Preparation and characterization of *cis*- and *trans*-[Ru(OAc)(2mqn)$_2$NO] (OAc = acetate, 2mqn = 2-methyl-8-quinolinolate), and their mutual photoisomerization reactions

Eiichi Miki*, Hiroharu Masano, Hitoshi Iwasaki, Hiroshi Tomizawa, Kunihiko Mizumachi, Tatsujiro Ishimori
Department of Chemistry, College of Science, Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171 (Japan)

Mikio Tanaka, Takashi Nagai
Laboratory of Chemistry, Nippon Medical School, Kosugi, Nakahara-ku, Kawasaki 211 (Japan)

and Noriharu Nagao*
Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioicho, Chiyoda-ku, Tokyo 102 (Japan)

(Received July 8, 1992)

Abstract

A mixture of hydrated nitrosylruthenium(III) chloride and 2-methyl-8-quinolinol (H2mqn) (1:4 molar ratio) in acetic acid aqueous solution adjusted to pH 5.5 and warmed at *c.* 70 °C for 2 h led to preparation of *cis*-[Ru(OAc)(2mqn)$_2$NO] which has *cis*(0,0) and *trans*(N,N) configuration for the ligating atoms of the 2mqn ligands. The *trans* isomer was photochemically prepared from the *cis* isomer in CH_2Cl_2 using an Xe lamp as the light source. The photoisomerization in deaerated CH_2Br_2 was examined at -5 to 30 °C using a super high-pressure Hg lamp (436 nm). Quantum yields of the *cis* to *trans* and the *trans* to *cis* isomerizations were $1–2.5 \times 10^{-3}$ and $8–11 \times 10^{-3}$, respectively. Solvent effect studies by adding liquid paraffin to the CH_2Br_2 solution on the photoreaction and the NO scramble on the irradiation in the presence of ^{15}NO gas showed that Ru–NO bond rupture takes part in the isomerization.

Introduction

The NO^+ ligand behaves as a weak σ-donor and a strong π-acceptor, characteristics which affect the synthesis, reactivity and structures of metal nitrosyls [1]. The {Ru(II)–NO^+} type of mononitrosyl complex tends to form an octahedral six-coordinate configuration. Geometrically isomeric pairs of [RuCl(N-O)$_2$NO] (H(N-O) = 8-quinolinol or 2-methyl-8-quinolinol), *cis*-1 and *cis*-2, were prepared and their structures were determined by X-ray analysis [2, 3]. The Cl atom in the isomers is *cis* to the NO group and the O atom of one of the quinolinolato ligands is *trans* to the NO group. The *cis*-1 isomer is in *cis*(0,0) and *trans*(N,N) configurations for the ligating atoms, N and O, of the two quinolinolato ligands, and the *cis*-2 isomer is in *cis*(0,0) and *cis*(N,N). The Ru–O bond distance *trans* to NO is clearly shorter than the Ru–O distance *cis* to NO, reflecting the stronger π-donation of the oxygen *trans* to the NO group. Other *cis* geometrical isomers could not be isolated.

The precursor complexes of the bis complexes, *cis*-[RuX$_3$(N-O)NO]$^-$ (X = Cl or Br), were isolated as the tetramethylammonium salts. The X-ray analysis showed that all the X are coordinated *cis* to NO and the 8-quinolinolato oxygen is *trans* to NO, and the Ru–O bond distance is comparable with the Ru–O bond *trans* to NO for the *cis*-1 and *cis*-2 complexes [4]. These results suggest that the phenolic oxygen anion is a stronger π-donor than the nitrogen atom in the quinoline ring.

Halide and acetate ions may behave as σ- and π-donors [5, 6], suggesting the possibility of preparing the *trans* type of bis complex in which the anion is *trans* to NO. For the {Ru(II)–NO^+} type of nitrosylruthenium complex, some geometrical isomerizations induced by a thermal reaction have been reported [6–10]. However, there has been no report on photoinduced geometrical isomerization for the nitrosylruthenium complexes although photoinduced denitro-

---

*Authors to whom correspondence should be addressed.

sylations of transition metal nitrosyls have been reported [11]. Recently, we have photochemically prepared *trans*-[RuX(2mqn)$_2$NO] (X = Cl or Br; H(2mqn) = 2-methyl-8-quinolinol) from the *cis*-1 and *cis*-2. The *trans* isomer is in *trans*(O,O) and *trans*(N,N) configurations for the 2mqn [12].

In this paper, we report the preparation of *cis*-1 type [Ru(OAc)(2mqn)$_2$NO] (OAc = acetate ion) and its *trans* isomer, and their mutual photoisomerizations in CH_2Cl_2 using an Xe lamp as the light source. Kinetics of the isomerizations at 436 nm is carried out in CH_2Br_2 using a super high-pressure Hg lamp as the light source. The isomerization is also examined in the presence of ^{15}NO (^{15}N at.% = 99).

Experimental

Measurements

IR spectra were measured in Nujol mull with JASCO A-202 and IR-F spectrophotometers. Electronic spectra were recorded using an Hitachi U-3410 spectrometer. ^1H and ^{13}C NMR spectra in chloroform-d$_1$ were recorded on JEOL-GSX 270N and 400 spectrometers at room temperature using TMS as internal standard. The field desorption (FD) mass spectra in the *m/z* range 0–1500 were measured by a combined FD unit on an Hitachi M-80 double-focusing mass spectrometer equipped with an Hitachi M-003 data processing system. The complex was dissolved in CH_2Cl_2 and placed on a carbon emitter. The measurement conditions were as follows: the emitter currents, 15–20 mA; the cathode potential, −4 kV; the ion accelerating potential, 3 kV.

Preparation

*cis-[Ru(OAc)(2mqn)$_2$NO] (I)**

A mixture of hydrated nitrosylruthenium(III) chloride (1.0 mmol) dissolved in hot water (30 cm^3) and freshly recrystallized 2-methyl-8-quinolinol (4.0 mmol) in 1 mol dm^{-3} acetic acid aqueous solution (20 cm^3) was adjusted to pH 5.5 with a sodium hydroxide aqueous solution and warmed at *c.* 70 °C for 2 h to precipitate a reddish-brown product. After the crude product was dissolved in CH_2Cl_2, the solution was charged on a silica-gel column (Wakogel C-200, ϕ 2.5×25 cm) and eluted with 40 vol.% ethylacetate–CH_2Cl_2. The faint first band was [RuCl(2mqn)$_2$NO]. The effluent of the major second band was concentrated on a rotary evaporator. Diethyl ether was slowly added to the solution which was stored overnight in a refrigerator. The reddish-brown product was filtered off and dried in air. Yield 35%. *Anal.* Found: Ru, 19.7; C, 51.8; H, 3.8; N, 8.3. Calc. for $C_{22}H_{19}N_3O_5Ru$: Ru, 20.0; C, 52.2; H, 3.8; N, 8.3%. IR (Nujol): ν(NO) at 1846 cm^{-1}, ν(C=O) of OAc at 1623 cm^{-1}. UV (CH_2Cl_2, 2.00×10^{-4} mol dm^{-3}): 24 800 (log ϵ 3.83), 37 300 (4.7), 41 800 (4.5) cm^{-1}. UV (CH_2Br_2, 2.03×10^{-4} mol dm^{-3}): 24 400 (3.81) cm^{-1}.

*trans-[Ru(OAc)(2mqn)$_2$NO] (II)***

The *cis* complex (0.1 mmol) dissolved in CH_2Cl_2 (20 cm^3) and then deaerated with dinitrogen, in a Pyrex vessel was irradiated by an Xe lamp (300 W) through a combination of a UV cutoff filter (less than 360 nm) (UV 36, Hoya) and a water filter for *c.* 4 h at room temperature. The solution was darkened. After the solvent had been evaporated, the residue dissolved in CH_2Cl_2 was charged on a silica-gel column (Wakogel C-200, ϕ 2.5×25 cm) and eluted with 20–40 vol.% ethylacetate–CH_2Cl_2. The faint first band was [RuCl(2mqn)$_2$NO] which was prepared by irradiation of the Xe lamp, the major second band being the *trans* complex (yield (20%), and the major third band being the starting complex (recovered 60%). *Anal.* Found: C, 51.8; H, 3.7; N, 8.2. Calc. for $C_{22}H_{19}N_3O_5Ru$: C, 52.2; H, 3.8; N, 8.3%. IR (Nujol): ν(NO) at 1825 cm^{-1} with a shoulder at 1815 cm^{-1}, ν(C=O) of OAc at 1664 cm^{-1}. UV (CH_2Cl_2, 3.52×10^{-4} mol dm^{-3}): 25 000 (log ϵ 3.77), 37 200 (4.7), 41 000 (4.5) cm^{-1}. UV (CH_2Br_2, 2.21×10^{-4} mol dm^{-3}): 24 800 (3.78) cm^{-1}.

Both **I** and **II** are unstable even when stored in the dark, thus they were chromatographically purified just before use.

Mutual photoisomerization reactions using an Xe lamp

A solution of **II** (0.1 mmol) dissolved in CH_2Cl_2 (20 cm^3) was exposed to an Xe lamp (300 W) for *c.* 4 h at room temperature. The same chromatographic separation for the preparation of **II** from **I** was performed. The yield of **I** was 60% and **II** was recovered in 20% yield.

Mutual photoisomerization reactions were also carried out in the presence of NO gas. Solutions of **I** or **II** (0.1 mmol) dissolved in CH_2Cl_2 (20 cm^3) were degassed by freeze–pump–thaw cycles. 1.0 mmol of NO was added to the reaction vessel, which was shaken under running water until the frozen solution thawed, and the solution was exposed to the Xe lamp. With **I** as a starting material, the yields of **II** and **I** were 26% and 74%. With **II** as a starting material, the yields of **I** and **II** were 70% and 25%.

Kinetics of mutual photoisomerization reactions using an Hg lamp

Apparatus

A super high-pressure Hg lamp (HBO 200 W, Osram) was used as the light source for the photoisomerization reactions. The 436 nm irradiation light was isolated by using a combination of a Shimadzu-Bausch & Lomb

---

*The formal name is (*OC*-6-22)-acetatobis(2-methyl-8-quinolinolato-*O*,*N*)nitrosylruthenium(III).

**The formal name is (*OC*-6-43)-acetatobis(2-methyl-8-quinolinolato-*O*,*N*)nitrosylruthenium(III).

SP-200 monochrometer and a UV cutoff filter (less than 360 nm) (UV 36). The reactant and product were separated using a JASCO TRIROTAR-V HPLC apparatus equipped with a C_{18}-10 silica gel reversed phase column (Finepak SIL C18, JASCO). Methanol–water (volumetric ratio 8:2) was used as eluent. The amounts of **I** and **II** were determined at 365 nm with a JASCO UVIDEC-100-2V equipped with a Shimadzu C-R6A Chromatopac data processor. To examine the degree of scrambling of NO on irradiation, irradiation in the presence of ^{15}NO (^{15}N at.% = 99) at 25 °C was studied, by measuring the absorbance ratio of the ^{15}NO stretching band area to the ^{14}NO band in coordinated NO for **I** or **II** in CH_2Cl_2 using a Perkin-Elmer 1600 FT-IR spectrometer. For examining the solvent effect on the isomerizations at 25 °C, mixtures of CH_2Br_2 and liquid paraffin (Uvasol, Merck) were used as solvents. The viscosity of the reaction solution was measured using a YAMCO model VM-1A-L viscometer (Yamaichi Electric Ind.).

Procedure

Irradiation under stirring was carried out in the temperature range of -5 to 30 °C using a 1.0 cm length quartz cell capped with a silicon rubber disk laminated with Teflon film. After complex **I** or **II** had been dissolved in CH_2Br_2 or liquid paraffin–CH_2Br_2 and deaerated by passing dinitrogen, the solution (exactly 3 cm^3) was placed in a quartz cell and capped under a dinitrogen atmosphere. The concentration was prepared to *c.* 1×10^{-3} mol dm^{-3} with absorbance *c.* 5 at 436 nm. Two quartz cells containing the solution were prepared. For one of them, irradiation was continued for 5 to 6 h until the photostationary state was achieved between the *trans* and the *cis* isomers to obtain the apparent equilibrium constant. The reaction was analyzed as a first-order reaction along with the reverse reaction. For another cell, an 8×10^{-3} cm^3 (8μl) was sampled through the disk by micro syringe at regular intervals (*c.* 5 min) during irradiation up to 20 min to obtain apparent rate constants. Quantum yields for the *cis* to *trans* and for the *trans* to *cis* isomerizations, ϕ_1 and ϕ_2, were calculated from the apparent rate constants.

For isomerizations in the presence of ^{15}NO, the CH_2Br_2 solution of **I** or **II** (*c.* 1×10^{-3} mol dm^{-3}, 3 cm^3) was first degassed by freeze–pump–thaw cycles and ^{15}NO gas was introduced into the quartz cell with a vacuum Teflon cock using a vacuum line (molar ratio of ^{15}NO to the complex is *c.* 20). After the solution had been separately irradiated for 1, 2, 3 or 5.5 h, the solvent and the residual gas were removed. A small portion of the residue was dissolved in CH_2Br_2, and **I** and **II** were analyzed by HPLC. Another major portion was dissolved in CH_2Cl_2, and **I** and **II** were separated on a silica-gel column (Wakogel C-300, ϕ 0.5×4.5 cm) as mentioned above. The absorbance of the ^{14}NO and ^{15}NO stretching vibrations for **I** and **II** was measured in CH_2Cl_2 using a CaF_2 liquid cell (0.5 mm length).

Incident light intensity was determined using tris(oxalato)ferrate(III) chemical actinometer [13].

Results and discussion

Identification of cis- and trans-[Ru(OAc)(2mqn)₂NO]

FD mass spectra of **I** and **II** showed the molecular ions and its isotopic peaks in the *m/z* 501–511 region. No other peaks were observed in the region of *m/z* 0–1500. The observed relative intensities agreed with those calculated for the isotopic abundances for all the constituent elements of the complexes. For **I**: *m/z* (observed relative intensity, calculated one) 501 (15.5, 15.0), 502 (5.0, 4.0), 503 (6.0, 5.8), 504 (31.2, 36.1), 505 (39.4, 43.7), 506 (55.2, 56.9), 507 (100, 100), 508 (24.9, 24.8), 509 (51.2, 55.0) 510 (15.2, 13.9), 511 (2.1, 2.3), 512 (0, 0.3); *sd* = 0.024. For **II**: *m/z* (observed relative intensity, calculated one) 501 (15.8, 15.0), 502 (4.4, 4.0), 503 (5.2, 5.8), 504 (36.6, 36.1), 505 (43.2, 43.7), 506 (55.9, 56.9), 507 (100, 100), 508 (27.3, 24.8), 509 (56.3, 55.0), 510 (15.0, 13.9), 511 (1.3, 2.3), 512 (0, 0.3); *s.d.* = 0.011.

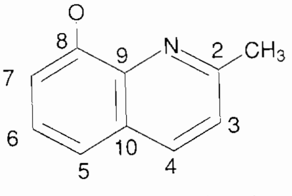
The elemental analyses were also consistent with formulae proposed for the complexes, suggesting that **I** and **II** are monomeric and geometrical isomers of each other.

$^1H\{^1H\}$ and $^{13}C\{^1H\}$ COSY spectra and ^1H non-decoupling spectra with NOE were measured. The quarternary carbons were confirmed by measuring ^1H off-resonance decoupling. Assignment of the NMR data for H2mqn and its metal chelates are in accord with Howie *et al.* [14].

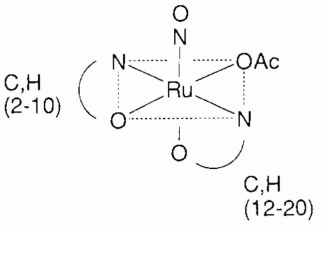
The $^1H\{^1H\}$ and $^{13}C\{^1H\}$ COSY NMR spectra of **II** are shown in Figs. 1 and 2. The ^1H and $^{13}C\{^1H\}$ chemical shifts and their assignments for **II** are as follows*. ^1H

---

*Numbering of the hydrogens and the carbons for 2mqn is basically as follows:



Numbering for complex **I** is as follows: where 2mqn is represented by N⌒O.



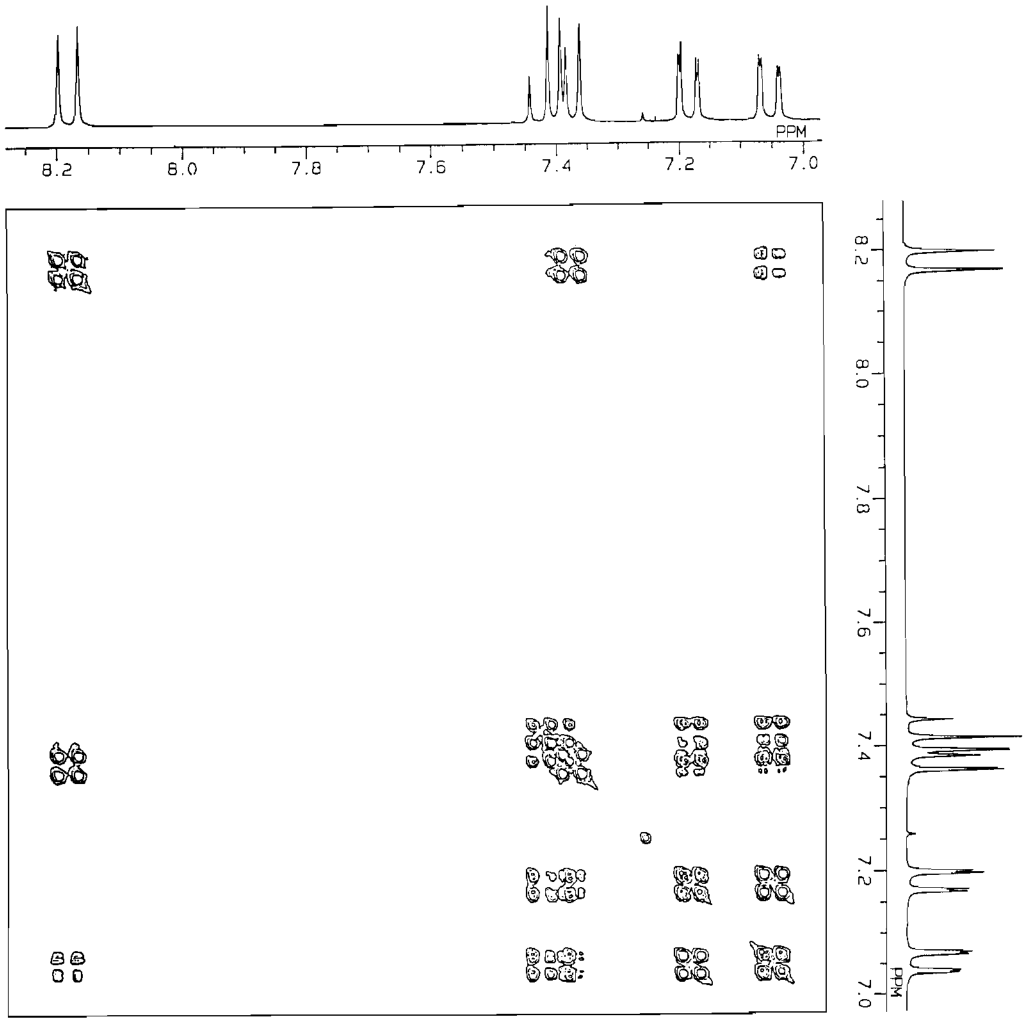


Fig. 1. $^1H\{^1H\}$ COSY spectrum of *trans*-[Ru(OAc)(2mqn)$_2$NO] in $CDCl_3$.

NMR ($CDCl_3$): $\delta = 1.23$ (3H, s, CH_3COO^-), 3.35 (6H, s, C2-CH_3), 7.05 (2H, d, $J = 8$ Hz, H5), 7.18 (2H, d, $J = 8$ Hz, H7), 7.38 (2H, d, $J = 8$ Hz, H3), 7.41 (2H, t, $J = 8$ Hz, H6), 8.18 (2H, d, $J = 8$ Hz, H4). ^{13}C NMR ($CDCl_3$): $\delta = 23.7$ (CH_3COO^-), 24.7 (C2-CH_3), 113.2 (C5), 114.6 (C7), 124.0 (C3), 128.4 (C10), 129.2 (C6), 139.4 (C4), 143.1 (C9), 162.4 (C2), 167.5 (C8), 175.6 (CH_3COO^-).

A signal attributable to the methyl hydrogens of 2mqn groups was observed at $\delta = 3.35$ and the resonance of the methyl carbons at $\delta = 24.7$, indicating that the two methyl groups in **II** are equivalent. The NMR data indicate that **II** is the *trans* isomer with *trans*(O,O) and *trans*(N,N) of the two 2mqn ligands consistent with the steric hindrance of the methyl groups in 2mqn.

The number of resonance lines for the ^{13}C NMR spectrum of **I** suggests that two of the 2mqn are in structurally different environments. Of the resonances due to C8 and C18, the latter was assigned to the 2mqn whose phenolic oxygen is *trans* to NO because NO is a strong π-electron acceptor. The ^1H and $^{13}C\{^1H\}$ NMR chemical shifts and their assignments for **I** are as follows*. ^1H NMR ($CDCl_3$): $\delta = 1.83$ (3H, s, CH_3COO^-), 2.94 (3H, s, C12-CH_3), 3.29 (3H, s, C2-CH_3), 6.94 (1H, d, $J = 8$ Hz, H7), 7.00 (1H, d, $J = 7$ Hz, H17), 7.10 (1H, d, $J = 7$ Hz, H15), 7.11 (1H, d, $J = 7$ Hz, H5), 7.35–7.42 (4H, m, H3, H13, H6, H16), 8.14 (1H, d, $J = 9$ Hz, H4), 8.24 (1H, d, $J = 8$ Hz, H14). ^{13}C NMR ($CDCl_3$): $\delta = 23.1$ (CH_3COO^-), 24.0 (C12-CH_3), 27.3 (C2-CH_3), 113.6 (C15), 114.3 (C5), 115.2 (C7), 115.3 (C17), 124.1 (C3), 124.3 (C13), 128.5 (C10), 128.9 (C20), 129.4 (C6 or C16), 129.5 (C16 or C6), 139.0 (C4), 140.1 (C14), 143.0 (C9), 143.8 (C19), 160.8 (C2), 161.6 (C12), 164.2 (C8), 167.7 (C18), 177.1 (CH_3COO^-).

Except for the acetato carbon resonance, the spectral pattern and the chemical shifts, especially the differences between the chemical shifts of C3 and C13 and of C9 and C19, were very similar to those for *cis*-1 type

---

*See footnote on p. 131.

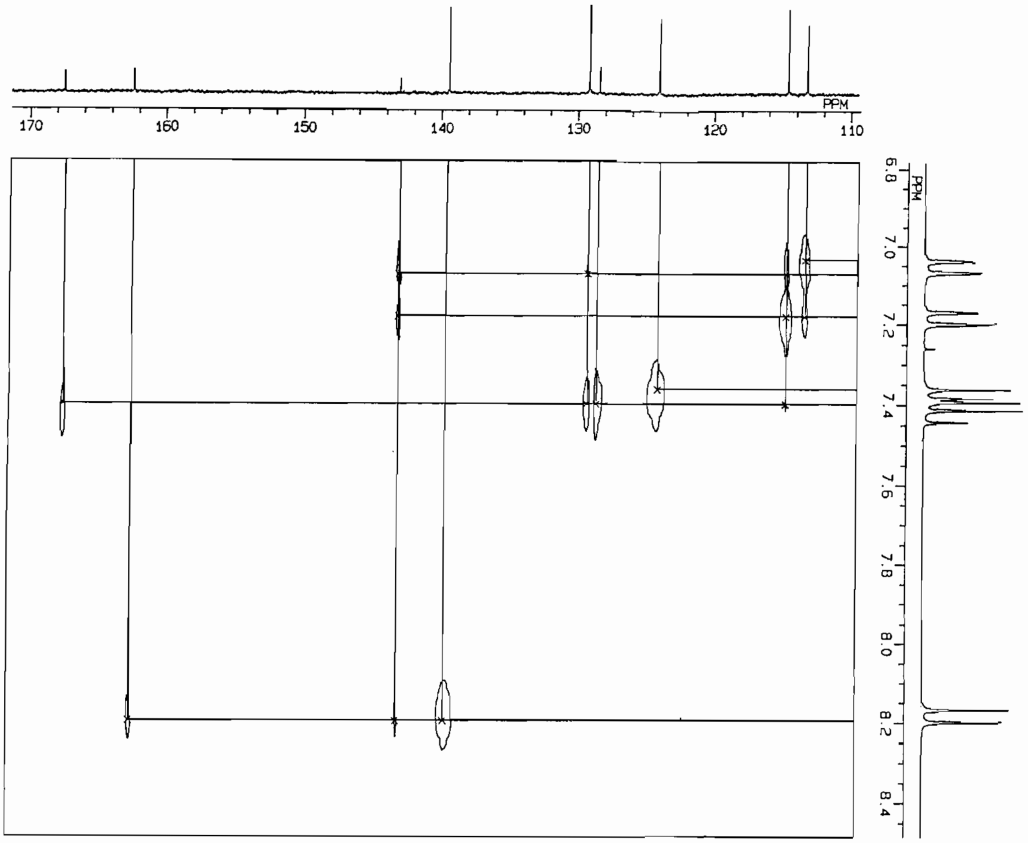


Fig. 2. $^{13}C\{^1H\}$ COSY spectrum of *trans*-[Ru(OAc)(2mqn)$_2$NO] in $CDCl_3$.

[RuCl(2mqn)$_2$NO] whose structure was determined to be in *cis*(0,0) and *trans*(N,N) configurations [2].

The ^1H resonance peaks of the two methyl group for *cis*-1 and *cis*-2 types of [RuX(2mqn)$_2$NO] were observed at $\delta = 3.06$ and 3.27, and at 1.82 and 3.14 for X = Cl, respectively, and at $\delta = 2.96$ and 3.04, and at 1.83 and 3.14 for X = Br, respectively [2]. For **I**, these were observed at $\delta = 2.94$ and 3.29. The differences between the resonances of each pair except for the methyl groups were also very similar to those of *cis*-1 [RuX(2mqn)$_2$NO] but not to those of the *cis*-2 isomer. Another important criterion is the difference between the chemical shifts due to C8 and C18. The resonances for the *cis*-1 and *cis*-2 types of [RuX(N-O)$_2$NO] (X = Cl or Br; N-O = 8-quinolinolato, 2-methyl-, 4-methyl-, 2,4-dimethyl-, 2-ethyl and 5-chloro-8-quinolinolato) were separately observed at $\delta = c.$ 164–168 and 163–169 [15]. For *cis*-1 type complexes, the difference was 1.2–3.5 ppm, while for *cis*-2 type complexes it was 4.4–5.4 ppm. For **I**, the resonances due to C8 and C18 were observed at $\delta = 164.2$ and 167.7, the difference being 3.5 ppm. Thus, **I** was determined to be *cis*-1 type.

The NO stretching vibration was observed at 1846 cm^{-1} for **I** and 1825 cm^{-1} for **II**, indicating that **I** and **II** are the {Ru(II)–NO$^+$} type [1].

The dπ(Ru) → π^*(NO) charge-transfer band for the {Ru(II)–NO$^+$} type of nitrosylruthenium(III) complex has been reported to be observed in the 21 000–23 800 cm^{-1} region with $\epsilon < 50$ mol^{-1} dm^3 cm^{-1} [5, 6, 16]. The dπ(Ru) → π^*(2mqn) bands for **I** and **II** were observed at *c.* 25 000 cm^{-1} with log $\epsilon = 3.8$. The dπ(Ru) → π^*(NO) band is apparently obscured by the more intense dπ(Ru) → π^*(2mqn) band. The charge transfer bands in the 2mqn ligands for **I** and **II** were observed at *c.* 37 000 cm^{-1} with log $\epsilon = 4.7$ and at *c.* 41 000 cm^{-1} with log $\epsilon = 4.5$.

Only the *cis*-1 type of acetato complex was prepared by the present thermal reaction although both *cis*-1 and *cis*-2 types were prepared in the case of the chloro and bromo ligands [2, 12]. The *trans* isomer could not be prepared by the thermal reaction as observed for the chloro and bromo complexes.

Photoisomerization reactions

Using coordinating solvents, acetonitrile or DMF, the *trans* and *cis* isomers were decomposed with NO elimination on irradiation with an Xe lamp even if the solvent was deaerated. In aerated CH_2Cl_2 or CH_2Br_2, the isomers were also considerably decomposed on irradiation. On the other hand, in deaerated CH_2Cl_2 or CH_2Br_2, the mutual isomerization reactions proceeded without decomposition of the complexes in the presence of NO gas. The ratio of the recovered *trans* isomer to prepared *cis* isomer using the *trans* isomer as the starting material was almost equal to that of the prepared *trans* isomer to recovered *cis* isomer using the *cis* isomer as the starting material. This observation indicates that a photostationary state is present on irradiation. In the absence of NO gas, the same stationary state was achieved with a little decomposition in the deaerated solvents.

Kinetics

Kinetics of the isomerization was examined in the absence of NO gas at 436 nm where both the complexes show absorption bands attributable to $d\pi(Ru) \rightarrow \pi^*(2mqn)$ and $d\pi(Ru) \rightarrow \pi^*(NO)$ charge-transfer. As the concentration of the complex photochemically prepared in the initial step was estimated to be *c*. 10^{-5} mol dm^{-3}, molar extinction coefficients of the *trans* and *cis* isomers in *c*. 10^{-3}–10^{-5} mol dm^{-3} were measured. The molar extinction coefficients of the *trans* isomer at 436 and 365 nm were constant within experimental error in the concentration range, while those of the *cis* isomer increased with decrease of the concentration*. Thus, the concentration effect for the *cis* isomer was corrected in the analysis of the kinetics. No clear change of the electronic spectra was observed during isomerization, therefore the reaction was followed by the HPLC technique. Notwithstanding strict deaeration of the solution, less than 5% of the total complexes was decomposed because air leakage caused the complexes to be decomposed when the reaction solution was sampled through the disk by micro syringe.

The course of isomerization is shown in Fig. 3. The molar ratio of the *cis* isomer to the *trans* isomer gradually approached 3 and was invariably on more than 4 h irradiation. The *cis* isomer was in equilibrium with the *trans* isomer whether the *trans* or *cis* isomer was the starting material, indicating that a photostationary state is present on irradiation.

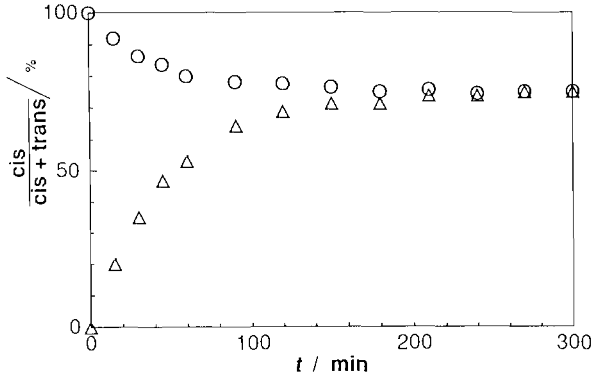


Fig. 3. Time course of isomerization of *trans*- and *cis*-[Ru(OAc)(2mqn)$_2$NO] in CH$_2$Br$_2$ at 25 °C. ○, *cis* to *trans*; initial concentration of *cis* isomer, 1.00×10^{-3} mol dm^{-3}. △, *trans* to *cis*; initial concentration of *trans* isomer, 1.00×10^{-3} mol dm^{-3}. The ratio was separately analyzed after continuous irradiation up to the corresponding time.

TABLE 1. Quantum yields of isomerization in CH$_2$Br$_2$ at 436 nm irradiation: initial concentration of the complex, 1.00×10^{-3} mol dm^{-3}

Temperature (°C)	$\phi_1 \times 10^{-3}$	$\phi_2 \times 10^{-3}$
−5	1.2	7.8
0	1.4	7.9
5	1.6	8.3
10	1.8	9.5
15	1.9	9.6
20	2.0	9.3
25	2.3	10.3
30	2.5	10.9

ϕ_1 = the quantum yield for *cis* to *trans* isomerization; ϕ_2 = the quantum yield for *trans* to *cis* isomerization; the values are accurate to ±10%.

Table 1 shows the quantum yields for the *cis* to *trans* and the *trans* to *cis* isomerizations, ϕ_1 and ϕ_2. The quantum yields using the *cis* isomer were almost equal to those using the *trans* isomer within experimental error although the former tended to be smaller than the latter. The quantum yield increased with increase of temperature. The plot of ln ϕ_1 or ln ϕ_2 against T^{-1} showed a linear relation, suggesting that only one Arrhenius type of process takes part in the photochemical process. Phosphorescence could not be observed for either the *cis* or *trans* isomer in 1,2-dichloroethane at 77 K, indicating that the lowest energy excited state is very short lived or is a non-emitting state. The lowest energy excited state is considered to be $d\pi(Ru) \rightarrow \pi^*(2mqn)$, $d \rightarrow d^*$, or $d\pi(Ru) \rightarrow \pi^*(NO)$ taking into consideration the photochemistry study of [RuCl(bpy)$_2$NO]$^{2+}$ by Callahan and Meyer [16]. The linear relation of the quantum yield against T^{-1} indicates that the photochemical primary process does not depend on temperature, but the secondary process originating from a reaction intermediate produced by the primary process depends on temperature [17]. The activation energies for the secondary process of the *cis* to *trans* and of the *trans* to *cis* isomerizations are estimated to be 15 (±1.5) and 5.5 (±0.6) kJ mol^{-1}, respectively.

The isomerization from the *cis* or *trans* isomer in CH$_2$Br$_2$ examined in the presence of ^{15}NO gas (^{15}N

---

*For the *cis*-1 isomer: ϵ (mol^{-1} dm^3 cm^{-1}) 3490 (1.40×10^{-3} mol dm^{-3}), 3510 (2.23×10^{-4}), 3580 (6.98×10^{-5}), 3740 (1.74×10^{-5}) at 365 nm; 4840 (1.40×10^{-3}), 4850 (2.23×10^{-4}), 4930 (6.98×10^{-5}), 4950 (1.74×10^{-5}) at 436 nm. For the *trans* isomer: 3750 (9.68×10^{-4}), 3770 (1.55×10^{-4}), 3730 (1.94×10^{-5}) at 365 nm; 3730 (9.68×10^{-4}), 3740 (1.55×10^{-4}), 3710 (1.94×10^{-5}) at 436 nm.

at.% = 99) on 436 nm irradiation showed exchange of coordinated NO for ^{15}NO. Neither the exchange of the NO nor the isomerization was observed without irradiation. The ^{14}NO and ^{15}NO stretching bands for the *cis* isomer separated chromatographically after irradiation were observed at 1861 and 1823 cm^{-1}, and those for the *trans* isomer at 1845 and 1808 cm^{-1}, respectively, in CH_2Cl_2. The ratio of the ^{15}NO to the ^{14}NO absorption intensity gradually increased with increase of the irradiation time using the *cis* or the *trans* isomer as the starting material. After irradiation for more than 5.5 h, the ratios of ^{15}NO to ^{14}NO in the *cis* and *trans* isomers were 1.5 and 1.3, respectively, in using the *cis* isomer as the starting material. Using the *trans* isomer, the ratios in the *cis* and *trans* isomers were 3 and 2, respectively. The ratio is expected to be 20, the starting ratio of ^{15}NO to NO in the complex after the exchange of the coordinated NO for ^{15}NO gas was attained at equilibrium. However, the observed ratios were smaller than 20 because of unsatisfactory stirring of the solution with NO gas due to restriction of the apparatus during the irradiation. The irradiation of the *cis* isomer in stirring the apparatus by hand every 15 min was also carried out at the same scale. The ratio of ^{15}NO to ^{14}NO of the *cis* isomer separated chromatographically was 2.7 after 2 h irradiation and was 19 after 5.5 h. This ratio was almost equal to the starting molar ratio of ^{15}NO to *cis* isomer, 20. The isomerization and the exchange of NO were attained in equilibration in almost the same time scale if the stirring in the presence of NO is satisfactory. Therefore, the same photochemical process seems to participate in the isomerization and the exchange of NO.

The effect of solvent on the isomerization was examined on 20 min irradiation at 25 °C in 5, 10, or 20 vol.% liquid paraffin–CH_2Br_2 solutions with viscosities 1.1, 1.2 and 1.4 mPa s, respectively. The quantum yields, ϕ_1 and ϕ_2 in the 5 and 10 vol.% solutions were almost equal to those in the CH_2Br_2 solution and only 5% of the complexes was decomposed to produce denitrosylated species of a dark green color. In the 20 vol.% solution, 15% of the complexes was decomposed to produce the denitrosylated species. These observations suggest that the liberated NO does not readily recombine with Ru in the presence of liquid paraffin added to the CH_2Br_2 solution.

The results obtained from the irradiation in the presence of ^{15}NO and the solvent effect show that irradiation of the $d\pi(Ru) \rightarrow \pi^*(NO)$ charge-transfer band triggers the bond rupture between the Ru and NO which is involved in the isomerization.

It has been reported that denitrosylation proceeds when nitrosyl complexes are exposed to UV–Vis light [11, 16]. Excited-state resonance Raman spectroscopic studies on nitrosyl complexes by Zink and co-workers show that a linear to bent geometry change of the metal–NO group is induced by electron transfer from the metal to NO followed by a cleavage of the metal–NO bond on irradiation near the $d\pi(Ru) \rightarrow \pi^*(NO)$ charge-transfer band. According to the photoisomerization mechanism proposed by Ford and co-workers [18], the possible isomerization mechanism in the present study is as follows. Homolytic cleavage of the bent Ru–NO bond of the intermediate was caused by irradiation to producing a denitrosylated five-coordinate intermediate with a square-pyramidal configuration which retains the symmetry of the reactant. The denitrosylated species rearranges to another denitrosylated species with a square-pyramidal configuration which retains the symmetry of the product via a trigonal-bipyramidal intermediate to undergo isomerization. These two square-pyramidal species recombine with NO to form the isomeric reactant and product. The activation energy for the rearrangement process of the denitrosylated species corresponds to that calculated from dependence of the quantum yield on temperature.

The isomerization proceeds with liberation and recombination of NO in a halocarbon medium having a poor coordinating ability which does not disturb the recombination.

Acknowledgements

The authors express their thanks to Dr Mikio Hoshino of the Institute of Physical and Chemical Research for kindly measuring the phosphorescence. The present work was partially supported by the Shinsei fund and by Teikoku Printing Inks Mfg. Co, Ltd.

References

1 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev., 13* (1974) 339; K. G. Caulton, *Coord. Chem., Rev., 14* (1975) 317; F. Bottomley, *Coord. Chem. Rev., 26* (1978) 7; F. Bottomley, in P. S. Braterman (ed.), *Reactions of Coordinated Ligands,* Vol. 2, Plenum, New York 1989, pp. 115–222; D. M. P. Mingos and D. J. Sherman, *Adv. Inorg. Chem., 34* (1989) 293.

2 Y. Kamata, T. Kimura, R. Hirota, E. Miki, K.Mizumachi and T. Ishimori, *Bull. Chem. Soc. Jpn., 60* (1987) 1343.

3 Y. Kamata, E. Miki, R. Hirota, K. Mizumachi and T. Ishimori, *Bull. Chem. Soc. Jpn., 61* (1988) 594.

4 E. Miki, K. Harada, Y. Kamata, M. Umehara, K. Mizumachi, T. Ishimori, M. Nakahara, M. Tanaka and T. Nagai, *Polyhedron, 10* (1990) 583.

5 A. F. Schreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm and J. D. Gunter, *Inorg. Chem., 11* (1972) 880.

6 S. Pell and J. N. Armor, *Inorg. Chem., 12* (1973) 873.

7 F. Bottomley, E. M. R. Kiremine and S. G. Clarkson, *J. Chem. Soc., Dalton Trans.,* (1975) 1909.

8 T. Fukuchi, E. Miki, K. Mizumachi and T. Ishimori, *Chem. Lett.,* (1987) 1133.

9 A. B. Nikol'skii, A. M. Popov, T. S. Repinskaya, Yu. N. Kukushkin and M. B. Egorova, *Sov. J. Coord. Chem., 13* (1987) 529.

10 A. B. Nikol'skii, A. M. Popov, M. B. Egorova and V. V. Khorunshii, *Sov. J. Coord. Chem., 15* (1989) 800.

11 Po-Hsin Liu and J. I. Zink, *Inorg. Chem., 16* (1977) 3165; W. Evans and J. I. Zink, *J. Am. Chem. Soc., 103* (1981) 2635; Y. Y. Yang and J. I. Zink, *J. Am. Chem. Soc., 107* (1985) 4799; G. Stochel and Z. Stasicka, *Polyhedron, 4* (1985) 1887; R. K. Coll, J. E. Fergusson and T. Sian Keong, *Aust. J. Chem., 39* (1986) 1161; M. Hoshino, S. Arai, M. Yamaji and Y. Hama, *J. Phys. Chem., 90* (1986) 2109; R. K. Coll, J. E. Fergusson, V. McKee, C. T. Page, W. T. Robinson and T. Sian Keong, *Inorg. Chem., 26* (1987) 106; M. Kubota, M. K. Chan, D. C. Boyd and K.R. Mann, *Inorg. Chem., 26* (1987) 3261; J.-H. Perng and J. I. Zink, *Inorg. Chem., 27* (1988) 1403; M. Hoshino and M. Kogure, *J. Phys. Chem., 93* (1989) 5478.

12 H. Kamata, Y. Konishi, Y. Kamata, E. Miki, K. Mizumachi, T. Ishimori, T. Nagai and M. Tanaka, *Chem. Lett.,* (1988) 159.

13 G. J. Ferraudi, *Elements of Inorganic Photochemistry,* Wiley–Interscience, New York, 1988, p. 17.

14 J. K. Howie, P. Bosserman and D. T. Sawyer, *Inorg. Chem., 19* (1980) 2293.

15 E. Miki *et al.*, unpublished work.

16 R. W. Callahan and T. J. Meyer, *Inorg. Chem., 16* (1977) 574.

17 G. B. Poter, V. Balzani and L. Moggi, *Advances in Photochemistry,* Vol. 9, Wiley, New York, 1974, p. 147.

18 L. H. Skibsted, D. Strauss and P. C. Ford, *Inorg. Chem., 18* (1979) 3171; P. C. Ford, D. Wink and J. Di Benedetto, in S. J. Lippard (ed.), *Progress in Inorganic Chemistry,* Vol. 30, Wiley, New York, 1983, pp. 213–271.