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Mixed-Valence State of Halo-1′-ethylbiruthenocenium(II,IV)$^+$Y$^-$ and Halo-1′-acetylbiruthenocenium(II,IV)$^+$Y$^-$ Salts

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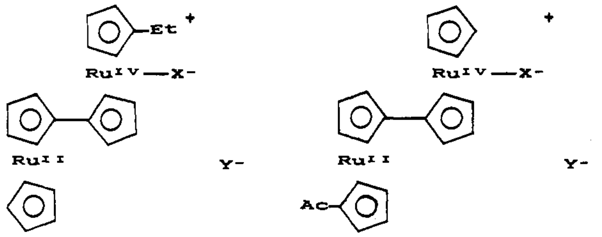
1′-Ethylbiruthenocene, RcRcEt, prepared by the reduction of 1′-acetylbiruthenocene, RcRcAc, with $LiAlH_4$–$AlCl_3$, is oxidized by haloruthenocenium(IV)$^+$Y$^-$ salts, [RcHX]$^+$Y$^-$ (X = I, Br, Cl; Y = PF_6, I_3), giving mixed-valence halo-1′-ethylbiruthenocenium(II,IV), [$Ru^{II}Cp(H_4C_5C_5H_4)(C_5H_4C_2H_5)Ru^{IV}X$]$^+Y^-$ salts, [RcRcEtX]$^+$Y$^-$ (**1–3**), in which the electron exchange reaction accompanied by halogen migration is observed between the Ru^{II} and Ru^{IV} in acetone and other solvents. The activation energy of the reaction, E_a, is found to be within the range 34–39 kJ/mol in acetone, which is larger than the corresponding values for halobiruthenocenium(II,IV) salts, [RcRcX]$^+$Y$^-$, probably because of steric hindrance of the Et group. On the other hand, the E_a value is too large to be determined by variable-temperature ^{1}H-NMR spectroscopy on mixed-valence halo-1′-acetylbiruthenocenium(II,IV) salts, [RcRcAcX]$^+$Y$^-$ (**4–6**), due to the strong electron-attracting effect of acetyl group.

Introduction

Although a large number of studies about one-electron exchange reactions, such as mixed-valence biferrocenium salts and oxo-centered trinuclear iron carboxylates, have been reported,[2-7] multielectron exchange reactions have been paid little attention. The most interesting studies of 2e$^-$ electron transfer have been reported on Pt^{II} and Pt^{IV} systems.[8-10] Recently, interesting studies of intermolecular 2e$^-$ exchange reaction with the halogen migration between the formal Ru^{II} and Ru^{IV} have been reported by Taube et al. and Kirchner et al. on the ruthenocene(II)/haloruthenocenium(IV), RcH/RcHX$^+$ (Rc; ruthenocenyl $CpRu(C_5H_4)$), and osmocene(II)/haloosmocenium(IV), OcH/OcHX$^+$ (Oc; osmocenyl $CpOs(C_5H_4)$), systems.[11-15] Recently, we reported on the electron exchange reactions of mixed-valence halobiruthenocenium$^+$Y$^-$, [RcRcX]$^+$Y$^-$, and halodialkylbiruthenocenium$^+$Y$^-$, [$RcRcR_2X$]$^+$Y$^-$ (R = Et, Pr), salts in acetone and other solvents, by means of ^{1}H- and ^{13}C-NMR spectroscopy. In these studies, NMR signals due to trapped-valence state of the Ru^{II} and Ru^{IV} observed below ca. 200 K moved together and eventually fused into the signal due to the averaged-valence state over Ru^{II} and Ru^{IV} on the NMR time scale, as temperature increased.[16-20] The Ea value of the reaction increases in the order, [$RcRcPr_2X$]$^+$ > [$RcRcEt_2X$]$^+$ > [RcRcX]$^+$. From the results of cyclic voltammograms of RcRc, $RcRcEt_2$, and $RcRcPr_2$, it is concluded that the order is not due to an electronic effect but is probably due to the steric hindrance of alkyl groups.[20]

Chart I



	X	Y		X	Y
1	I	I_3	4	I	I_3
2	Br	PF_6	5	Br	PF_6
3	Cl	PF_6	6	Cl	PF_6

In the present studies, we describe syntheses of RcRcEt, its mixed valence salts, [RcRcEtX]$^+$Y$^-$ (**1–3**, see Chart I), and related

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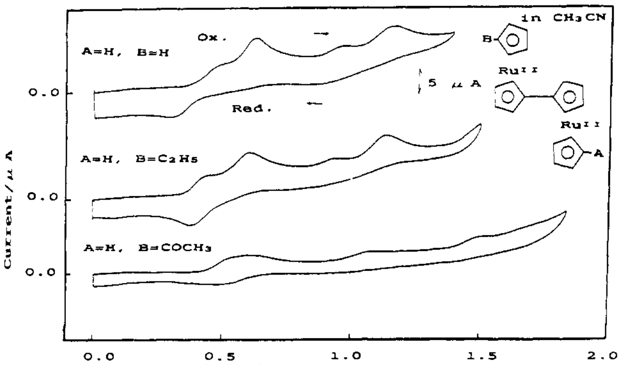

Figure 1. Cyclic voltammograms of RcRc (a), RcRcEt (b) and RcRcAc (c) in acetonitrile. (sweep rate 100 mV s^{-1}).

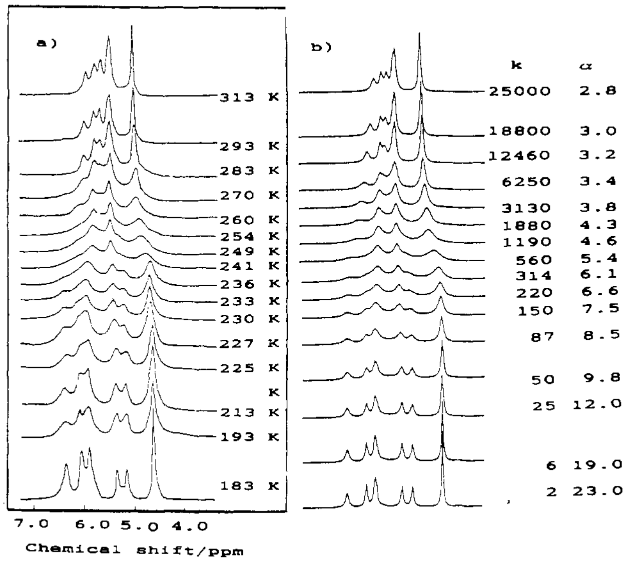

Figure 2. Temperature dependent 90-MHz ^{1}H-NMR spectra of **1** (a) in CD_3COCD_3, at indicated temperatures, and the calculated ^{1}H-NMR spectra of **1** (b).

salts, $[RcRcAcX]^+Y^-$ (**4**–**6**), and the effect of substituent on electron transfer between Ru^{II} and Ru^{IV} in the salts investigated by means of ^{1}H-NMR spectroscopy.

Experimental Section

Syntheses. 1′-Monoacetylbiruthenocene, RcRcAc (2.0 g, 3.98 mmol), prepared by the reaction with RcRc and CH_3COCl–$BF_3{\cdot}Et_2O$ in CH_2Cl_2,[19,20] was added to a dry ethereal solution (100 cm^3) of anhydrous aluminum chloride (5.0 g) and lithium aluminum hydride (2.0 g); the yellow solution immediately lost its color. After water was added, the organic phase was extracted with benzene, and the benzene layer was washed with water, dried, and evaporated. RcRcEt was separated by alumina-column chromatography using a hexane–benzene (1:1) mixture, and was recrystallized from a benzene–hexane mixture as pale yellow crystals (1.8 g, 3.68 mmol; yield 92%). Anal. Calcd for $C_{22}H_{22}Ru_2$: C, 54.08; H, 4.54. Found: C, 54.10; H, 4.64. ^{1}H-NMR ($CDCl_3$): δ_H = 4.68 (2H, t, J = 1.7 Hz), 4.64 (2H, t, J = 1.6Hz), 4.48 (5H, s), 4.47 (2H, t, J = 1.7 Hz), 4.45 (2H, t, J = 1.6 Hz), 4.42 (2H, t, J = 1.7 Hz), 4.37 (2H, t, J = 1.7 Hz), 2.10 (2H, q, J = 7.5 Hz), 1.02 (3H, t, J = 7.5 Hz). δc = 201.49 (1C), 91.66 (1C), 87.17 (1C), 87.37 (1C), 76.24 (2C), 73.84 (2C), 73.64 (2C), 73.32 (2C), 73.12 (5C), 72.02 (2C), 71.88 (5C), 28.83 (1C).

Iodoethylbiruthenocenium(II,IV)$^+I_3^-$ (**1**) and iodoacetylbiruthenocenium(II,IV)$^+I_3^-$ (**4**) salts were prepared by a method similar to that used for $[RcRcI]^+I_3^-$.[17–20] Anal. Calcd for $C_{22}H_{22}Ru_2I_4$: C, 26.52; H, 2.23. Found: C, 26.56; H, 2.30. Calcd for $C_{22}H_{20}ORu_2I_4$: C, 26.16; H, 2.00. Found: C, 26.85; H, 2.06. Salts **2** and **3** were prepared by oxidation in the similar manner as applied for $[RcRcEt_2Cl]^+PF_6^-$ reported previously.[20] Anal. Calcd for $C_{22}H_{22}Ru_2BrPF_6$: C, 37.04; H, 3.11. Found: C, 36.97; H, 3.44. Calcd for $C_{22}H_{22}Ru_2ClPF_6$: C, 39.50; H, 3.32. Found: C, 39.78; H, 3.55. Salts **5** and **6** were prepared by the oxidation of RcRcAc with the corresponding $[RcHX]^+PF_6^-$ (X = Br, Cl) salts in the similar conditions as that used for salts **2** and **3**, respectively. Anal. Calcd for $C_{22}H_{20}ORu_2BrPF_6$: C, 36.32; H, 2.77. Found: C, 36.03; H, 2.95. Calcd for $C_{22}H_{20}ORu_2ClPF_6$: C, 38.69; H, 2.95. Found: C, 39.09; H. 2.95.

Table I. ^{1}H Chemical Shifts of RcRcEt and Related Compounds in Acetone, Chloroform,[a] and a Mixed Solution of Chloroform and Acetonitrile (1:1)[b]

compd	temp/K	chem shifts δ/ppm
RcRc[a]	298	4.68, 4.44, 4.48
RcRcEt[a]	298	4.68, 4.64, 4.48, 4.47, 4.45, 4.42, 4.37 2.10 ($-CH_2-$), 1.02 ($-CH_3$)
RcRcAc[a]	298	5.01, 4.72, 4.70, 4.68, 4.50, 4.47, 2.08 ($-CH_3$)
1	183	4.67, 5.22, 5.40 $(C_5H_4)(C_5H_5)Ru^{II}$ 5.85 sh, 5.90, 6.11, 6.41 $[(C_5H_4)(C_5H_4Et)Ru^{IV}I]^+$ 2.54 ($-CH_2-$), 1.04 ($-CH_3$)
	298	4.98, 5.42, 5.56, 5.72, 5.85 2.46 ($-CH_2-$), 1.09 ($-CH_3$)
2	183	4.72, 5.30 $(C_5H_4)(C_5H_5)Ru^{II}$ 5.74, 5.87, 6.32 $[(C_5H_4)(C_5H_4Et)Ru^{IV}Br]$ 2.54 ($-CH_2-$), 1.00 ($-CH_3$)
	293	4.90, 5.20, 5.30, 5.47, 5.59, 6.05 2.49 ($-CH_2-$), 1.10 ($-CH_3$)
3	183	4.76, 5.31 $(C_5H_4)(C_5H_5)Ru^{II}$ 5.81, 5.90, 6.30 $[(C_5H_4)(C_5H_4Et)Ru^{IV}Cl]$ 2.40 ($-CH_2-$), 1.00 ($-CH_3$)
	323	4.95, 5.20, 5.45, 5.56, 5.60 sh, 6.00 2.36 ($-CH_2-$), 1.11 ($-CH_3$)
4[b]	213	4.79, 5.04, 5.06 sh, 5.13 $(C_5H_4)(C_5H_4Ac)Ru^{II}$ 5.56, 5.81, 6.06 $[(C_5H_4)(C_5H_5)Ru^{IV}I]^+$ 2.10 ($-CH_3$)
	343	4.84, 5.08, 5.13 $(C_5H_4)(C_5H_4Ac)Ru^{II}$ 5.68, 5.81, 6.06 $[(C_5H_4)(C_5H_5)Ru^{IV}I]^+$ 2.15 ($-CH_3$)
5[b]	213	4.80, 5.02, 5.11 $(C_5H_4)(C_5H_4Ac)Ru^{II}$ 5.23, 5.74, 5.92 $[(C_5H_4)(C_5H_5)Ru^{IV}Br]^+$ 2.11 ($-CH_3$)
	323	4.84, 5.04, 5.13 $(C_5H_4)(C_5H_4Ac)Ru^{II}$ 5.42, 5.76, 5.96 $[(C_5H_4)(C_5H_5)Ru^{IV}Br]^+$ 2.16 ($-CH_3$)
6[b]	213	4.81, 5.02, 5.12 $(C_5H_4)(C_5H_4Ac)Ru^{II}$ 5.23, 5.73, 5.93 $[(C_5H_4)(C_5H_5)Ru^{II}Cl]^+$ 2.13 ($-CH_3$)
	323	5.94, 5.75, 5.36 $(C_5H_4)(C_5H_4Ac)Ru^{II}$ 5.18, 5.02, 4.88 $[(C_5H_4)(C_5H_5)Ru^{II}Cl]^+$ 2.19 ($-CH_3$)

Physical Measurements. ^{1}H-NMR spectra of **1** and related compounds were recorded on a JEOL FX-90Q spectrometer at 89.59 MHz using TMS as a standard. An NM-VTS unit was used to control the prove temperature within ±1 °C. The assignment of the signal of the RcRcEt was by selective proton-decoupling experiments. Electronic spectra were measured in CH_3CN with a Hitachi spectrophotometer, Model 220, at room temperature. Cyclic voltammograms were obtained with a HB-104 function generator and HA-301 potentiostat (Hokuto Denko) with standard three-electrode configuration. A working electrode (platinum button) and an Ag/AgCl reference were connected via a salt bridge of CH_3CN containing 0.1 mol dm^{-3} $[(C_4H_8)_4N]ClO_4$ as supporting electrolyte. The scan rate was 100 mV s^{-1}.

Results and Discussion

Salts 1 and 4. The effect of the ethyl and acetyl group on RcRcEt and RcRcAc compared with RcRc was investigated by use of cyclic voltammography. It is well known that a reversible one-electron oxidation peak is observed for ferrocene near 0.4 V and a much higher irreversible two-electron oxidation peak for RcH near 0.9 V.[21–25] Actually, RcH shows an irreversible two-electron oxidation peak in CH_3CN (E_{ox} = 0.85 V and E_{red} 0.49

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Table II. Activation Parameters for **1** and Related Compounds from 90-MHz ^{1}H-NMR Spectroscopy at 298 K

compd	E_a/kJ mol^{-1}	ΔE/kJ mol^{-1}	ΔG^*/kJ mol^{-1}	ΔH^*/kJ mol^{-1}	ΔS^*/J K^{-1} mol^{-1}
1	38.4 ± 1.0	8.6 ± 0.5	48.9 ± 0.4	35.9 ± 1.0	–43.6 ± 4.7
2	35.8 ± 0.9	7.4 ± 0.5	47.6 ± 0.4	33.3 ± 0.9	–48.0 ± 4.4
3	34.5 ± 0.9	6.1 ± 0.5	47.2 ± 0.4	32.0 ± 0.9	–51.0 ± 4.4
$[RcRcI]^+I_3^-$	36.4 ± 0.6	0	49.1 ± 0.2	34.0 ± 0.6	–50.7 ± 2.7
$[RcRcBr]^+PF_6^-$	34.0 ± 0.5	0	46.8 ± 0.3	31.5 ± 0.5	–51.3 ± 2.7
$[RcRcCl]^+PF_6^-$	32.8 ± 0.5	0	45.5 ± 0.3	30.3 ± 0.5	–51.0 ± 2.7

V) in the present study. On the other hand RcRc gives four irreversible oxidation peaks (E_{ox} = 0.48, 0.63, 0.96, and 1.16 V, as shown in Figure 1a) in the same conditions. A recent interesting study shows that RcH gives a quasi-reversible one-electron oxidation peak in non-coordinating media (0.1 M tetrabutylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, TBA^+TFPB^-, as supporting electrolyte in CH_2Cl_2); i.e., monocationic ruthenocenium, $[Cp_2Ru^{III}]^+$, is stabilized when the extremely weakly coordinating $TFPB^-$ is used as the supporting anion in CH_2Cl_2.[26] Therefore, the electrochemical study of RcRc in CH_3CN suggests that the first oxidation peak on RcRc is assigned the formation of $RcRc^+$, and the second, third, and fourth peaks to those of $RcRc^{2+}$, $RcRc^{3+}$, and $RcRc^{4+}$, respectively. The corresponding four E_{ox} peaks are found for RcRcEt (0.43, 0.61, 0.93, 1.13 V; see Figure 1b) and these values are a little smaller (ca. 0.02–0.05 V) than the corresponding values of RcRc, because of an electron-donating effect of the ethyl group. RcRcAc also gives four oxidation peaks (E_{ox} = 0.52, 0.62, 1.05, and 1.48 V; see Figure 1c). Although the E_{ox} values of first and second peaks correspond well with those of RcRc and RcRcEt, those of third and fourth oxidation peaks are much larger than those of RcRc and RcRcEt, due to the electron-attracting effect of the acetyl group. Therefore, the Ru atom in the $(C_5H_4)CpRu$ moiety in RcRcAc is expected to be oxidized easier by $[RcHX]^+PF_6^-$ salts compared with the $(C_5H_4Ac)CpRu$ moiety.

Figure 2a shows the temperature dependency of the 90-MHz ^{1}H-NMR spectra of **1** in acetone-d_6 together with their computer simulation in Figure 2b, and the ^{1}H chemical shift values (δ) of **1** and related compounds are listed in Table I. Analogously to symmetrical $[RcRcI]^+I_3^-$ and $[RcRcEt_2I]^+I_3^-$ systems,[18-20] ^{1}H-NMR spectra of **1** exhibit a remarkable temperature dependence, and no ^{1}H-NMR spectra versus concentration change of **1** (0.03–0.0001 mol dm^{-3}) was obtained. Therefore, there occurs an intramolecular electron exchange reaction between the Ru^{II} and Ru^{IV} atoms.

The unbalanced trapped valence state ($Ru^{II}Ru^{IV}$) of **1** is reflected on the spectrum observed at 183 K; i.e., seven lines (δ = 6.41, 6.11, 5.90, 5.85 sh, 5.40, 5.22, and 4.67) are observed in the 4–7 ppm region. In analogy with the δ values of symmetrical $[RcRcI]^+I_3^-$ and $[RcRcEt_2I]^+I_3^-$ salts at 183 K, the seven lines are assigned as follows: 6.41 (2H), 5.85 sh (2H) ppm to the ring protons of $H_{2,5}$, $H_{3,4}$; 6.11 (2H), 5.90 (2H) ppm to $H_{2',5'}$, $H_{3',4'}$ for the $(C_5H_4)(C_5H_4Et)Ru^{IV}$ side; 5.40 (2H), 5.22 (2H) ppm to $H_{2,5}$, $H_{3,4}$; 4.67 (5H) ppm for the $Cp(C_5H_4)Ru^{II}$ side. The methylene and methyl signals of the ethyl group are found to be 1.04 (t, 3H) and 2.54 (q, 2H) ppm. Hence, the formula of salt **1** can be given as $[Ru^{II}Cp(H_4C_5C_5H_4)(C_5H_4Et)Ru^{IV}I]^+I_3^-$ at 183 K, species **A**. It can be concluded that the electron-rich Ru atom in $(C_5H_4)(C_5H_4Et)Ru^{II}$ side is oxidized easier by I_2 compared with that in the $(C_5H_4)CpRu^{II}$ side. But the presence of the broader seven lines compared with the symmetrical $[RcRcI]^+I_3^-$ and $[RcRcEt_2I]^+I_3^-$ systems even at 183 K suggests that presence of a small amount of other species such as $[IRu^{IV}Cp(H_4C_5C_5H_4)(C_5H_4Et)Ru^{II}]^+I_3^-$, (**B**), could not be ruled out either.

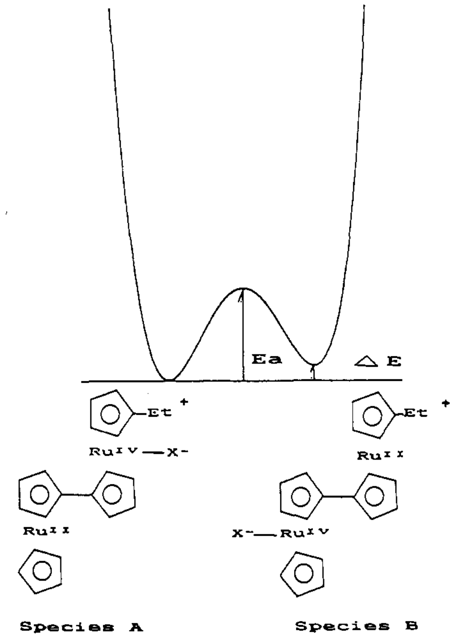

Figure 3. Potential well diagrams for the nonsymmetrical mixed-valence system $Ru^{II}Ru^{IV}$. The left well is for the $[Ru^{II}Cp(H_4C_5C_5H_5)(C_5H_4Et)Ru^{IV}I]^+$ cation (**A**) and the right well is for the $[IRu^{IV}Cp(H_4C_5C_5H_5)(C_5H_4Et)Ru^{II}]^+$, cation (**B**).

When the sample is heated, the seven lines broaden and eventually the lines change into three much broader lines at 241 K. Above 241 K, the ring peaks become sharper, and five broader lines are observed even at 313 K. In comparison with the temperature dependency of the symmetrical biruthenocenium systems, the $[RcRcI]^+$ and $[RcRcEt_2I]^+$ cations, the temperature dependency of **1** is more complicated because cation $[RcRcEtI]^+$ is asymmetric.

In Figure 3 a simplified double-well potential energy diagram is depicted for the asymmetrical system. The left well is for species **A** and the right well is for species **B**. The ΔE value is the zero-point energy difference between the two wells, and the E_a value is the activation energy of the **A** and **B** species. The population ratio of the two site is defined as $\alpha = P_a/P_b$, where P_a is population of the A site and P_b is the B site. The α values can be estimated from the δ values of the nonsubstituted main Cp ring, as shown in Figure 2b. When the temperature is raised, the population of the B site increases; therefore, the α value decreases: e.g., 23.0 ± 2.0 at 183 K, 8.5 ± 0.5 at 227 K, and 2.8 ± 0.2 at 313 K. The computer simulation of the temperature-dependent NMR spectra of the salt is shown in Figure 2b in the 4–7 ppm region, using the model of chemical exchange between the two sites proposed by Abragam.[27] The value of k varies at small intervals in the spectral calculations used to obtain the best fit of the calculated spectrum to the observed one. The Arrhenius plot of ln k (defined as $k = 1/\tau$) vs $1/T$ shows a good straight line, and the error is estimated by least-squares fitting of the data. The E_a value is found to be 38.4 ± 1.0 kJ/mol and Gibbs free energy, ΔG^*, and enthalpy of activation, ΔH^*, are found to be 48.9 ± 0.4 and 35.9 ± 1.0 kJ/mol, respectively (see Table II). The energy difference between the two wells, ΔE, is found to be 8.6 ± 0.5 kJ/mol, from plotting of ln α vs $1/T$. Due to the

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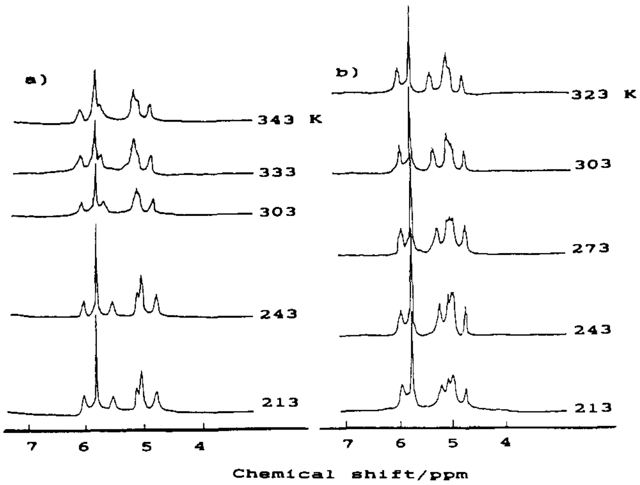

Figure 4. Temperature-dependent 90-MHz ^{1}H-NMR spectra of **4** (a) and **5** (b) in mixed solution $CD_3CN/CDCl_3$ (1/1) at indicated temperatures.

relatively small ΔE value compared with E_a (ca. 4.5 times smaller), a remarkable temperature dependency in NMR spectra is observed for **1**. The similar temperature dependencies in ^{1}H-NMR spectra for **1** are obtained in other solutions, such as $CDCl_3$ and CD_3CN.

On the other hand, the ΔE and E_a values are too large to be estimated from the ^{1}H-NMR spectra on **4**. Figure 4a shows temperature dependent ^{1}H-NMR spectra on **4** in mixed solution ($CDCl_3/CD_3CN$ = 1/1) because **4** is less stable in acetone at higher temperatures. Seven sharp lines (δ = 4.79, 5.04, 5.06 sh, 5.13, 5.56, 5.81, and 6.06) are observed in the 4–7 ppm region at 213 K. In contrast to the spectra for **1** at 213 K, a nonsubstituted Cp ring signal is observed at lower field (δ = 5.81); i.e., an electron-rich Ru atom on the $(C_5H_4)CpRu^{II}$ side is preferentially oxidized by I_2 giving a $[(C_5H_4)CpRu^{IV}I]^+$ moiety. The formula of **4** is given as $[Ru^{II}(C_5H_4COCH_3)(H_4C_5C_5H_4)CpRu^{IV}I]^+I_3^-$ at 213 K; this conclusion corresponds well with the results of the cyclic voltammogram. Although six slightly broader lines are observed at 343 K, the spectra show no appreciable temperature dependency; therefore, the structure of **4** is expected to remain intact even at 343 K.

Although the $[RcHX]^+PF_6^-$ salts (X = Cl, Br) dissolved in acetone and acetonitrile give green-yellow solutions, $[RcRcX]^+Y^-$ and $[RcRcEt_2X]^+Y^-$ salts give deep red-purple solutions, in which a new and strong absorption band is found in the 480-470 nm region.[18,20] In the electronic absorption spectrum of **1**, the new band is also observed at 485 sh nm along with the bands at 291 and 362 nm assigned as I_3- in CH_3CN. The band red-shifts slightly as compared with $[RcRcI]^+I_3$- (λ_{max} = 480 sh nm) and blue-shifts with $[RcRcEt_2I]^+I_3$- (490 sh nm). Although no temperature dependency of the NMR spectra is observed for **4**, a similar absorption band (λ_{max}, 470 sh nm) is observed. The assignment of the band is, however, not yet settled at the present time. The band is ascribable to the interaction between the Ru^{II} and Ru^{IV} in the mixed valence state, and the λ_{max} of the band is sensitive to the electronic effect of the substituent on the Cp ring: i.e., Et as the electron-donating effect increases slightly the λ_{max} value of the band and Ac as the electron-attracting effect decreases.

Salts 2, 3, 5, and 6. In order to compare the activation parameters for **2**, **3**, **5**, and **6** with those for **1** and **4**, the same NMR studies have been carried out, and Figure 5 shows the temperature dependent ^{1}H-NMR spectra of **2** (a) and **3** (b) at the indicated temperatures. Five sharp lines (δ = 6.32, 5.87, 5.74, 5.30, 4.72) are observed at 183 K in the 4–7 ppm region for **2**. As in the case of **1**, the former three lines are assigned as the ring protons of $H_{2,5}$, $H_{3,4}$ (6.32, 5.74 ppm) and ethyl-substituted Cp ring (5.87 ppm) of the $[(C_5H_4)(C_5H_4Et)Ru^{IV}Br]^+$ side and the latter two lines are assigned to those of $H_{2,5}$, $H_{3,4}$ (5.30 ppm) and nonsubstituted Cp-ring (4.72 ppm) of the Ru^{II} side. When the temperature (219–248 K) is raised, these lines are broadened, and four broader lines are observed at 229 K, which is lower than that of **1** (241 K). As mentioned in previous reports, a similar observation is already found for $[RcRcBr]^+$ and $[RcRcEt_2Br]^+$ salts as compared with corresponding $[RcRcI]^+$ and $[RcRcEt_2I]^+$ salts.[18-20] Although five broad lines are observed for **1** (see Figure 2a) at 293 K, six lines, which consist of two sharp lines (δ = 4.90 and 5.47) with strong intensities and four lines (δ = 5.20, 5.30, 5.59, and 6.05) with low intensities, are observed. The values of k and α at 293 K are estimated to be ca. 25 100 ± 150 s^{-1} and 3.0 ± 0.2, respectively, by fitting the calculated spectra to those observed. The k values are 1.2–1.3 times larger than the corresponding values of **1**, suggesting a smaller E_a value for **2** than that of **1**. Actually the E_a value of **2** is found to be 35.8 ± 0.9 kJ/mol from the slope of the Arrhenius plot line. The ΔE value is found to be 7.4 ± 0.5 kJ/mol from the plots of ln α vs $1/T$, which is also slightly smaller than that of **1**.

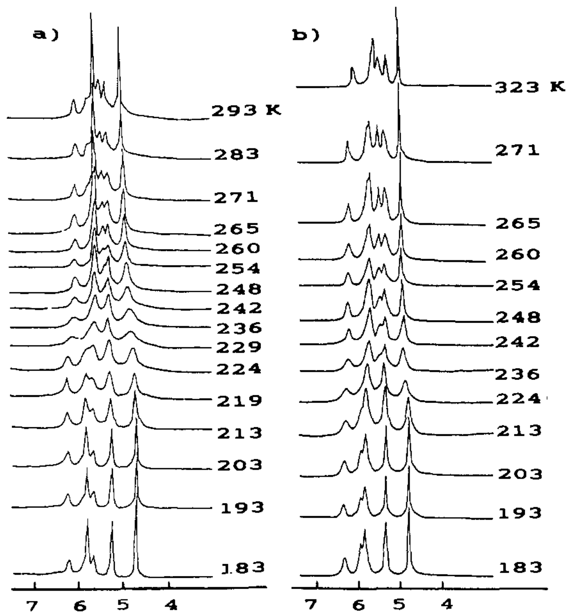

Figure 5. Temperature dependent 90-MHz ^{1}H-NMR spectra of **2** (a) and **3** (b) in CD_3COCD_3 at indicated temperatures.

Similar spectral features are observed for **3** (see Figure 5b). Five relatively sharp lines are observed at 183 K. As the temperature is increased, these lines are broadened and four broader lines are observed at 224 K. Above 224 K, these lines become sharper and five lines and one shoulder (5.60 ppm) are observed even at 271 K, while **1** and **2** give much broader lines at 271 K, suggesting a larger k value for **3** as compared with the values for **1** and **2**. Actually, the k value is estimated to be ca. 16 700 ± 120 s^{-1} for **3**, while the value is found to be ca. 7100 ± 100 s^{-1} and 6400 ± 100 s^{-1}, for **2** and **1**, respectively at 271 K. From the plots of ln $k - 1/T$ and ln $\alpha - 1/T$ for **3**, a little smaller E_a (34.5 ± 0.9 kJ/mol) and ΔE (6.1 ± 0.5 kJ/mol) values are obtained as compared with those of **1** and **2**.

Thus the intramolecular electron transfer rate between Ru^{II} and Ru^{IV} with halogen migration increases in the order **3** > **2** > **1**. In other words, the E_a values of the salt are ranked as **1** > **2** > **3**. The order is the opposite of that observed for mononuclear $RcH/[RcHX]^+Y^-$ systems. The reason of the difference may be ascribed to the different mechanisms of the intra- ($[RcRcEtX]^+Y^-$) and intermolecular ($RcH/[RcHX]^+Y^-$) electron transfer associated with the exchange of the X atoms. In the case of intramolecular electron transfer, a smaller ionic radius of Cl^- leads to less distortion of the intermediate cation, giving a smaller E_a for $[RcRcEtCl]^+$ compared with the values for $[RcRcEtBr]^+$ and $[RcRcEtI]^+$.

Table III. Electronic Spectra Data for Salt 1 and Related Compounds in CH_3CN (250–900 nm)

compd	λ_{max}/nm (ϵ in parentheses)
1	291 (21800), 362 (13480), 485 sh (2600)
2	354 (7760), 485 (5010)
3	348 (12020), 478 (7943)
4	291 (35400), 360 (19400), 470 sh (3160)
5	348 (9487), 467 (5750)
6	340 (12200), 466 (3980)
$[RcRcI]^+I_3^-$	290 (13200), 360 (8520), 480 sh (1590)
$[RcRcBr]^+PF_6^-$	335 (8920), 480 (5600)
$[RcRcCl]^+PF_6^-$	340 (12500), 470 (7080)
$[RcRcEt_2I]^+I_3^-$	291 (20900), 362 (12900), 490 sh (2400)
$[RcRcEt_2Br]^+PF_6^-$	357 (9970), 491 (6610)
$[RcRcEt_2Cl]^+PF_6^-$	348 (12020), 484 (7590)

As in the case of 1, the characteristic absorption band is observed for 2 (λ_{max} = 485 nm) and 3 (λ_{max} = 478 nm) in CH_3CN. The λ_{max} values are about average compared with one of the corresponding values of $[RcRcX]^+PF_6^-$ and $[RcRcEt_2X]^+PF_6^-$ (X; Br, Cl) (see Table III), because the electron-donating effect of Et group to the Ru in $[RcRcEtX]^+$ decreases by about half compared with that of $[RcRcEt_2X]^+$.

RcRcAc was oxidized by $[RcHX]^+PF_6^-$ (X = Br, Cl) giving diamagnetic salts 5 and 6, respectively. Although 2 and 3 give temperature-dependent NMR spectra, 5 and 6 show no appreciable temperature dependency (as shown in Figure 4b for 5) Six sharp lines are observed for 5 in mixed solution ($CDCl_3/CD_3CN$ (1/1)) at 213 K in the 4–7 ppm region. Three lines (δ = 4.80, 5.02, and 5.11) are due to the Ru^{II} side and the other three lines (δ = 5.23, 5.74, and 5.92) to the Ru^{IV} side; in particular the nonsubstituted Cp ring signal (5.74 ppm) is found at lower field. At higher temperature (323 K), the δ values of the main Cp ring and other lines change slightly, as in the case of 4. Therefore, the formula of 5 is given as $[BrRu^{IV}Cp(H_4C_5C_5H_4)(C_5H_4Ac)Ru^{II}]^+PF_6^-$ in the solution at 213–323 K on the NMR time scale. Results similar to those for 5 are also obtained for 6. Even for the Cl^- salt (less steric hindrance in intermediate cations due to the smaller ionic radius of Cl^-), NMR spectra are observed without temperature dependency.

All the results obtained in the present studies suggest that 1–3 give large temperature-dependent NMR spectra while NMR spectra for 4–6 show no temperature dependency. In other words, 4–6 are considered as valence-trapped on the NMR time scale. The reason why no temperature-dependent NMR spectra were observed for the latter salts should be the much higher oxidation potentials of the $(C_5H_4Ac)Ru^{II}Cp$ side; i.e., the only Ru^{II} atom in $(C_5H_4)Ru^{II}Cp$ side is oxidizable and the Ru^{IV}–X bond is formed.

Salts 5 and 6 dissolved in acetonitrile and acetone giving deep red-purple solutions. As in the case of 4, a new absorption band is also found at 467 nm for 5 and at 466 nm for 6. Although small blue shifts (10–20 nm as compared with the values for 2 and 3) are observed, the presence of the bands suggests some interaction between the Ru^{II} and Ru^{IV} in 4 and 5, e.g., a much slower rate for the electron exchange reaction between the two Ru atoms.

From the observations described above we conclude that there occurs an intramolecular electron exchange reaction between Ru^{II} and Ru^{IV} with halogen migration in the mixed-valence states of 1–3 in acetone and other solutions on the NMR time scale. The E_a values are found to be 38.4 ± 1.0, 35.8 ± 0.9, and 34.5 ± 0.9 kJ/mol for 1, 2, and 3, respectively. These values are larger (ca. 2 kJ/mol) than the corresponding values for symmetrical $[RcRcX]^+Y^-$ salts probably because of the steric hindrance of the Et group in 1–3.

The ΔE values are found to be 8.6 ± 0.5, 7.4 ± 0.5 and 6.1 ± 0.5 kJ/mol for 3, 2, and 1, respectively; therefore, at lower temperatures (less than ca 200 K) the formula of the cations for 1–3 is given as trapped-valence type: $[Ru^{II}Cp(H_4C_5C_5H_4)(C_5H_4Et)Ru^{IV}X]^+$ (X; I, Br, Cl). Because of much larger ΔE and E_a values as compared with those for 1–3, 4–6 show no appreciable temperature dependency by a thermal process; i.e., the formula of the cations in 4–6 is given as trapped-valence type: $[XRu^{IV}Cp(H_4C_5C_5H_4)(C_5H_4Ac)Ru^{II}]^+$ even at higher temperature (343 K). However, it is possible to obtain the averaged valence state, $Ru^{III}Ru^{III}$, even at lower temperatures (213 K), by an optical process for 4–6.