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Mixed valence state associated with halogen migration in diruthenocenylmethane and its related compounds

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Abstract

Diruthenocenylketone (RcCORc, **1**) as a precursor of diruthenocenylmethane ($RcCH_2Rc$, **2**), was first prepared in 30% yield in a one-step reaction of ruthenocene (RcH) with butyllithium (BuLi) and *N,N*-dimethylcarbamyl chloride. Reaction of **2** with I_2 and iodoruthenocenium(IV)$^+PF_6^-$ ($[RcHI]^+PF_6^-$) gives mixed valence salts formulated as $[Ru^{II}Cp(C_5H_4CH_2C_5H_4)CpRu^{IV}I]^+Y^-$ ($Y = I_3$ (**3**), PF_6 (**4**)) in which the intramolecular electron exchange reaction associated with iodine migration between the Ru^{II} and Ru^{IV} atoms is observed. The activation energy of the reaction (E_a) is estimated to be 31.0 ± 0.6 kJ mol^{-1} for **3** in acetone, which is smaller than the corresponding value of a mixed valence $[RcRcI]^+I_3^-$ salt (36.5 ± 0.6 kJ mol^{-1}). Reaction of **2** with the $[RcHCl]^+PF_6^-$ or $[RcHBr]^+PF_6^-$ salts gives an *α,α*-diruthenocenylmethylium$^+PF_6^-$ salt formulated as $[Ru^{II}Cp(C_5H_4CH^+H_4C_5)CpRu^{II}]PF_6^-$ (**5**).

Keywords: Crystal structures; Mixed valence complex; Ruthenium complexes; Ruthenocenylmethane complexes

1. Introduction

Although a large number of studies about one-electron exchange reactions, such as mixed valence biferrocenium salts and oxo-centered trinuclear iron carboxylates, has been reported [1–7], little attention has been paid to multielectron exchange reactions. The most interesting studies of two-electron transfer have been reported on Pt^{II} and Pt^{IV} systems [8–10]. Interesting studies of intermolecular two-electron exchange reactions associated with the migration of halogen atom between the formal Ru^{II} and Ru^{IV} have been reported by Taube and co-workers [11] and Kirchner et al. [12–14] 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 [15]. The line broadening in their ^1H NMR spectra supports the fact that the rate constants of the electron exchange for the RcH/$RcHX^+$ system are larger than the corresponding values for the OcH/$OcHX^+$ systems. In addition, it has been reported that the rate increases in the order $Cl < Br < I$ for both systems.

Our recent results of ^1H and ^{13}C NMR spectroscopic studies of binuclear mixed valence halobiruthenocenium$^+Y^-$ ($[RcRcX]^+Y^-$) and halodialkylbiruthenocenium$^+Y^-$ ($[RcRcR_2X]^+Y^-$; R = Et, Pr) salts in acetone and other solvents indicate that a trapped valence state (Ru^{II},Ru^{IV}) at lower temperature changes into an averaged valence state (Ru^{III},Ru^{III}) with increased temperature. As for the kinetic behavior, the E_a value of the electron exchange reaction increases in the order $[RcRcPr_2X]^+ > [RcRcEt_2X]^+ > [RcRcX]^+$. In addition, the rate of the exchange reaction is reversed from that in the mononuclear systems, i.e. the rate increases in the order $I < Br < Cl$ for the binuclear system [16–19]. Another characteristic feature of binuclear systems is the generation of a strong absorption band at 480–490 nm in their electronic spectra.

More recently, the crystal structure of iodobiruthenocenium tetrafluoroborate ($[RcRcI]^+BF_4^-$) has been determined by X-ray analysis [20]. As has been observed in all other structures of neutral RcRc, biferrocene and mixed-valence biferrocenium salts, the two Cp rings are transoid with respect to the fulvenide ligand, as shown in Fig. 1. An iodine atom is coordinated to the Ru(1) side, causing the Cp ring attached to the Ru(1) to incline greatly (the dihedral angle between the Cp and fulvalene ligand is found to be 42.4°). The Ru(1)–I

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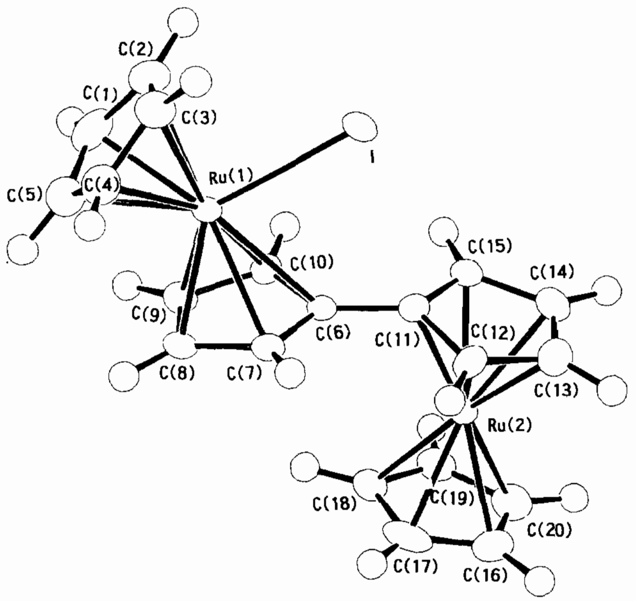

Fig. 1. ORTEP drawing of the [Rc^{II}Cp(C$_5$H$_4$C$_5$H$_4$)CpRu^{IV}I]$^+$ cation with the numbering scheme of the atoms.

distance (2.717(2) Å) corresponds well to that of the [RcHI]$^+$ cation (2.732(3) Å [21]), and the distance between Ru(2) and I (5.398(5) Å) indicates no bond formation between them. The average distance between the Ru(1)–Cp ring center (1.879(7) Å) is longer than that on the Ru(2) side (1.812(3) Å). The longer distance in the Ru(1)–Cp ring is ascribed to the increase in the oxidation state of Ru from Ru^{II} to Ru^{IV}. Based on these results, the cation is formulated as [Ru^{II}Cp(C$_5$H$_4$C$_5$H$_4$)CpRu^{IV}I]$^+$ in the solid state. The distance between Ru(1) and Ru(2) is found to be 5.464(4) Å showing no interaction between them. Because of a higher steric hindrance of the ruthenocene moieties in the *cis* conformation, the structure of the cation is expected to remain intact in the *trans* conformation in acetone or other organic solutions. Hence, it is reasonable to conclude that the mechanism of electron exchange reaction between the Ru^{II} and Ru^{IV} atoms in solution is not due to direct interaction between them. The question, however, remained as to whether the electron exchange occured through the migration of X atoms or through the fused fulvalene ligand, (C$_5$H$_4$)(C$_5$H$_4$), as in the case of mixed valence biferrocenium salts. In order to answer this question, we synthesized compound **2**, its mixed valence salts **3** and **4**, and related salt **5**, and investigated their properties by means of cyclic voltammograms and ^{1}H and ^{13}C NMR spectroscopy.

2. Experimental

2.1. Syntheses of 1 and 2

Salazar and Cowan reported a high yield (86%) synthesis of diferrocenylketone using monobromoferrocene and *N,N'*-carbamyl chloride [22]. Analogously, we successfully synthesized new compound **1** using (CH$_3$)$_2$NCOCl, BuLi and RcH as follows (the reason for using RcH in place of monobromoruthenocene is due to the ineffective high yield synthetic routes of monobromoruthenocene). RcH (2.0 g, 8.65 mmol) dissolved in dried diethyl ether (300 cm^3) was placed in a three-necked flask. To this solution, BuLi (8 cm^3, 8.65 mmol) dissolved in dried hexane (50 cm^3) was added dropwise at room temperature over about 20 min and then the reaction mixture was stirred for 10 h under nitrogen. To the solution, freshly distilled *N,N*-dimethylcarbamyl chloride (0.424 cm^3, 4.4 mmol) dissolved in dried hexane (100 cm^3) was added over 1 h and the mixture was stirred at room temperature for 12 h. The reaction mixture was poured into an aqueous solution of HCl. The reaction mixture was extracted with benzene and the organic phase was washed with water, dried and evaporated. Products were purified by column chromatography on silica. RcH (1.2 g, recovery 60%) was eluted first with a hexane–benzene (1:1) mixture. The second fraction eluted by a mixture of ethyl acetate–benzene (1:3) included compound **1**. The crude product of **1** was recrystallized from a benzene–hexane (1:1) mixture to give well-formed yellow crystals (0.7 g, 1.43 mmol, yield 33%). *Anal.* Calc. for C$_{21}$H$_{18}$ORu$_2$: C, 52.06; H, 3.74. Found: C, 52.20; H, 3.80%. ^{1}H NMR (CDCl$_3$): δ_H 5.27 (2H, t, J = 1.7 Hz), 4.74 (2H, t, J = 1.7 Hz), 4.59 (5H, s) ppm. ^{13}C NMR (CDCl$_3$): δ_c 195.5 (1C), 84.6 (2C), 72.6 (8C), 72.2 (10C) ppm. IR spectroscopic data (KBr): 3101.8, 1626.1, 1464.1, 1408.2, 1392.7, 1375.4, 1352.2, 1329.1, 1290.5, 1197.9, 1101.5, 1024.3, 1001.2, 900.8, 835.3, 808.3, 765.8, 679.0, 601.8, 574.8, 482.3, 443.7 cm^{-1}.

The third fraction eluted with a benzene–ethyl acetate (1:1) mixture gave an unidentified oily product. The fourth fraction eluted with a benzene–ethyl acetate–methanol (1:1:1) mixture gave 1,1'-diruthenocenoylruthenocene (RcCORcCORc), which was recrystallized from a benzene–hexane mixture to give yellow–orange crystals (0.4 g, 0.54 mmol, yield 19%). *Anal.* Calc. for C$_{32}$H$_{26}$O$_2$Ru$_3$: C, 51.53; H, 3.51. Found: C, 51.50; H, 3.49%. ^{1}H NMR (CDCl$_3$): δ_c 5.31 (4H, t, J = 1.7 Hz), 5.23 (4H, t, J = 1.7 Hz), 4.77 (8H, t, J = 1.7 Hz), 4.58 (10H, s), ^{13}C NMR (CDCl$_3$): δ_c 194.8 (2C), 85.7 (2C), 84.0 (2C), 74.5 (4C), 73.9 (4C), 72.9 (4C), 72.4 (4C), 72.3 (10C) ppm.

The new compound **2** was obtained in a high yield by reduction of **1** with AlCl$_3$ and LiAlH$_4$, as follows. RcCORc (1.0 g, 2.05 mmol) was added to a dry ethereal solution (50 cm^3) containing a large excess of anhydrous aluminum chloride (3 g) and lithium aluminum hydride (2.0 g); the solution, which lost its color during the reaction, was stirred for 30 min at room temperature under nitrogen, then water was added carefully to the reaction mixture, and the mixture was extracted with benzene. The benzene layer was washed with water, dried and evaporated. $RcCH_2Rc$ was separated by column chromatography on silica using a benzene–hexane (1:1) mixture, and recrystallized from a benzene–hexane mixture to give pale yellow crystals (0.8 g, 1.69 mmol; yield 82%). *Anal.* Calc. for $C_{21}H_{20}Ru_2$: C, 53.15; H, 4.25. Found: C, 53.69; H, 4.28%. ^1H NMR ($CDCl_3$): δ_H 4.51 (4H, t, $J = 1.7$ Hz), 4.49 (10H, s), 4.44 (4H, t, $J = 1.6$ Hz), 3.14 (2H, s) ppm. ^{13}C NMR ($CDCl_3$): δ_c 92.2 (2C), 71.0 (4C), 70.6 (10C), 69.4 (4C), 30.0 (1C) ppm. IR spectral data (KBr): 3088.3, 2922.4, 2853.0, 1464.1, 1433.2, 1408.2, 1290.5, 1248.1, 1221.1, 1099.5, 1024.3, 997.3, 923.9, 804.4, 763.9, 439.8 cm^{-1}.

2.2. *Syntheses of salts 3, 4 and 5*

Salt **3** was prepared by a method similar to that used for the preparation of $[RcRcI]^+I_3^-$ [5]. *Anal.* Calc. for $C_{21}H_{20}Ru_2I_4$: C, 25.68; H, 2.05. Found: C, 24.98; H, 1.94%. IR spectroscopic data (KBr): 3090.2, 2924.4, 1533.6, 1406.2, 1099.5, 1053.2, 1018.3, 1001.3, 908.6, 841.0, 819.8, 655.9, 578.7, 416.7 cm^{-1}.

Salt **4** was prepared by adding **2** (100 mg, 0.21 mmol in 50 cm^3 of CH_2Cl_2) to a stoichiometric amount of $[RcHI]^+PF_6^-$ in 50 cm^3 of CH_2Cl_2. The reaction mixture was stirred for 1 h and evaporated to dryness. RcH was removed by extraction with benzene, and the remaining solid was recrystallized from a dichloromethane–hexane mixture to give red–brown crystals of **4**. *Anal.* Calc. for $C_{21}H_{20}Ru_2IPF_6$: C, 33.79; H, 2.70. Found: C, 33.82; H, 2.67%. IR spectroscopic data (KBr): 3128.8, 2926.3, 1531.6, 1483.4, 1442.9, 1410.1, 1385.0, 1101.5, 1026.2, 850.7, 833.3, 740.7, 557.5, 418.6 cm^{-1}.

Salt **5** was prepared by a method analogous to that used for $[FcCH^+Rc]PF_6^-$ using $[RcHX]^+PF_6^-$ (X = Br, Cl) [8]. *Anal.* Calc. for $C_{21}H_{19}Ru_2PF_6$: C, 40.78; H, 3.10. Found: C, 39.99; H, 3.22%. IR spectroscopic data (KBr): 3128.8, 2928.2, 2858.8, 1626.1, 1516.2, 1487.3, 1446.7, 1412.0, 1101.5, 833.3, 740.7, 557.5, 461.0, 414.7 cm^{-1}.

2.3. *Physical measurements*

^1H NMR spectra were determined as described elsewhere [18,19]. The spectral line was simulated by using the method reported previously for the chemical exchange between the equivalent sites proposed by Abragam [23]. Cyclic voltammograms were determined using an HB-104 function generator and an HA-301 potentiostat (Hokuto Denko) with standard three-electrode configuration. A working electrode (platinum button) and Ag/AgCl reference were connected via a salt bridge of CH_3CN containing $[(C_4H_9)_4N]ClO_4$ 0.1 mol dm^{-3} as supporting electrolyte. The scan rate was 100 mV s^{-1}.

3. Results and discussion

3.1. *Salts 3 and 4*

In order to discuss the results of these studies, it is desirable to investigate the oxidation potentials for **1** and **2**. The cyclic voltammograms of **1** and **2** in acetonitrile are shown in Fig. 2. Compound **1** gives two irreversible two-electron oxidation peaks (E_{ox}: 1.01 and 1.17 V), which are much higher than those found in RcH and RcRc, due to the electron attractive nature of the carbonyl group (–CO–). Compound **1** could not be oxidized by iodine or $[RcHI]^+I_3^-$. Compound **2** gives two lower irreversible two-electron oxidation peaks (E_{ox}: 0.78 and 0.97 V). As already shown in the previous studies [19,24], RcH shows one irreversible two-electron oxidation peak (E_{ox}: 0.85 V [19]) in CH_3CN; the first peak can be attributed to the oxidation of $RcCH_2Rc$ to $[RcCH_2Rc]^{2+}$ and the second to that of $[RcCH_2Rc]^{2+}$ to $[RcCH_2Rc]^{4+}$, suggesting there may be a little interaction between the two Ru atoms in **2**.

It has been reported by Muller-Westerhoff et al. that [1.1]ruthenocenophane ([1.1]RcP) gives a reversible two-electron peak at an anomalously lower oxidation potential around 380 mV, which is ascribed to an antiferromagnetic interaction between Ru^{III} and Ru^{III} [25]. Actually, a Ru^{III}–Ru^{III} single bond (2.953 Å) is observed in the X-ray diffraction study of $[1.1]RcP^{2+}(BF_4^-)_2$ [26]. The absence of such a lower oxidation peak in **2** indicates that there is no antiferromagnetic interaction between the two Ru^{III} atoms in $[RcCH_2Rc]^{2+}$ cations because of the more flexible structure of the $[CpRu(C_5H_4)CH_2(C_5H_4)RuCp]^{2+}$ cation compared with that in $[1.1]RcP^{2+}$.

Compound **2** was oxidized by an equivalent amount of I_2 and $[RcHI]^+PF_6^-$ giving diamagnetic monocationic salts **3** and **4**, respectively. Fig. 3 shows the temperature dependent ^1H NMR spectra of **3**. The chemical shift values (δ_H) are listed in Table 1. The temperature dependence of the ^1H NMR spectrum observed for **3** in acetone-d_6 solutions at 180 K is similar to that observed for **4**; no significant differences with various

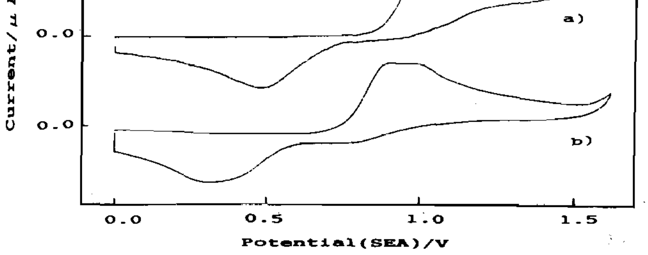

Fig. 2. Cyclic voltammograms of **1** (a) and **2** (b) in acetonitrile (sweep rate 100 mV s^{-1}).

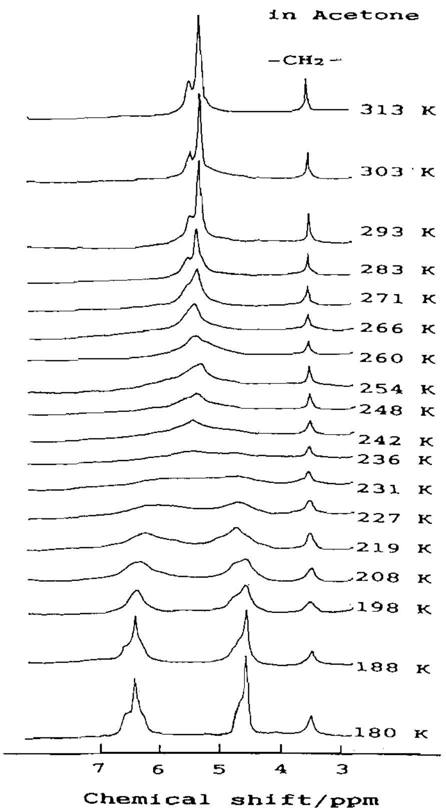

Fig. 3. Temperature-dependent ^1H NMR spectra of **3** in acetone at indicated temperatures.

Table 1
^1H chemical shifts of **2**, salts **3** and **4**, and related compounds in acetone

Compound	Temp. (K)	Chemical shift δ_H		
2	298	4.41, 4.51	($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Ru^{II}$
		4.45	(C_5H_5)	
		3.11	($-CH_2-$)	
RcH	298	4.51	(C_5H_5)	
	183	4.51	(C_5H_5)	
$[RcHI]^+I_3$	298	6.38	(C_5H_5)	
	183	6.43	(C_5H_5)	
3	180	6.55, 6.32	($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Ru^{IV}$
		6.40	(C_5H_5)	
		4.63, 4.57	($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Ru^{II}$
		4.57	(C_5H_5)	
		3.45	($-CH_2-$)	
	313	5.60, 5.42	($H_{2,5}$, $H_{3,4}$)	
		5.44		
		3.59	($-CH_2-$)	
4	180	6.55, 6.32	($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Ru^{IV}$
		6.40	(C_5H_5)	
		4.63, 4.57	($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Ru^{II}$
		4.57	(C_5H_5)	
		3.45	($-CH_2-$)	
5	183	5.62[b], 5.57[b]	($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Ru^{II}$
		5.03	(C_5H_5)	
		7.63	($-CH^+-$)	
	293	5.61, 5.48	($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Ru^{II}$
		5.02	(C_5H_5)	
		7.72	($-CH^+-$)	

b = broad line.

counter anions are observed as in the case of $[RcRcI]^+Y^-$ ($Y = I_3$, PF_6, BF_4, CCl_3COO–CCl_3COOH) [27]. Two sharp strong lines (δ_H: 6.40 and 4.57) are observed at 180 K. Based on the results of our previous studies [16–19], the former value corresponds well to the Cp ring of the Ru^{IV} side and the latter to that of Ru^{II}, i.e. the cation is formulated as the trapped valence (Ru^{II},Ru^{IV}) type $[Ru^{II}Cp(C_5H_4CH_2C_5H_4)CpRu^{IV}I]^+$ in acetone at 180 K.

The chemical shift difference ($\Delta\delta_H$: 1.83) of the Cp ring between the Ru^{II} and Ru^{IV} sides (which is a slightly smaller value ($\Delta\delta_H$: 1.92) for mononuclear RcH (δ_H: 4.51) and $[RcHI]^+I_3^-$ (δ_H: 6.43)) is significantly larger than the value for $[RcRcI]^+I_3^-$ ($\Delta\delta_H$: 1.44), suggesting less interaction between the $Ru^{II}Cp(C_5H_4)$ and $[IRu^{IV}Cp(C_5H_4)]^+$ moieties in **3** compared with that in $[RcRcI]^+I_3^-$ because of the separation of the moieties by the non-conjugated $-CH_2-$ group.

The linewidths of the spectrum in the higher temperature region are broadened and the coalescence temperature (T_c) is found around 236 ± 2 K (T_c: 246 K for $[RcRcI]^+I_3^-$ [18]). Above T_c, the lines become sharper with no chemical shifts difference between the $Ru^{II}Cp(C_5H_4)$ and $[IRu^{IV}Cp(C_5H_4)]^+$ moieties. Although all attempts to determine the temperature dependence of the ^{13}C NMR spectra of **3** and **4** failed because of the lower stability of **3** and **4** in acetone (above ~250 K) compared with the mixed valence salts $[RcRcI]^+Y^-$ ($Y = I_3$ and PF_6), the NMR spectroscopic observation clearly indicates that a rapid electron exchange reaction occurs between the Ru^{II} and Ru^{IV} atoms in salts **3** and **4**.

Sharp NMR lines are observed for $[RcRcI]^+I_3^-$ in acetone at 180–213 K, while relatively broader lines are observed for **3** even at 180 K, suggesting the smaller E_a value for **3** compared with that for $[RcRcI]^+I_3^-$. To estimate E_a and other kinetic parameters, the computer simulation of the temperature-dependent ^1H NMR spectra was carried out by procedures reported previously [18]. From the plots of T^{-1} versus log k (k is defined as τ^{-1}, τ is mean lifetime), a smaller E_a value (31.0 ± 0.6 kJ mol^{-1}) is obtained for **3** compared with the values of other iodobiruthenocenium and iododialkylbiruthenocenium salts ($[RcRcI]^+I_3^-$: 36.5 ± 0.6 kJ mol^{-1}, $[RcRcEt_2I]^+I_3^-$: 39.2 ± 0.6 kJ mol^{-1}) under the same conditions. Other activation parameters, $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, are found to be 50.4 ± 0.3 kJ mol^{-1}, 29.5 ± 0.6 kJ mol^{-1} and -70.1 ± 3.0 J K^{-1} mol^{-1}, respectively (49.1 ± 0.2 kJ mol^{-1}, 34.0 ± 0.6 kJ mol^{-1} and -50.7 ± 2.7 J K^{-1} mol^{-1}, $[RcRcI]^+I_3^-$, respectively [18]). The reason that **3** gives a smaller E_a value and lower T_c compared with the corresponding values of $[RcRcI]^+I_3^-$ is probably due to the stability of the intermediate structure, such as $[Cp(C_5H_4CH_2C_5H_4)Ru^{III}\cdots I\cdots Ru^{III}Cp]^+$, with a more flexible structure of the cation.

Based on the results of the present studies such as the smaller E_a value of **3** compared with those of $[RcRcI]^+I_3^-$ and $[RcRcEt_2I]^+I_3^-$ and the X-ray diffraction study on $[RcRcI]^+BF_4^-$ [20], the mechanism of the electron exchange reaction in **3**, **4** and similar binuclear systems could be explained by assuming iodine migration between Ru^{II} and Ru^{IV}. Moreover, the fact that the much smaller E_a values estimated for binuclear $[RcRcBr]^+PF_6^-$ (29.2 kJ mol^{-1}) and $[RcRcCl]^+PF_6^-$ (28.1 kJ mol^{-1} [15]) systems compared with the value of mononuclear $RcH/[RcHBr]^+PF_6^-$ (41.7 kJ mol^{-1}) and $RcH/[RcHCl]^+PF_6^-$ [1] systems suggests a different mechanism of the electron exchange reaction associated with the migration of halogen atoms in solution (the intramolecular reaction for $RcH/[RcHX]^+$ and the intermolecular reaction for $[RcRcX]^+$ systems).

This mechanism is quite different from that found in a number of mixed valence biferrocenium systems. Temperature-dependent ^{57}Fe Mössbauer spectra (from a trapped valence $Fe^{II}Fe^{III}$ state to an averaged valence state) are observed for mixed valence biferrocenium, dihalogenobiferrocenium and dialkylbiferrocenium salts depending upon the substituted group on the Cp rings and upon the counter anions [28], while temperature-independent spectra are also observed for the mixed valence diferroceniummethane triiodide salt ($[FcCH_2Fc]^+I_3^-$) [29] and disubstituted biferrocenium salts [28]. It is known that the electron exchange between Fe^{II} and Fe^{III} in biferrocenium salts and related compounds takes place through the fused fulvalene ligand in the solid state.

Fig. 4(a) (b) and (c) shows FT-IR spectra of **2**, **3** and $[RcHI]^+I_3^-$, respectively. The strong band found in the 900–800 cm^{-1} region is associated with the C–H bending mode. Based on the IR studies of adducts of RcH (such as $RcH–HgX_2$ (X=Cl, Br) [30]) and of ferrocenium salts, it is found that the band shifts toward the higher frequency regions (~ 50 cm^{-1}) compared with that of neutral RcH and FcH, respectively. Based on the C–H bending modes found for **2** (804.4 cm^{-1}) and $[RcHI]^+I_3^-$ (844.9 cm^{-1}), two kinds of broader peaks are observed for **3** at 841.0 and 819.8 cm^{-1} attributed to the $[Cp(C_5H_4)Ru^{IV}I]^+$ moiety and the $Cp(C_5H_4)Ru^{II}$ moiety, respectively. The results suggest that the structure of **3** remains in a trapped valence conformation indicated as $[CpRu^{II}(C_5H_4CH_2C_5H_4)Ru^{IV}CpI]^+PF_6^-$ just as in the case of $[RcRcI]^+BF_4^-$ in the solid state, although further X-ray diffraction studies are needed to confirm the structure of **3** and **4** (Scheme 1).

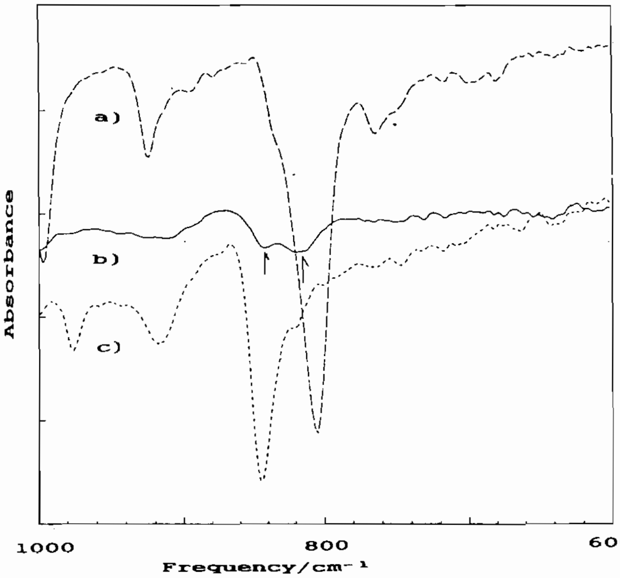

Fig. 4. FT-IR spectra of **2** (a), **3** (b) and $[RcHI]^+I_3^-$ (c).

3.2. *Salt 5*

In order to prepare mixed valence $[RcCH_2RcBr]^+PF_6^-$ and $[RcCH_2RcCl]^+PF_6^-$ salts, **2** was oxidized by $[RcHBr]^+PF_6^-$ and $[RcHCl]^+PF_6^-$ under the same conditions used for the preparation of $[RcRcBr]^+PF_6^-$ and $[RcRcCl]^+PF_6^-$ [17,18]. The elemental analysis data show the chemical formula to be $C_{21}H_{19}Ru_2PF_6$ for the oxidized product **5** in which neither chlorine nor bromine atoms are included. The salt **5** is more stable in acetone compared with **3** and **4**. The ^{1}H and ^{13}C NMR spectra are shown in Fig. 5(a) and (b), respectively. While temperature-dependent NMR spectra are observed for **3** and **4**, **5** shows temperature-independent NMR spectra from 183 to 293 K (slightly broader NMR lines are obtained only at 183 K). Three sharp lines (δ_H: 5.61, 5.48, 5.02) are observed at 293 K. The former two lines can be assigned to $H_{2,5}$ and $H_{3,4}$ and the latter main line to hydrogen atoms in the Cp rings. Although two kinds of lower field shift of the non-substituted ring proton signal ($\Delta\delta_H$: 1.95 and 0.12) are observed for mixed valence salts **3** and **4**, only a single $\Delta\delta_H$ (0.58) value is observed for **5**, suggesting equivalent oxidation states in both the Ru atoms in **5**.

One of the most striking spectral features is the presence of a broad signal at the lower field (δ_H: 7.72), although no signal is observed for the original $RcCH_2Rc$, **3** and **4** in this region. Moreover, the bridged methylene signal is observed (δ_H: 3.11) for $RcCH_2Rc$, while the corresponding signal disappears in the spectrum of **5**.

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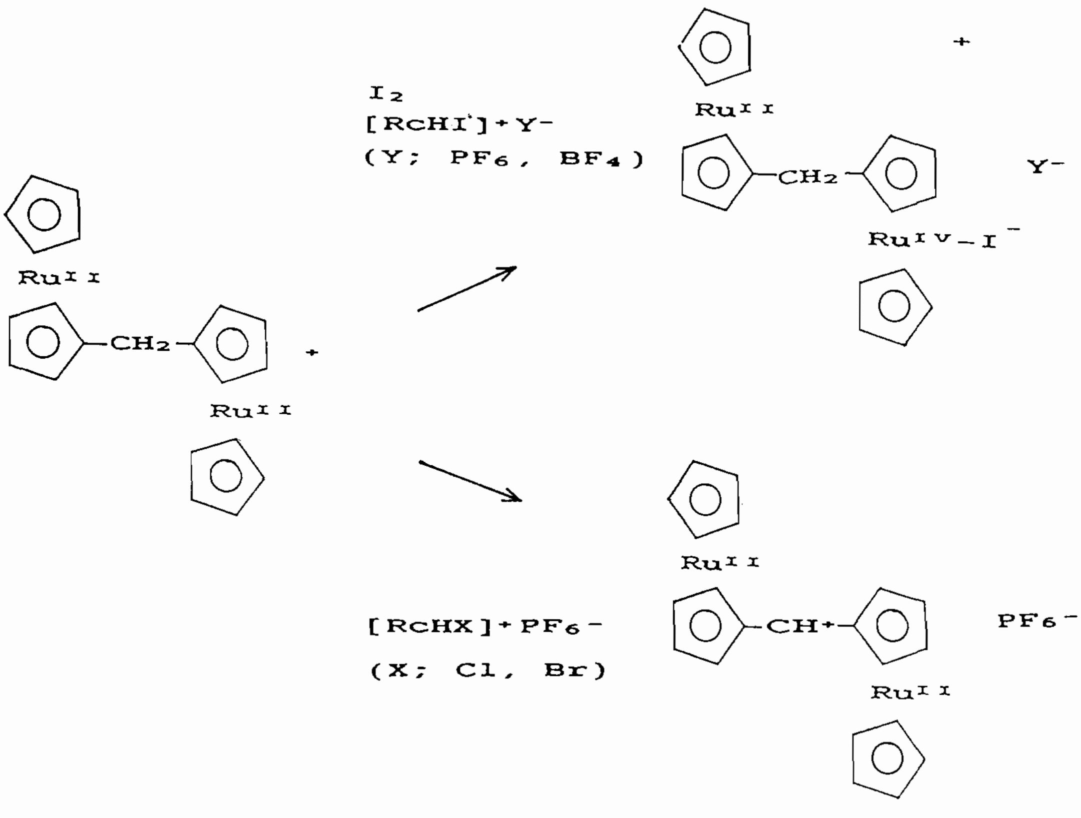
[1] No E_a value was estimated because of a small temperature dependence in ^{1}H NMR spectra in the temperature range 83–358 K [15].



Scheme 1.

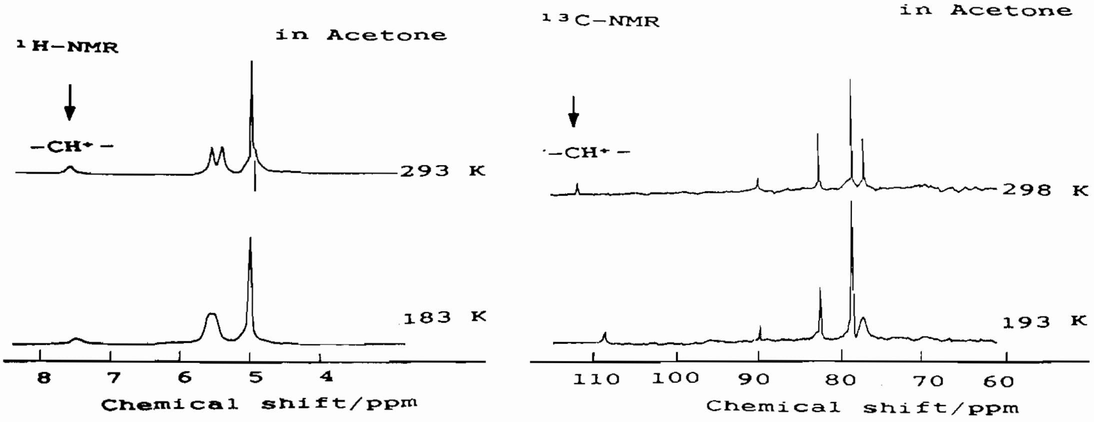


Fig. 5. ^{1}H NMR spectra and ^{13}C NMR spectra of 5 at indicated temperatures.

Similar results are obtained for ^{13}C NMR spectra of 5. A main signal assigned to the Cp ring is found at δ_C 79.0 and two signals assigned to $C_{2,4}$, $C_{3,4}$ are found at δ_C 82.9 and 77.6 at 298 K (Table 2). The lower field shift ($\Delta\delta_C$: 7.6–11.1) is observed for 5 compared with the corresponding values of 2. A new and weak signal observed at δ_C 111.8 shows a good correlation with the lower shielded proton signal (δ_H: 7.72) found in a selective proton-decoupling experiment on 5 at 298 K.

Recently, similar observations have been reported. Ferrocenylruthenocenylmethane ($RcCH_2Fc$) reacts with $[RcHX]^+PF_6^-$ salts (X = Cl, Br), giving a deep purple diamagnetic α,α-ferrocenylruthenocenylmethylium$^+$-PF_6^- ($[RcCH^+Fc]PF_6^-$) salt [31]. In the ^{13}C and ^{1}H NMR spectroscopic study of this salt, the $-CH^+-$ proton and carbon atoms are found to resonate at a lower field, δ_H 7.85–8.00 at 183–313 K and δ_C 111.3–117.8 at 183–323 K, respectively. Therefore, the signal of 5 at lower field can be assigned to $-CH^+-$ and 5 should be formulated as $[Ru^{II}Cp(C_5H_4CH^+C_5H_4)CpRu^{II}]PF_6^-$. The cationic state of the $-CH^+-$ group may be stabilized by the softer e_{2g} electrons of Ru^{II} forming a weak interaction ($-CH^+-\cdots Ru^{II}$), causing

Table 2
^{13}C chemical shifts of **2**, salts **3** and **4** and related compounds in acetone

Compound	Temp. (K)	Chemical shift δ_C	
2	298	93.3	(C_1)
		71.8, 70.0	($C_{2,5}$, $C_{3,4}$)
		71.2	(C_5H_5)
		31.6	($-CH_2-$)
5	298	90.1	(C_1)
		82.9, 77.6	($C_{2,5}$, $C_{3,4}$)
		79.0	(C_5H_5)
		111.8	($-CH^+-$)
	193	90.3	(C_1)
		82.9, 77.7^b	($C_{2,5}$, $C_{3,4}$)
		79.1	(C_5H_5)
		108.6	($-CH^+-$)

b = broad line.

a lower field shift in the ^1H and ^{13}C NMR spectra of **5**.

From the results obtained in the present studies, it has been found that $RcCH_2Rc$ reacts with I_2 and $[RcHI]^+PF_6^-$ giving mixed valence salts formulated as $[Ru^{II}Cp(C_5H_4CH_2C_5H_4)CpRu^{IV}I]^+Y^-$ ($Y = I_3$, PF_6), in which intramolecular electron transfer associated with migration of iodine atoms between the Ru^{II} and Ru^{IV} atoms occurs, as described in $[Ru^{II}Cp(C_5H_4CH_2C_5H_4)CpRu^{IV}I]^+ \rightleftharpoons [IRu^{IV}Cp(C_5H_4CH_2C_5H_4)CpRu^{II}]^+$. It has also been found that $RcCH_2Rc$ reacts with $[RcHCl]^+PF_6^-$ or $[RcHBr]^+PF_6^-$ giving an α,α-diruthenocenylmethylium$^+PF_6^-$ ($[RcCH^+Rc]PF_6^-$) salt. The difference in the mechanism of the two kinds of reactions can be interpreted by assuming the greater stability of the Ru^{IV}–I bond compared to the Ru^{IV}–Br or Ru^{IV}–Cl bond because the soft Ru atom has a larger affinity to a soft base such as the I atom rather than to hard bases such as Cl and Br atoms. The stable Ru^{IV}–I bond may also prevent the formation of the carbenium ion. The lower stability of the Ru^{IV}–Cl and Ru^{IV}–Br bonds explains why **2** reacts with $[RcHX]^+PF_6^-$ (X = Br, Cl) giving the carbenium ion. Further X-ray diffraction studies may provide more reliable evidence for the structure of **5**.

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