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^1H -NMR spectroscopic studies of anion and solvent effects on mixed-valence iodobiruthenocenium(II, IV) salts

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Abstract

Oxidation of 1,1'-biruthenocene with iodobiruthenocenium(IV) $^+Y^-$ salts in CH_2Cl_2 gives iodo-1,1'-biruthenocenium(II,IV) $^+Y^-$ salts ($Y = \text{PF}_6, \text{BF}_4, 2,4,6\text{-(NO}_2)_3\text{C}_6\text{H}_2\text{O}, \text{CCl}_3\text{COO} \cdot \text{CCl}_3\text{COOH}$). The electron exchange reaction between Ru^{II} and Ru^{IV} with iodide migration was investigated by temperature-dependent ^1H -NMR spectroscopy in CD_3COCD_3 and the mixed-solvent solutions $\text{CDCl}_3\text{-CD}_3\text{COCD}_3$, $\text{CDCl}_3\text{-CD}_3\text{CN}$ and $\text{CCl}_4\text{-CD}_3\text{COCD}_3$ with a range of mixing ratios. The activation energy of the reaction increases as the concentration of low dielectric constant solvent increases.

1. Introduction

Taube and coworkers [1] and Kirchner *et al.* [2–5] reported the intermolecular two-electron exchange reactions in ruthenocene(II)–haloruthenocenium(IV) (RcH-RcHX^+) ($\text{Rc} = \text{ruthenocenyl CpRu(C}_5\text{H}_4)$) and osmocene(II)–haloosmocenium(IV) (OcH-OcHX^+) ($\text{Oc} = \text{osmocenyl CpOs(C}_5\text{H}_4)$) ($X = \text{Cl, Br, I}$) systems accompanied by halogen migration. The line broadening in their ^1H -NMR spectra supports the fact that the rate constants of the electron exchange are larger for the RcH-RcHX^+ system than for the OcH-OcHX^+ systems because the Os-X bond has a higher stability than the Ru-X bond. In addition, the rate increases in the order $\text{Cl} < \text{Br} < \text{I}$ for both systems.

Our recent results of ^1H and ^{13}C NMR spectro-

scopic studies for binuclear mixed-valence halo-biruthenocenium(II, IV) salts, $[\text{RcRcX}]^+Y^-$ ($X = \text{I, Br, Cl}$ and $Y = \text{PF}_6, \text{I}_3$) indicate that a trapped-valence state ($\text{Ru}^{\text{II}}\text{-Ru}^{\text{IV}}$) at lower temperatures changes to an averaged-valence state ($\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}$) by increasing the temperature in acetone and acetonitrile solutions [6–9]. As for the kinetic behaviour, the activation energy of the electron exchange reaction is much smaller for the intramolecular process in the binuclear system than for the intermolecular process in the mononuclear mixture system [10]. In addition, the rate of the halogen migration between Ru^{II} and Ru^{IV} is reversed from that in the intermolecular process, *i.e.* the rate increases in the order $\text{I} < \text{Br} < \text{Cl}$ for the binuclear system. Another characteristic feature of the binuclear systems is the generation of a strong absorption band at 480–490 nm in the electronic spectra [7–9]. This paper aims at investigating the intramolecular electron exchange reaction accompanied by the halogen migration with respect to effects of the counter-anion and solvent

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using 90 MHz ¹H NMR spectroscopy for iodo-1,1''-biruthenocenium(II, IV)⁺Y⁻ (Y⁻ = I₃⁻ (1); PF₆⁻ (2); BF₄⁻ (3); 2,4,6-(NO₂)₃C₆H₂O⁻ (4); CCl₃COO⁻·CCl₃CO-

OH (5)) and related salts in the mixed-solvents systems CDCl₃-CD₃COCD₃, CDCl₃-CD₃CN and CCl₄-CD₃COCD₃ with various mixing ratios (Scheme 1).

TABLE 1. ¹H chemical shifts of R_cR_c and related salts (1-5) at the indicated temperature

Compound	Solvent	Temperature (K)	Chemical shifts δ (ppm)
R _c R _c	(CD ₃) ₂ CO	298	4.68, 4.44 (H _{2,3} , H _{3,4}), 4.48(Cp)
		183	4.69, 4.43 (H _{2,3} , H _{3,4}), 4.46(Cp)
1	CDCl ₃ (CD ₃) ₂ CO	298	4.67, 4.47 (H _{2,3} , H _{3,4}), 4.51(Cp)
		183	6.41, 6.05, 5.76 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.33, 5.19, 4.61 Cp(C ₅ H ₄)Ru ^{II}
2	(CD ₃) ₂ CO	323	5.72, 5.62, 5.30
		183	6.41, 6.05, 5.78 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.35, 5.21, 4.64 Cp(C ₅ H ₄)Ru ^{II}
2	CDCl ₃ -(CD ₃) ₂ CO (1/1)	300	5.71, 5.62, 5.30
		183	6.27, 5.95, 5.71, [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.23, 5.11, 4.57 Cp(C ₅ H ₄)Ru ^{II}
2	CDCl ₃ -(CD ₃) ₂ CO (3/1)	303	5.71, 5.56, 5.31
		183	6.24, 5.91, 5.64 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.16, 5.12, 4.57 Cp(C ₅ H ₄)Ru ^{II}
2	CDCl ₃ -(CD ₃) ₂ CO (5/1)	303	5.68, 5.51, 5.29
		208	6.23, 5.90, 5.59 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.12, 4.59 Cp(C ₅ H ₄)Ru ^{II}
2	CDCl ₃ -(CD ₃) ₂ CO (10/1)	303	5.26, 5.47, 5.64
		203	6.17, 5.85, 5.48 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.08, 4.55 Cp(C ₅ H ₄)Ru ^{II}
2	CDCl ₃	303	5.66, 5.41, 5.28
		203	6.18, 5.85, 5.24 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.10, 4.93, 4.55 Cp(C ₅ H ₄)Ru ^{II}
3	(CD ₃) ₂ CO	333	5.65, 5.36, 5.25
		183	6.41, 6.05, 5.80 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.36, 5.21, 4.64 Cp(C ₅ H ₄)Ru ^{II}
3	CDCl ₃ -(CD ₃) ₂ CO (2/1)	300	5.72, 5.63, 5.33
		183	6.31, 5.94, 5.70 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.21, 5.11, 4.57 Cp(C ₅ H ₄)Ru ^{II}
3	CDCl ₃ -(CD ₃) ₂ CO (5/1)	313	5.69, 5.53, 5.29
		183	6.22, 5.85, 5.52 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.06, 4.52 Cp(C ₅ H ₄)Ru ^{II}
3	CDCl ₃ -(CD ₃) ₂ CO (11/1)	333	5.66, 5.52, 5.29
		183	6.19, 5.84, 5.37 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.05, 5.00, 4.51 Cp(C ₅ H ₄)Ru ^{II}
3	CDCl ₃	333	5.68, 5.48, 5.29
		209	6.26, 5.91, 5.37 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.10, 4.99, 4.57 Cp(C ₅ H ₄)Ru ^{II}
4	(CD ₃) ₂ CO	333	5.65, 5.43, 5.27
		183	6.45, 6.06, 5.85 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.35, 5.18, 4.62 Cp(C ₅ H ₄)Ru ^{II}
4	CDCl ₃	303	8.65 picrate ⁻ 5.77, 5.69, 5.35
		209	8.64 picrate ⁻ 6.39, 6.02, 5.74 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.10, 4.58 Cp(C ₅ H ₄)Ru ^{II}
5	(CD ₃) ₂ CO	333	8.97 picrate ⁻ 5.63, 5.61, 5.28
		183	8.89 picrate ⁻ 6.46, 6.10, 5.83 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.39, 5.25, 4.68 Cp(C ₅ H ₄)Ru ^{II}
5	CDCl ₃	209	6.2-5.8, 5.36 [Cp(C ₅ H ₄)Ru ^{IV} I] ⁺ 5.15, 5.05, 4.60 Cp(C ₅ H ₄)Ru ^{II}
		333	5.68, 5.41, 5.31

2. Experimental details

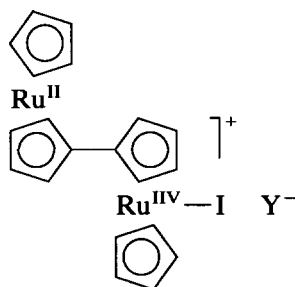
2.1. Syntheses

2.1.1. Preparation of salts 1–3

Salt **1** was prepared by the method reported previously [7]. Salt **2** was prepared as follows: R_cR_c (100 mg, 0.22 mmol) dissolved in 50 cm³ of CH₂Cl₂ was added to a stoichiometric amount of [R_cHI]⁺PF₆⁻ (109 mg, 0.22 mmol, prepared by the method given in the literature [1]) dissolved in 100 cm³ of CH₂Cl₂. The mixture was stirred for 1 h and the solvent was evaporated. After extraction of R_cH with benzene, **2** was obtained by recrystallization of the residues from a CH₂Cl₂–C₆H₁₄ mixture to give deep-purple crystals (136 mg, 0.19 mmol; yield, 86%). Anal. Found: C, 32.40; H, 2.50. C₂₀H₁₈Ru₂IPF₆ calc.: C, 32.80; H, 2.48%. Salt **3** was prepared by a method similar to that used for **2** using R_cR_c and [R_cHI]⁺BF₄⁻ ([R_cHI]⁺BF₄⁻ was prepared by the analogous method to [R_cHI]⁺PF₆⁻ using [R_cHI]⁺I₃⁻ and AgBF₄ [1]). Anal. Found: C, 34.78; H, 2.59. C₂₀H₁₈Ru₂IBF₄ calc.: C, 35.63; H, 2.69%.

2.1.2. Preparation of [R_cHI]⁺2,4,6-(NO₂)₃C₆H₂O⁻ (**4**) and [R_cHI]⁺CCl₃COO⁻·CCl₃COOH (**5**)

The precursors ([R_cHI]⁺2,4,6-(NO₂)₃C₆H₂O⁻ and [R_cHI]⁺CCl₃COO⁻·CCl₃COOH) for salts **4** and **5** were first obtained in this work. [R_cHI]⁺BF₄⁻ (300 mg, 0.67 mmol) dissolved in 50 cm³ of hot water (60°C) was added to an excessive amount of picric acid (1 g, 4.36 mmol) in water (30 cm³). The mixture was stirred for 30 min at 0°C to obtain crude precipitates, which were washed with water and dried. Recrystallization from a CH₂Cl₂–C₆H₁₄ mixture gave yellow crystals of the picrate (250 mg; yield, 64%). Anal. Found: C, 33.09; H, 2.17; N, 7.81. C₁₆H₁₂N₃O₇RuI calc.: C, 32.78; H, 2.06;



	Y
1	I ₃
2	PF ₆
3	BF ₄
4	picrate
5	CCl ₃ COO·CCl ₃ COOH

N, 7.17%. When CCl₃COOH was used in place of picric acid, crystals of [R_cHI]⁺CCl₃COO⁻·CCl₃COOH were obtained similarly. Anal. Found: C, 24.51; H, 1.64. C₁₄H₁₁Cl₆O₄RuI calc.: C, 24.59; H, 1.62%.

Salts **4** and **5** were prepared by methods similar to that used for **2** using [R_cHI]⁺2,4,6-(NO₂)₃C₆H₂O⁻ and [R_cHI]⁺CCl₃COO⁻·CCl₃COOH respectively in place of [R_cHI]⁺PF₆⁻. Anal. Found: C, 38.10; H, 2.48; N, 5.20. C₂₆H₂₀N₃O₇RuI calc.: C, 38.29; H, 2.47; N, 5.15%. Anal. Found: C, 31.30; H, 2.15. C₂₄H₁₉Cl₆O₄RuI calc.: C, 31.57; H, 2.10%.

2.2. NMR measurement

¹H NMR spectra were recorded using the method reported previously [8,10]. The simulated spectra were calculated using the model of chemical exchange between two equivalent sites proposed by Abragam [11].

3. Results and discussion

Table 1 summarized the chemical shifts observed for **1**–**5** in selected conditions of temperature and solvent with the assignments. The temperature dependences of the ¹H NMR spectra observed for **2**–**4** in acetone-*d*₆ solutions are very similar to that observed for **1**; no significant differences were obtained in the values of the chemical shifts at 183 K. The tendency that the well-resolved signals appeared after the coalescence of the signals at a temperature lower than the coalescence temperature *T*_c was also in common for **2**–**4** as well as for **1** (Fig. 1(a) shows the spectra for **2** in acetone-*d*₆). Hence, the behavior of the spectra is interpreted in

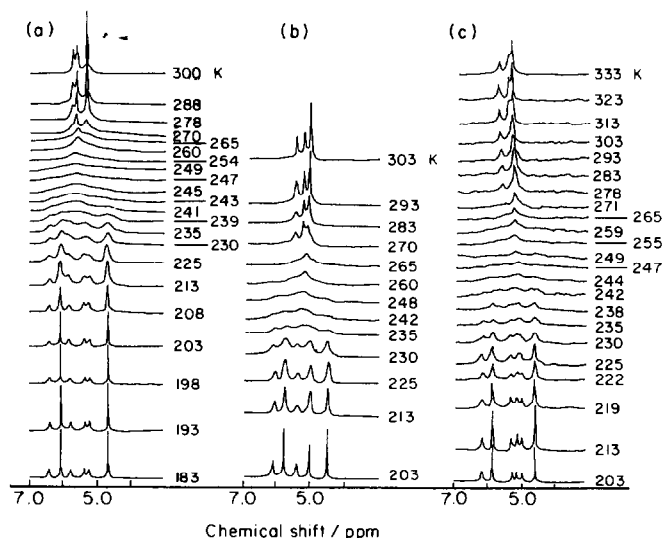


Fig. 1. Temperature-dependent 90 MHz ¹H NMR spectra of **2** in (a) (CD₃)₂CO, (b) CDCl₃–(CD₃)₂CO ([CDCl₃]/[(CD₃)₂CO] = 10/1) and (c) CDCl₃ at the indicated temperatures.

terms of the intramolecular electron exchange reaction with the migration of the iodide anion between Ru^{II} and Ru^{IV} in the respective solvents for 2–4 as well as 1. The computer simulation of the temperature-dependent ¹H NMR spectra of 2 in acetone-*d*₆ was carried out by procedures similar to that previously applied [8,10,11], and the simulated spectra agreed well with the observed spectra. The activation parameters for 2 listed in Table 2 are almost the same as those for 1, 3 and 4 in acetone-*d*₆. From these observations, it is concluded that the counter-anion Y⁻ has little influence on the electron exchange Ru^{II} and Ru^{IV} in acetone.

As is shown in Figs. 1(a)–1(c) for 2 and in Table 1 for 1–4, the spectral features are considerably affected by the change in the dielectricity of the solvent. Figure 1(b) shows ¹H NMR spectra of 2 in a mixed CDCl₃–CD₃COCD₃ solution with [CDCl₃]/[CD₃COCD₃] = 10/1. Five sharp lines are observed at 203 K and the main Cp ring signals of the Ru^{II} and Ru^{IV} are found to be 5.85 ppm and 4.55 ppm respectively. Both the signals shift to a higher field (0.20 ppm for Ru^{IV} and 0.09 ppm for Ru^{II}) compared with the corresponding values in acetone; in particular the shift for Ru^{IV} is larger. Such a high field shift was also observed for [RcHI]⁺PF₆⁻ alone in the present study; δ = 6.34 in CD₃COCD₃, 6.28 and 6.19 in CDCl₃–CD₃COCD₃

([CDCl₃]/[CD₃COCD₃] = 1/1 and 3/1 respectively) and 6.19 in CDCl₃. The larger high field shift of the Ru^{IV} compared with Ru^{II} gives smaller Δδ value (the difference between the chemical shifts of Ru^{IV} and Ru^{II}). The Δδ value decreases on decrease in the solvent with the higher dielectric constant (CD₃COCD₃) in the solvent mixtures from 1.41 ppm in CD₃COCD₃; that is the Δδ values are found to be 1.38, 1.34 and 1.31 ppm in CDCl₃–CD₃COCD₃ with [CDCl₃]/[CD₃COCD₃] ratios of 1/1, 3/1 and 5/1 respectively, 1.39, 1.35, 1.34 and 1.33 ppm in CCl₄–CD₃COCD₃ with [CCl₄]/[CD₃COCD₃] ratios of 1/3, 1/1, 2/1 and 3/1 respectively, and 1.30 ppm for 2 in CDCl₃. Results similar to those for 2 are obtained for 3 and other [RcRcX]⁺PF₆⁻ (X = Br, Cl) salts in CXCl₃–CD₃COCD₃ (X = D, Cl) and CDCl₃–CD₃CN.

The spectral bandwidths in the higher temperature region are broadened on decrease in the mixing ratio of CD₃COCD₃; for example three broader lines are found for 2 in CDCl₃–CD₃COCD₃ ([CDCl₃]/[CD₃COCD₃] = 10/1; see Fig. 1(b), curve for 303 K) and in CDCl₃ (see Fig. 1(c), curve for 333 K). The broadening causes an increase in the activation energy *E*_a as listed in Table 2 and shown in the Arrhenius plots in Fig. 2; for example, the values found to be about 37 kJ mol⁻¹ in CD₃COCD₃ for 2–4 increase to 38–49 kJ mol⁻¹ in CXCl₃–CD₃COCD₃ (X = D, Cl).

TABLE 2. Activation parameters of salts 1–3 at 298 K

Compound	Solvents	<i>E</i> _a (kJ mol ⁻¹)	Δ <i>G</i> [‡] (kJ mol ⁻¹)	Δ <i>H</i> [‡] (kJ mol ⁻¹)	Δ <i>S</i> [‡] (J K ⁻¹ mol ⁻¹)	
1	CD ₃ COCD ₃	36.5 ± 0.6	49.1 ± 0.2	34.0 ± 0.6	-51.0 ± 2.7	
	CD ₃ COCD ₃	37.0 ± 0.6	51.8 ± 0.2	34.5 ± 0.6	-58.0 ± 2.7	
2	CDCl ₃ –CD ₃ COCD ₃ (1/1)	38.1 ± 0.6	51.6 ± 0.2	35.6 ± 0.6	-53.8 ± 2.7	
	CDCl ₃ –CD ₃ COCD ₃ (3/1)	38.9 ± 0.7	52.0 ± 0.3	36.4 ± 0.7	-52.1 ± 3.4	
	CDCl ₃ –CD ₃ COCD ₃ (5/1)	39.4 ± 0.7	51.9 ± 0.3	36.9 ± 0.7	-50.4 ± 3.5	
	CDCl ₃ –CD ₃ COCD ₃ (10/1)	41.7 ± 1.0	52.2 ± 0.4	39.2 ± 1.0	-43.3 ± 4.7	
	CDCl ₃	46.4 ± 0.7	52.8 ± 0.3	43.9 ± 0.7	-30.2 ± 3.4	
	CCl ₄ –CD ₃ COCD ₃ (1/3)	39.4 ± 0.6	51.2 ± 0.3	36.7 ± 0.6	-48.7 ± 3.0	
	CCl ₄ –CD ₃ COCD ₃ (1/1)	43.1 ± 0.6	51.5 ± 0.3	41.6 ± 0.6	-33.2 ± 3.0	
	CCl ₄ –CD ₃ COCD ₃ (2/1)	46.4 ± 0.8	51.9 ± 0.4	43.9 ± 0.8	-26.9 ± 4.0	
	CCl ₄ –CD ₃ COCD ₃ (3/1)	46.7 ± 1.0	52.8 ± 0.2	44.2 ± 1.0	-28.6 ± 4.0	
	3	CD ₃ COCD ₃	37.1 ± 0.6	52.3 ± 0.3	34.6 ± 0.6	-59.6 ± 3.0
CDCl ₃ –CD ₃ COCD ₃ (2/1)		37.9 ± 0.6	51.3 ± 0.3	35.4 ± 0.6	-53.8 ± 3.0	
CDCl ₃ –CD ₃ COCD ₃ (5/1)		38.4 ± 0.8	52.6 ± 0.3	35.9 ± 0.8	-55.9 ± 3.7	
CDCl ₃ –CD ₃ COCD ₃ (11/1)		41.2 ± 1.2	52.8 ± 0.3	38.7 ± 1.2	-47.0 ± 5.0	
CDCl ₃		45.7 ± 0.8	53.1 ± 0.3	45.0 ± 0.8	-27.3 ± 3.7	
CCl ₄ –CD ₃ COCD ₃ (1/3)		38.8 ± 0.6	52.5 ± 0.3	36.3 ± 0.6	-54.2 ± 3.0	
CCl ₄ –CD ₃ COCD ₃ (1/1)		42.4 ± 0.8	52.9 ± 0.3	39.9 ± 0.8	-43.7 ± 3.7	
CCl ₄ –CD ₃ COCD ₃ (3/1)		46.4 ± 1.2	53.0 ± 0.4	43.9 ± 1.2	-30.7 ± 5.4	
4		CD ₃ COCD ₃	37.1 ± 0.6	51.9 ± 0.4	34.6 ± 0.6	-58.1 ± 3.4
		CDCl ₃ –CD ₃ COCD ₃ (1/1)	37.7 ± 0.6	52.1 ± 0.4	35.2 ± 0.6	-56.7 ± 3.4
	CDCl ₃ –CD ₃ COCD ₃ (3/1)	38.9 ± 0.8	51.9 ± 0.5	36.4 ± 0.8	-52.0 ± 4.4	
	CDCl ₃ –CD ₃ COCD ₃ (7/1)	41.7 ± 1.2	52.6 ± 0.5	39.2 ± 1.2	-45.0 ± 5.7	
	CDCl ₃	49.1 ± 0.8	52.7 ± 0.5	46.6 ± 0.8	-20.5 ± 4.4	

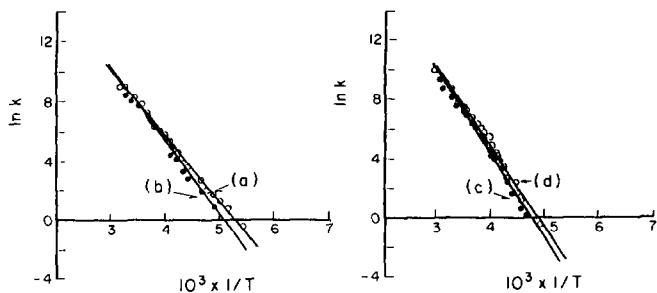


Fig. 2. The Arrhenius plots of $\log k$ vs. $1/T$ for 2 in CD_3COCD_3 (line a), CDCl_3 - CD_3COCD_3 ($[\text{CDCl}_3]/[\text{CD}_3\text{COCD}_3]=10/1$) (line b) and CDCl_3 (line c) and for 3 in CDCl_3 (line d).

The ^1H NMR spectra of 2–4 in CDCl_3 are shown in Fig. 3 in the 4–7 ppm and 271–333 K temperature regions. The spectral shape and the shifts vary considerably from salt to salt in contrast with the similar results observed for the acetone solutions. As listed in Table 1, the variation in the shifts is more marked for Ru^{IV} than for Ru^{II} in the trapped-valence state. A conductivity study on $[\text{RcHI}]^+\text{CF}_3\text{SO}_3^-$ [4] supports the dissociation of the salt in a high dielectric constant solvent and ion pair formation in a low dielectric constant solvent. Hence, the variation should be due to the ion pair formation between the $[\text{RcRcI}]^+$ cation, mainly on the Ru^{IV} side, and the Y^- anion in CDCl_3 , whereas the $[\text{RcRcI}]^+\text{Y}^-$ salts in this study should be dissociated into the free cation in acetone without any influence of the anion on the ^1H NMR spectrum.

A distinctive effect due to the ion pair formation was observed for 5. Although the spectrum of acetone solution at 183 K gives bands with shifts very similar to those for 1–4, the bands for Ru^{IV} in 5 are considerably broadened in comparison with the others. In acetone, 5 appears to decompose above 266 K; the intensity of the bands for the Ru^{II} increases and that for Ru^{IV} side decreases probably because of $\text{Ru}^{\text{IV}}\text{-I}$ bond cleavage. However, the salt is stable in CD_3CN and CDCl_3 and a

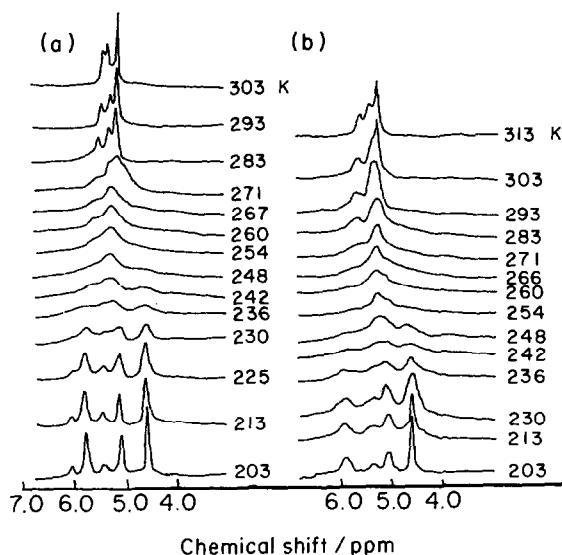


Fig. 4. Temperature-dependent 90 MHz ^1H NMR spectra of 5 in CDCl_3 - CD_3CN with $[\text{CDCl}_3]/[\text{CD}_3\text{CN}]$ ratios of (a) 1/1 and (b) 7/1 at the indicated temperatures.

temperature dependence of the ^1H NMR spectra was observable, as shown in Fig. 4 ($[\text{CDCl}_3]/[\text{CD}_3\text{CN}] = 1/1$ for Fig. 4(a) and 7/1 for Fig. 4(b)). Five lines are observed at 203 K (Fig. 4(a)); three broad lines assigned to Ru^{IV} and two sharp lines to Ru^{II} . The three broad lines for Ru^{IV} become broader as the concentration of CDCl_3 increases (see Fig. 4(b)). Moreover, three much broader lines for Ru^{IV} and higher T_c (265 K, the highest of the present salts 2–5) are observed in CDCl_3 . The spectral features of 5 are interpreted in terms of the electron exchange between Ru^{II} and Ru^{IV} and of the ion pair formation favourable in a low dielectric constant solvent.

The sharp singlet at 8.65 ppm assigned to the picrate-H in acetone at 183 K for 4 did not show any temperature dependence apart that due to the Cp ring of the cation. However, the band shows a low field shift

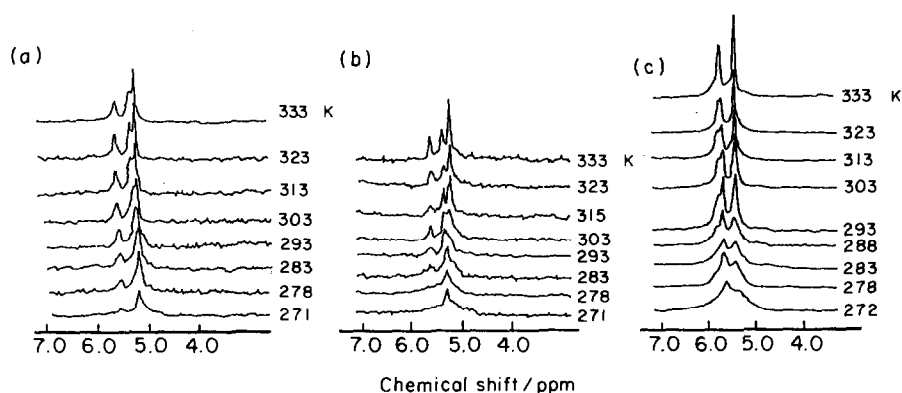


Fig. 3. ^1H NMR spectra of 2–5 in CDCl_3 at the indicated temperatures.

on increasing the amount of CDCl₃ in the mixed solvents with CD₃COCD₃; that is, the chemical shift values are found to be 8.80, 8.88 and 8.91 ppm in CDCl₃-CD₃COCD₃ with [CDCl₃]/[CD₃COCD₃] ratios of 1/1, 3/1 and 7/1 respectively, and 8.97 ppm in CDCl₃ at 209 K. Such a large low field shift is not observed for picric acid alone; the band at 9.09 ppm in CD₃COCD₃ gives 9.09, 9.09, 9.10 and 9.15 ppm under the same conditions for **4**. The *E*_a value of 49.1 kJ mol⁻¹ in CDCl₃ is the largest of the salts **1**-**4**. Since the picrate is the bulkiest anion in those examined in this study, the steric interaction appears to be effective in increasing the *E*_a value accompanied by ion pair formation.

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