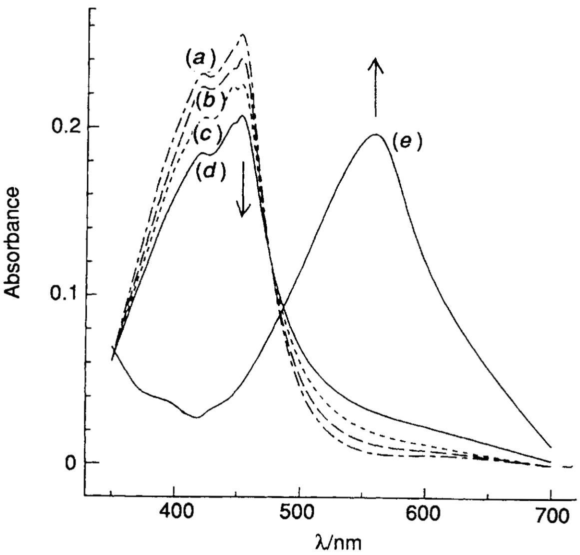


Fig. 5 Change of absorption spectrum of a dichloromethane solution of Λ-[Ru(phen)$_3$]Cl$_2$ (1.2 × 10^{-5} mol dm^{-3}) with time under illumination from 400 nm light at 26 °C. The light intensity was 1000 lux. The spectrum was recorded at 0 (*a*), 120 (*b*), 300 (*c*) and 600 s (*d*) after illumination. Curve (*e*) is the final spectrum after 5 h

$$\text{d}[\text{Ru(phen)}_3\text{Cl}_2]/\text{d}t = -k_dI[\text{Ru(phen)}_3\text{Cl}_2] \qquad (12)$$

The change in the CD spectrum with time was studied under the same conditions as in Fig. 5. In contrast to Fig. 2, the absorbance due to Λ-[Ru(phen)$_3$]Cl$_2$ decreases with no appearance of a new spectrum. More interestingly, the rate of the decrease in absorbance in the CD spectrum is much larger than that of the decrease in the concentration of Λ-[Ru(phen)$_3$]Cl$_2$. For example, the concentration of Λ-[Ru(phen)$_3$]Cl$_2$ had decreased by 4.5% 120s after irradiation (the second curve in Fig. 5), while the amplitude of the CD spectrum had decreased by 39% at this time. The results imply that, under illumination, Λ-[Ru(phen)$_3$]Cl$_2$ racemizes before it dissociates the ligand. The photoinduced racemization rate was estimated from the change in the CD spectrum, taking account of the decrease in the reactant due to the decomposition reactions. For the change of I from 250 to 3 × 10^3 lux, the rate of racemization was found to be proportional to I as in equation (13) with

$$\text{d(e.e.)}/\text{d}t = -k_rI\text{(e.e.)} \qquad (13)$$

k_r = (3.0 ± 0.2) × 10^{-6} lux^{-1} s^{-1}, about ten times larger than k_d. When the dissociation of Λ-[Ru(phen)$_3$]Cl$_2$ is complete after 5 h at 26 °C and 1000 lux, no optical activity is detected in the CD spectrum of the [Ru(phen)$_2$Cl$_2$] produced.

Comparison of Photochemical Behaviours Between [Ru(bipy)$_3$]Cl$_2$ *and* [Ru(phen)$_3$]Cl$_2$.—The preceding results indicate that photodissociation is predominant for [Ru(bipy)$_3$]Cl$_2$, while photoracemization is predominant for [Ru(phen)$_3$]Cl$_2$. Based on the proposed Scheme 1 for [Ru(bipy)$_3$]Cl$_2$, we postulate that the monodentate ligand in [Ru(phen)$_2$(phen*)Cl]Cl (phen* = monodentate phen) is so firmly co-ordinated that the process leading to racemization of the intermediate occurs before the phen* is dissociated.

It is not clear at the present stage what is the main cause for the different photochemical behaviours of these complexes.

One possible reason may lie in the difference in the flexibility of the ligands. The free pyridyl moiety of bipy* in [Ru(bipy)$_2$(bipy*)Cl]Cl may rotate around the C(1)–C(1′) bond of the bipy molecule. This rotation would result in delocalization of π electrons in each pyridyl group. As a result, the N–Ru^{II} bond is weakened due to the decrease in back donation from the Ru^{II} to the ligand. The rotation may also have an effect in decreasing k_{-1}. No such weakening of a N–Ru^{II} bond would take place in the case of phen* in [Ru(phen)$_2$(phen*)Cl]Cl, since the ligand remains planar even if one of the N–Ru^{II} bonds is cleaved. As a result, the ligand is more likely to attack the co-ordination sites of other ligands resulting in racemization in the dark rather than dissociate.

References

1 M. Gleria, F. Minto, G. Beggiato and P. J. G. Bortolus, *J. Chem. Soc., Chem. Commun.*, 1978, 285.

2 B. Durham, J. V. Caspar, J. K. Nagle and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4803.

3 B. Durham, J. L. Walsh, C. L. Carter and T. J. Meyer, *Inorg. Chem.*, 1980, **19**, 860.

4 A. M. Pyle, J. P. Rehmann, R. Meshoyrer, C. V. Kumar, N. J. Turro and J. K. Barton, *J. Am. Chem. Soc.*, 1989, **111**, 3051.

5 J. A. A. Sagues, R. D. Gillard, D. H. Smalley and P. A. Williams, *Inorg. Chim. Acta*, 1980, **43**, 211.

6 F. P. Dwyer, *Proc. R. Soc. N. S. W.*, 1949, **83**, 174.

7 A. J. MacCaffery, S. F. Mason and B. J. Norman, *J. Chem. Soc.*, 1969, 1428.

8 F. P. Dwyer, H. A. Goodwin and E. C. Gyarfas, *Aust. J. Chem.*, 1963, **16**, 42.

9 B. Bosnich, *Inorg. Chem.*, 1968, **7**, 178.

10 S. Tachiyashiki, K. Nakamaru and K. Mizumachi, *Chem. Lett.*, 1992, 1119.

11 J. K. Barton and E. Lolis, *J. Am. Chem. Soc.*, 1985, 107, 708.

12 N. Grover, N. Gupta and H. H. Thorp, *J. Am. Chem. Soc.*, 1992, **114**, 3390.

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