# Photochromic Reversible Substitution Reaction of Tridentate Schiff Base-Ruthenium(II) Complexes

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In acetonitrile, the chloro ligands of [$RuCl_2$(ppb-etol)($PPh_3$)] (**1**, ppb-etol=*N*-(2-diphenylphosphinobenzilidene)-2-hydroxyethylamine) are substituted with the solvent molecules to yield an equilibrium mixture of [RuCl($CH_3CN$)(ppb-etol)($PPh_3$)]Cl (**2**) and [Ru($CH_3CN$)$_2$(ppb-etol)($PPh_3$)]$Cl_2$ (**3**) at 50 °C in the dark. The reaction is accompanied by a color change from orange to yellow. Upon irradiation of UV-vis light, the color of the solution reverts to orange, and complexes **2** and **3** are converted again into complex **1**. The color change can be made repeatedly and a reversible photochromic reaction system is constructed.

There has been considerable interest in the photoreactivity of transition metal complexes, and the photochemistry of the *cis*-bis(bipyridine)ruthenium(II) moiety and its analogue has been studied extensively.[1] It is an attractive approach to construct a new photoreaction system in connection with the light-triggered molecular devices. We recently reported the photochemical substitution reactions of the ruthenium(II) complexes containing tetradentate Schiff base ligands.[2] Here, we report the bidirectional photo and thermal substitution reactions of ruthenium(II) complexes containing tridentate Schiff base ligands.

The tridentate Schiff base ligands were prepared by the reaction of 2-diphenylphosphinobenzaldehyde and 2-hydroxyethylamine or its derivative in ethanol. The solvent was evaporated and the pale yellow oily residue was used without purification for the synthesis of the complexes. Equimolecular quantities of [$RuCl_2(PPh_3)_3$] and ppb-etol (*N*-(2-diphenylphosphinobenzilidene)-2-hydroxyethylamine) were dissolved in dichloromethane and refluxed for 8 h. Red-orange crystals of [$RuCl_2$(ppb-etol)($PPh_3$)] (**1**)[3] were obtained from a dichloromethane-hexane solution. Since satisfactory crystals of complex **1** suitable for X-ray crystal analysis could not be obtained, X-ray structure determination was applied for [$RuCl_2${ppb-(1*R*,2*S*)-ephe}($PPh_3$)] (**4**)[4] (ppb-(1*R*,2*S*)-ephe=*N*-(2-diphenylphosphinobenzilidene)-(1*R*,2*S*)-norephedrine) which was prepared in a similar way. The geometry around the ruthenium atom is distorted octahedral with the tridentate Schiff base ligand and a triphenylphosphine molecule in the equatorial positions. Two chloro ligands occupy the *trans* position to each other. The absorption spectra of complexes **1** and **4** are quite similar. Thus the structure of complex **1** was assigned to the same *trans* configuration.

Complex **1** was dissolved in acetonitrile and left overnight at 25 °C in the dark to give a yellow solution, from which complex **2** was isolated by adding ether. Figure 1 shows the structure of [RuCl($CH_3CN$)(ppb-etol)($PPh_3$)]$^+$ (**2**).[5] An acetonitrile molecule occupies the *trans* position to a chloro ligand. Evidently, thermal substitution of a chloro ligand by an acetonitrile molecule occurred.

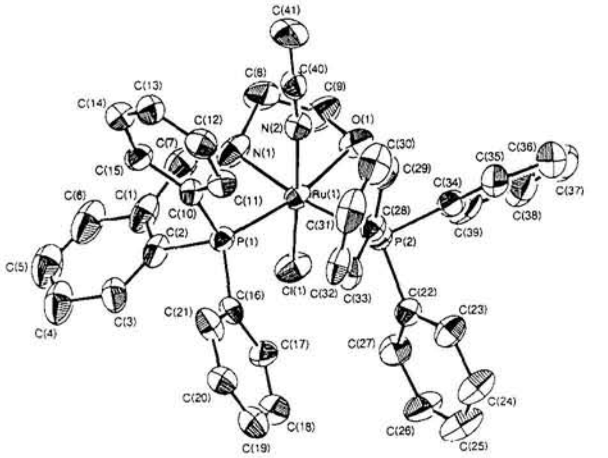


**Figure 1.** The structure of the cation [RuCl($CH_3CN$)(ppb-etol)($PPh_3$)]$^+$ (**2**).

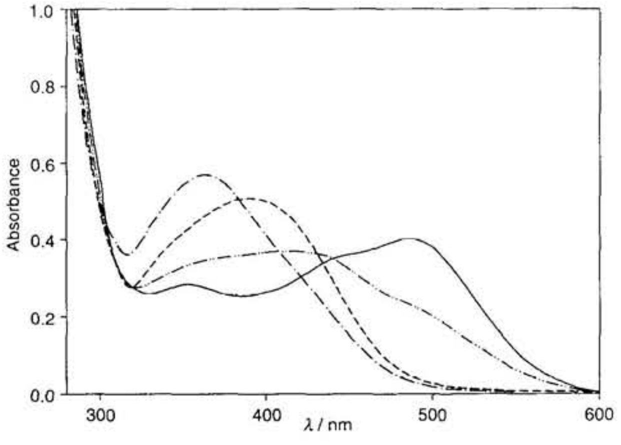


**Figure 2.** The absorption spectra of **a**; ——, **b**; - - - -, **c**; – · –, **d**; – ·· – in acetonitrile.

An acetonitrile solution of complex **2** exhibited a slight color change on heating at 50 °C in the dark. On exposure to sunlight at 25 °C, the color of the solution reverted to orange, but this reaction did not take place under room light. Figure 2 shows the absorption spectra of the complexes in acetonitrile in each stage. The spectral changes clearly showed that two-step thermal reaction occurs. The spectrum of complex **1** (**a**) gradually changed at first to **b** at 25 °C in 10 h, and then from **b** to **c** at 50 °C in 8 h in the dark. During each reaction, isosbestic points were retained. Spectrum **b** was almost identical with that of complex **2**, and the first step (**a** to **b**) was attributed to the substitution of a chloro ligand by an acetonitrile molecule. Unfortunately, we could not isolate the complex which was formed at 50 °C in acetonitrile, and we have no decisive evidence so far to assign its structure. Hodgson and co-workers[6] reported that the thermal substitution of [$RuCl_2$(*o*-bpy)] (*o*-bpy=1,2-bis(2,2′-bipyridyl-6-yl)ethane) in acetonitrile yielded stepwise [$RuCl(CH_3CN)$(*o*-bpy)]$^+$ and [$Ru(CH_3CN)_2$(*o*-bpy)]$^{2+}$. Thus, we anticipate that the product of our second step reaction is [$Ru(CH_3CN)_2$(ppb-etol)($PPh_3$)]$Cl_2$ (**3**). Spectrum **c** changed to **d** in 270 s by irradiation of UV-vis light (500 W xenon lamp) to the solution. Spectrum **d** is interpreted as that of a mixture of complexes **1** and **2**. Though prolonged heating and/or irradiation caused some decomposition of the complexes, the color change could be made repeatedly. Figure 3 shows the absorbance changes of an acetonitrile solution of complex **1** at 500 nm by repeated heating and irradiation of the solution.

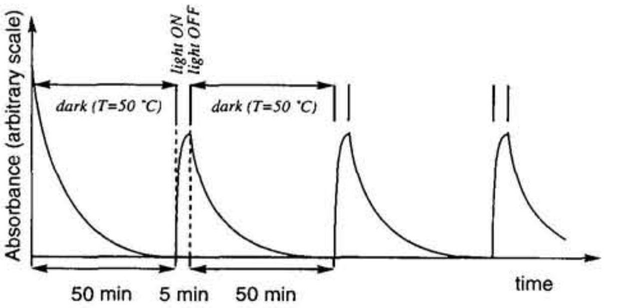


**Figure 3.** Absorbance changes of complex **1** at 500 nm in acetonitrile caused by repeated heating (50 °C) and irradiarion (500 W xenon lamp).

The time-course of the reaction was also followed by measuring $^1H$ NMR spectra in acetonitrile-$d_3$. Figure 4 displays the $^1H$ NMR spectral changes in the imine region of the complexes. The imine proton of complex **1** was observed as a doublet at 9.06 ppm owing to the coupling with $^{31}P$ of the triphenylphosphine molecule ($^4J_{P\text{-}H}$ = 9.5 Hz) (**a**). On standing the solution at 25 °C, the doublet at 9.06 ppm diminished with time and a new doublet attributable to complex **2** developed at 9.05 ppm ($^4J_{P\text{-}H}$ = 10.0 Hz) (**c**). In addition, another doublet appeared at 9.11 ppm ($^4J_{P\text{-}H}$ = 9.3 Hz) at 50 °C (**d**). The intensity ratio of the two doublets (9.05 and 9.11 ppm) was ca. 2:1 after equilibrium was reached. Upon irradiation, the doublet signals at 9.05 and 9.11 ppm diminished and disappeared, respectively, and that at 9.06 ppm increased instead. Upon heating the solution at 25 °C, the spectrum changed to **g**, which was practically identical with that of **c**.

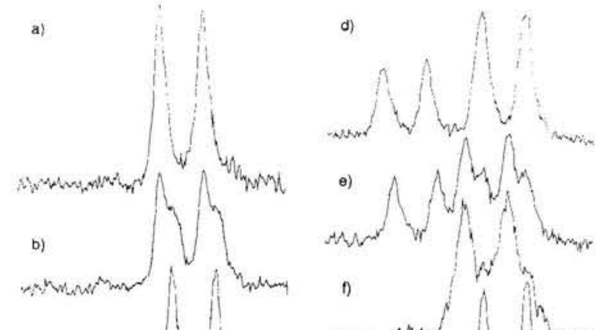
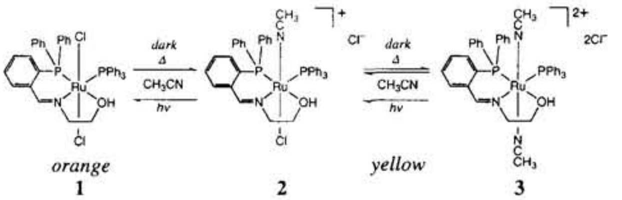


**Figure 4.** The $^1H$ NMR spectral changes in the imine region of the complexes in acetonitrile-$d_3$. **a**; complex **1**, **b**; t=1 h at 25 °C in the dark, **c**; t=10 h at 25 °C in the dark, **d**; t=8 h at 50 °C in the dark, **e**; irradiation of UV-vis light t=30 s at 25 °C, **f**; irradiation of UV-vis light t=270 s at 25 °C, **g**; t=12 h at 25 °C in the dark.

We supposed that the photo and thermal substitution reactions of the complexes occurred as follows.



Thus the thermal substitution reaction of the chloro ligands of complex **1** occurs to yield an equilibrium mixture of complexes **2** and **3**, and they reverts to complex **1** on photolysis in acetonitrile. Although the functional importance of such photoswitching reaction of complex **1** (Figure 3) is still uncertain, this is, to our knowledge, the first report of the photochromic reaction system of ruthenium(II) Schiff base complexes. The electronic and steric effects of the ligand and the wavelength dependence of the photoreactivity are under investigation.

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## References and Notes

1 For example, A. Julis, V. Balzani, F. Barigelleti, F. Campagna, P. Belser, and A. Von Zelewsky, *Coord. Chem. Rev.*, **84**, 85 (1988), and the references cited therein.

2 K. Nakajima, Y. Ando, H. Mano, and M. Kojima, *Inorg. Chim. Acta*, **274**, 184 (1998).

3 Anal. Found: C, 57.65; H, 4.79; N, 1.73%. Calcd for [$RuCl_2$(ppb-etol)($PPh_3$)]·$0.75CH_2Cl_2$ = $C_{39.75}H_{36.5}Cl_{3.5}NOP_2Ru$: C, 57.43; H, 4.43; N, 1.68%.

4 Anal. Found: C, 59.94; H, 4.59; N, 1.47%. Calcd for [$RuCl_2${ppb-(1*R*,2*S*)-ephe}($PPh_3$)]·$CH_2Cl_2$ = $C_{47}H_{43}Cl_4NOP_2Ru$: C, 59.88; H, 4.60; N, 1.49%. Crystallographic data for **4**: orthorhombic, space group $P2_12_12_1$, $a$ = 15.346(2), $b$ = 22.060(2), $c$ = 12.876(4) Å, V = 4359(2) Å$^3$, Z = 4, $D_c$ = 1.44 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 7.07 cm$^{-1}$, 5462 reflections measured ($2\theta_{max}$ = 55°), 4710 [|Fo|>3σ(|Fo|)] used in the refinement, $R$ = 0.031, $R_w$ = 0.039. The reflection intensities were collected on a Rigaku AFC7R diffractometer using graphite monochromated Mo Kα radiation. All calculations were performed using the Xtal 3.2 software.

5 Anal. Found: C, 59.17; H, 5.00; N, 3.56%. Calcd for [$RuCl(CH_3CN)${ppb-etol}($PPh_3$)]Cl·$1.5H_2O$ = $C_{41}H_{41}Cl_2N_2O_{2.5}P_2Ru$: C, 58.93; H, 4.94; N, 3.35%. Crystallographic data for **2**: monoclinic, space group $C2/c$, $a$ = 39.257(4), $b$ = 10.279(1), $c$ = 19.471(1) Å, $\beta$ = 100.28(1)°, V = 7731(1) Å$^3$, Z = 8, $D_c$ = 1.44 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 6.56 cm$^{-1}$, 11411 reflections measured ($2\theta_{max}$ = 60°), 7707 [|Fo|>3σ(|Fo|)] used in the refinement, $R$ = 0.048, $R_w$ = 0.074. The reflection intensities were collected on a Rigaku AFC7R diffractometer using graphite monochromated Mo Kα radiation. All calculations were performed using the Xtal 3.2 software.

6 Md. A. Masood, B. P. Sullivan, and D. J. Hodgson, *Inorg. Chem.*, **33**, 4611 (1994).