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^{1}H, ^{13}C-NMR and ^{57}Fe-Mössbauer spectroscopic studies of α,α-ferrocenylruthenocenylmethylium$^+$ ion

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Abstract

Ferrocenylruthenocenylmethane reacts with chloro- or bromoruthenocenium(IV)$^+$PF$_6^-$ salts, giving a deep-purple salt. The results of ^{57}Fe-Mössbauer, ^{1}H, and ^{13}C NMR spectroscopic studies on the salt suggest the formula α,α-ferrocenylruthenocenylmethylium hexafluorophosphate salt; [Fe^{II}Cp(C$_5$H$_4$CH$^+$C$_5$H$_4$)CpRu^{II}]PF$_6^-$ (1). The salt gives remarkably temperature dependent ^{1}H and ^{13}C NMR spectra, due to rotation about the exocyclic carbon atom (–CH$^+$–). The energy barrier of the rotation is estimated on the basis of ^{1}H NMR line simulation studies to be about 34.0 ± 0.6 kJ mol^{-1}. On the other hand, ferrocenylruthenocenylmethane reacts with iodoruthenocenium(IV)$^+$Y$^-$ (Y; BF$_4$, PF$_6$) salts, giving paramagnetic dicationic salts formulated from the results of ^{57}Fe-Mössbauer and NMR spectroscopic studies as [Fe^{III}Cp(C$_5$H$_4$CH$_2$C$_5$H$_4$)CpRu^{IV}I]$^{2+}$Y$_2^-$.

1. Introduction

Ferrocenylruthenocene, abbreviated as FcRc (Fc, ferrocenyl; Rc, ruthenocenyl), has an interesting structure because Fc and Rc moieties are bonded directly [1]. One of the most distinctive features of FcH and RcH chemistries is illustrated in the reaction with iodine as follows; the reaction of FcH and RcH with I$_2$ in benzene or other solvents gives paramagnetic ferrocenium [Cp$_2$Fe^{III}]$^+$I$_3^-$ and diamagnetic iodoruthenocenium [Cp$_2$Ru^{IV}I]$^+$I$_3^-$ salts, respectively [2]. We already reported that FcRc reacts with a large excess of I$_2$, giving a diamagnetic black precipitate analyzed as FcRcI$_4$ [3]. ^{57}Fe-Mössbauer spectra on the

salt show well separated two lines at 78 and 300 K (quadrupole splitting, QS, values; 2.16 mm s^{-1} both at 78 and 300 K), suggesting the Fe to be low-spin Fe^{II}; *i.e.*, the Fe is not oxidized by I$_2$, although the Fe is oxidized more easily than the Ru judging from the results of cyclic voltammetry of FcRc [4]. All the results of ^{13}C-CP/MAS NMR and ^{57}Fe-Mössbauer spectroscopies indicate the formula [Fe^{II}Cp(H$_4$C$_5$-C$_5$H$_4$)CpRu^{IV}I]$^+$I$_3^-$.

Ferrocenylruthenocenylmethane, abbreviated as FcCH$_2$Rc, reacts with a large excess of I$_2$ giving a paramagnetic black salt analyzed as FcCH$_2$RcI$_7$ (2) as shown in Scheme 1 [5]. ^{57}Fe-Mössbauer spectra for 2 show a broad single line at 78 and 300 K, suggesting that the ferrocenyl moiety is oxidized to ferrocenium ion. Therefore, the formula of the salt is to be [Fe^{III}Cp(C$_5$H$_4$CH$_2$C$_5$H$_4$)CpRu^{IV}I]$^{2+}$ (I$_3^-$)$_2$; *i.e.*, the

Fc and Rc moieties react with iodine independently because the two moieties are separated by methylene group [5].

In the present studies, $FcCH_2Rc$ was oxidized by [haloruthenocenium(IV)]$^+PF_6^-$ salts, $[RcHX]^+PF_6^-$ (X = Cl, Br), giving a deep purple diamagnetic PF_6^- salt, 1. The salt 1 is easily soluble in organic solvents, such as acetone and acetonitrile, giving deep purple solutions, whereas most ferrocenium salts give green-blue solutions; e.g., 2 gives a typical ferrocenium green–blue solution (λ_{max}: 296, 360 nm (ascribed to I_3^-), and 625 nm (ascribed to ferrocenium ion)). On the basis of the present studies, 1 is found to be $[Fe^{II}Cp(C_5H_4CH^+C_5H_4)CpRu^{II}]^+PF_6^-$. In order to clarify the oxidation behaviour of these salts, ^{57}Fe-

Mössbauer, ^{1}H and ^{13}C NMR spectroscopic studies were carried out on 1 and the related salts 2–5.

2. Experimental section

2.1. Syntheses

The compounds, $FcCH_2Rc$, diferrocenylmethane ($FcCH_2Fc$), and 2 were obtained by the method reported previously [5,6]. Salt 1 was prepared by the following method. $FcCH_2Rc$ (100 mg; 0.23 mmol) dissolved in 30 ml of CH_2Cl_2 was added to a stoichiometric amount of chlororuthenocenium$^+PF_6^-$ (96 mg; 0.23 mmol), $[RcHCl]^+PF_6^-$, dissolved in 100 ml of CH_2Cl_2. The reaction mixture was stirred for 30 min and then RcH was removed by extraction of the reaction mixture
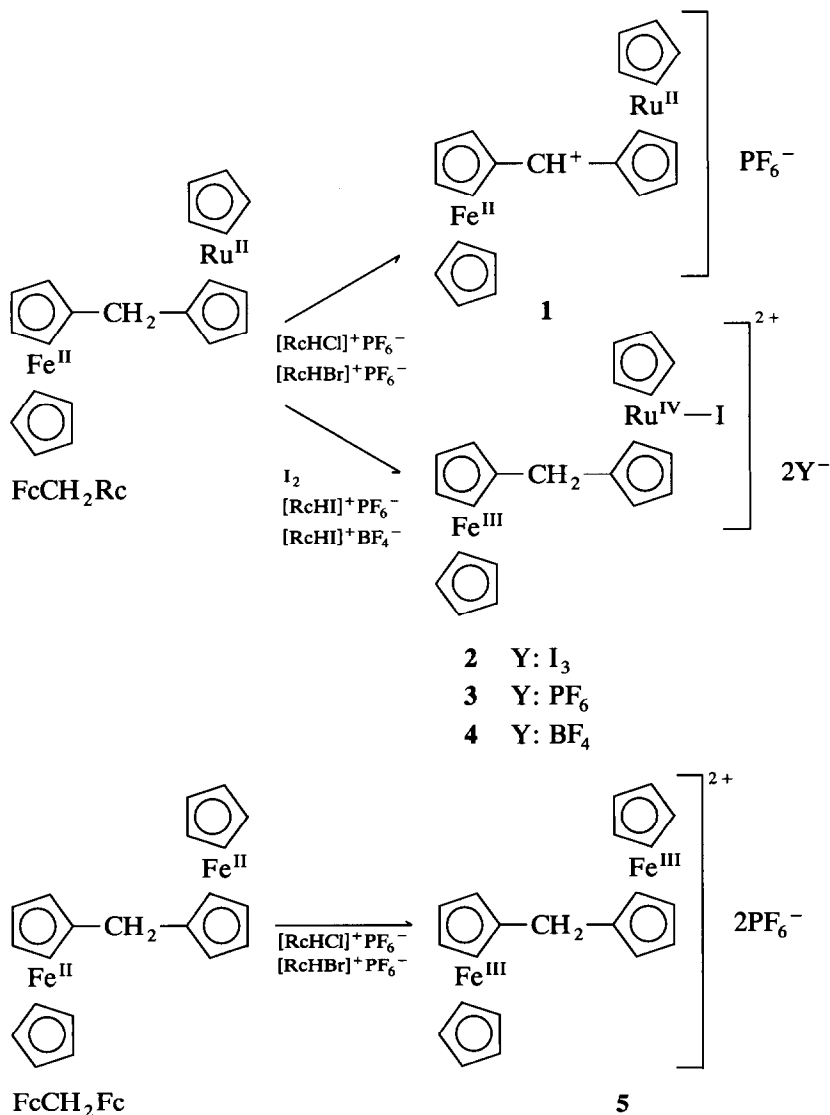
Scheme 1.

with benzene after the solvent was removed. The remaining solid was recrystallized from a dichloromethane/n-hexane mixture to give deep purple crystals of 1 (60 mg, 0.11 mmol; yield 46%). The salt 1 was also obtained by using bromoruthenocenium$^+$PF$_6$$^-$, [RcHBr]$^+PF_6$$^-$ in place of [RcHCl]$^+$PF$_6$$^-$. Anal. Found: C, 43.70; H, 3.43. C$_{21}$H$_{19}$FeRuPF$_6$ Calc.: C, 44.00; H, 3.34%. Ir (KBr): 3113.4, 2924.4, 1514.3, 1410.1, 1392.7, 1257.7, 1219.1, 1105.3, 1059.0, 1032.0, 1001.1, 951.0, 827.5, 736.9, 684.8, 557.5, 505.4, 484.2, 434.0, 407.0 cm^{-1}. Visible spectra (CH$_3$CN): λ$_{max}$ 524 nm (ε 3648 M^{-1} cm^{-1}), 380sh (3700), 320 (11250).

Salt 3 was prepared by the same method as that used for 1 by using [RcHI]$^+$PF$_6$$^-$ in place of [RcHCl]$^+$PF$_6$$^-$. Anal. Found: C, 29.91; H, 2.40. C$_{21}$H$_{20}$FeRuIP$_2$F$_{12}$ Calc.; C, 29.81; H, 2.38%. Ir (KBr): 3119.2, 1514.3, 1410.1, 1105.3, 1055.2, 1005.0, 839.1, 499.6, 424.4, 416.7 cm^{-1}. Visible spectra (CH$_3$CN): λ$_{max}$ 516 nm (ε 1100 M^{-1} cm^{-1}), 350 (3950), 288 (9530), 257 (9525).

Salt 4 was prepared by the same method as that used for 3 by using [RcHI]$^+$BF$_4$$^-$ in place of [RcHI]$^+$PF$_6$$^-$. Anal. Found: C, 34.93; H, 2.88. C$_{21}$H$_{20}$FeRuIB$_2$F$_8$ Calc.; C, 34.56; H, 2.76%. Ir (KBr); 3099.9, 1512.3, 1410.1, 1084.1, 1033.9, 833.3, 586.4, 534.3, 520.8, 501.5 cm^{-1}. Visible spectra (CH$_3$CN): λ$_{max}$ 505 nm (ε 943 M^{-1} cm^{-1}), 350sh (2830), 280 (8500), 253 (13500).

The dicationic di(ferrocenylium)methane^{2+}(PF$_6$$^-$)$_2$, (FcCH$_2$Fc^{2+}(PF$_6$$^-$)$_2$ salt 5 was prepared by the same method as that used for 1 by using FcCH$_2$Fc in place of FcCH$_2$Rc. Anal. Found: C, 37.32; H, 2.90. C$_{21}$H$_{20}$Fe$_2$P$_2$F$_{12}$ Calc.; C, 37.42; H, 2.99%. Visible spectra (CH$_3$CN): λ$_{max}$ 627 nm (ε 384 M^{-1} cm^{-1}), 267 (6990). Ir (KBr): 3113.4, 1473.8, 1421.7, 1126.5, 1060.9, 1033.9, 1010.8, 829.5, 557.5 cm^{-1}.

2.2. Measurements

Both the ^{1}H and ^{13}C NMR spectra in solution were recorded with a JEOL FX-90Q Fourier Transform NMR spectrometer at 89.59 and 22.5 MHz, respectively, using TMS as a standard. An NM-VTS unit was used to control the probe temperatures which were measured to an accuracy of at least ±1°C. ^{57}Fe-Mössbauer spectra were recorded under the conditions similar to those applied in our previous report [4]. The isomer shifts were referred to metallic iron foil. The ^{57}Fe-Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks. Electronic absorption spectra were measured in acetonitrile with a JASCO Ubest-50 Spectrometer at room temperature. Cyclic voltammograms were obtained with a Hokuto Denko HB-104 function generator and HA-301 potentiostat combined with a standard three-electrode configuration. A working electrode of platinum button and
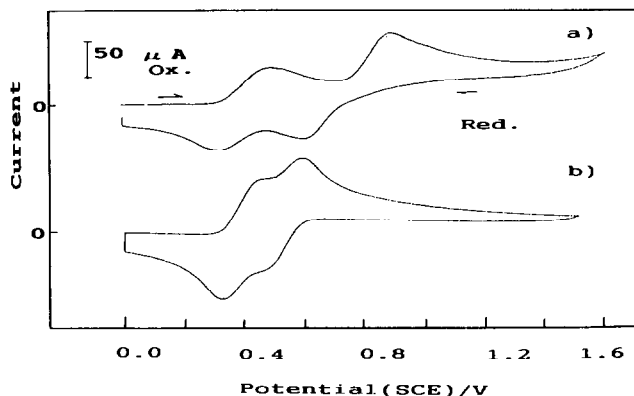

Fig. 1. Cyclic voltammograms of FcCH$_2$Rc (a) and FcCH$_2$Fc (b) in acetonitrile. (Sweep rate 200 mV s^{-1}).

an Ag/AgCl reference electrode were connected via a salt bridge of CH$_3$CN containing (0.1 mol dm^{-1}) [(n-C$_4$H$_9$)N]ClO$_4$. The scan rate was 200 mV s^{-1}.

3. Results and discussion

In order to discuss the results of these studies, it is desirable to investigate the half-wave redox potentials $E_{1/2}$ for FcCH$_2$Rc. The cyclic voltammogram of FcCH$_2$Rc in acetonitrile shows a reversible one-electron oxidation peak ($E_{1/2}$ 0.40 V) ascribed to ferrocene-type Fe^{II} to Fe^{III} and an irreversible two-electrons oxidation peak ($E_{1/2}$ 0.75 V) to that of ruthenocene-type Ru^{II} to Ru^{IV}, as shown in Fig. 1(a). The results above clearly indicate that the Ru is less easily oxidized than the Fe, which corresponds well to the results of the same studies of FcH ($E_{1/2}$ 0.45 V) and RcH ($E_{1/2}$ 0.65 V).

FcCH$_2$Rc dissolved in CH$_2$Cl$_2$ gives a clear yellow solution (λ$_{max}$ 322 nm, ε 297 M^{-1} cm^{-1}; 432 nm, 93 M^{-1} cm^{-1}). When the solution of RcHCl$^+$PF$_6$$^-$ in CH$_2$Cl$_2$ is added to this solution, the colour of the solution changes (remarkably) to deep-purple and the salt 1 of the same colour is isolated from the solution. The salt 1 can also be prepared by using RcHBr$^+$PF$_6$$^-$ in place of RcHCl$^+$PF$_6$$^-$. In contrast to the products of reaction of RcRc with RcHCl$^+$PF$_6$$^-$ and RcHBr$^+$PF$_6$$^-$ [7–9], the halogen atom (Cl, Br) is not contained in 1 based on the elemental analysis (Cl and Br) data.

Figure 2 shows ^{57}Fe-Mössbauer spectra for 1 at 298 K. No temperature dependences of the spectra are found in the range 298–78 K, and the QS and isomer shift (IS) values are found to be 2.19, 0.43 mm s^{-1} at 298 K and 2.24 and 0.52 mm s^{-1} at 78 K, respectively. Although the QS values are smaller than those of the original compound, FcCH$_2$Rc (2.41 and 2.44 mm s^{-1} at 298 and 78 K, respectively), the Mössbauer results

clearly show that the Fe in the oxidation product still remains as low-spin Fe^{II}. That the Fe in $FcCH_2Rc$ is not oxidized by $RcHX^+PF_6^-$ (X = Cl, Br) is quite different from what we expected from the results of the cyclic voltammogram of $FcCH_2Rc$.

To compare the results of 1, diferrocenylmethane ($FcCH_2Fc$) is prepared and the cyclic voltammogram, as shown in Fig. 1(b), shows two reversible one-electron oxidation peaks ($E_{1/2}$ 0.39 and 0.53 V), of which the first is attributed to the oxidation of $FcCH_2Fc$ to $FcCH_2Fc^+$ and the second to that of $FcCH_2Fc^+$ to $FcCH_2Fc^{2+}$. Because the $E_{1/2}$ value of the second oxidation peak is smaller than the value of RcH (0.65 V), $FcCH_2Fc$ is expected to be oxidized completely by $RcHX^+PF_6^-$ (X = Cl and Br), giving a dicationic ferrocenium cation $FcCH_2Fc^{2+}$. Actually, the oxidation of $FcCH_2Fc$ with $RcHX^+PF_6^-$ (X = Cl and Br) gives a green dicationic salt analyzed as $[FcCH_2Fc]^{2+}(PF_6^-)_2$ (5).

The salt 5 dissolves well in acetone, giving a typical green ferrocenium solution, which cannot give ^1H NMR spectra over a range of temperatures, because of its paramagnetism. ^{57}Fe-Mössbauer spectra give a typical ferrocenium broad single line in the range of 298 to 78 K (IS = 0.42 and 0.52 mm s^{-1} at 298 and 78 K, respectively), which clearly shows that the two Fe in $FcCH_2Fc$ are oxidized by $RcHX^+PF_6^-$ (X = Cl and Br) to give low-spin Fe^{III}, and that the formula of 5 is $[Fe^{III}Cp(C_5H_4CH_2C_5H_4)CpFe^{III}]^{2+}(PF_6^-)_2$.

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

Fig. 2. ^{57}Fe-Mössbauer spectra of salt 1 (a) and 3 (b) at 298 K.

In comparison with the studies on 1, we can conclude that the Ru in $FcCH_2Rc$ plays an important role in preventing the oxidation of Fe in $FcCH_2Rc$ with $RcHX^+PF_6^-$. In order to investigate the chemical state of the Fe and Ru in 1 in more detail, ^1H and ^{13}C NMR spectroscopic studies for 1 were carried out in acetone, as is shown in Figs. 3 and 4, and their chemical shifts are listed in Tables 1 and 2, respectively. The original compound $FcCH_2Rc$ gives seven sharp ^1H NMR lines in acetone and other solvents. On the basis of the same studies on FcH, RcH and FcRc, the three lines (δ_H = 4.49, 4.39 and 4.44) at the lower frequency side can be assigned to Cp-ring protons of the Ru^{II} side, the other three lines (δ_H = 4.10, 4.05 and 4.08) to those of the Fe^{II} side, and a line at δ_H = 3.28 to the signal of CH_2.

TABLE 1. ^{1}H NMR chemical shifts of FcCH$_2$Rc and of salt 1 in acetone

Compound	Temperature (K)	Chemical shift δ_H		
FcH$_2$Rc	298	4.49, 4.39	(H$_{2,5}$, H$_{3,4}$)	Cp(C$_5$H$_4$)Ru^{II}
		4.44	(C$_5$H$_5$)	
		4.10, 4.05	(H$_{2,5}$, H$_{3,4}$)	Cp(C$_5$H$_4$)Fe^{II}
		4.08	(C$_5$H$_5$)	
		3.28	(CH$_2$)	
1	183	6.36, 6.20,		Cp(C$_5$H$_4$)Ru^{II}
		6.08, 5.38	(H$_{2,3,4,5}$)	
		5.26	(C$_5$H$_5$)	
		5.01, 4.95,		Cp(C$_5$H$_4$)Fe^{II}
		4.81	(H$_{2,3,4,5}$)	
		4.38	(C$_5$H$_5$)	
		7.85	(CH$^+$)	
	313	6.17, 5.65	(H$_{2,5}$, H$_{3,4}$)	Cp(C$_5$H$_4$)Ru^{II}
		5.21	(C$_5$H$_5$)	
		4.94	(H$_{2,5}$, H$_{3,4}$)	Cp(C$_5$H$_4$)Fe^{II}
		4.46	(C$_5$H$_5$)	
		8.00	(CH$^+$)	

As shown in Fig. 3, 1 gives two sharp strong lines (δ_H = 5.26 and 4.38 at 183 K) and those are assigned to non-substituted Cp-ring protons of the Ru^{II} and Fe^{II} sides, respectively. Two kinds of lower field shift of the peak ($\Delta\delta_H$) are found to be 0.82 (Ru^{II} side) and 0.30 ppm (Fe^{II} side), as compared with the corresponding values of the original FcCH$_2$Rc (δ_H = 4.44 and 4.08). It seems more likely that there is a significant differ-

ence on the Ru^{II} side especially between the original FcCH$_2$Rc and 1.

In contrast with the original FcCH$_2$Rc, remarkably temperature dependent ^{1}H-NMR spectra are observed for 1. Four broad peaks (δ_H = 6.36, 6.20, 6.08, 5.38) ascribed to the H$_2$, H$_3$, H$_4$ and H$_5$ protons for the Ru^{II} side are observed separately at 183 K. The broadening of the signals is due not only to spin–spin coupling interaction but also to some dynamic behaviour. On increasing the temperature to 225 K, these four signals get broader, and finally two lines reappear at δ_H 6.17 (2H) and 5.65 (2H) at 313 K. A similar observation is made for the Fe^{II} side; i.e., three lines at 183 K (δ_H = 5.01, 4.95, 4.81) get broader with increasing temperature and a relatively sharp line reappears at 313 K. Moreover, one of the most interesting spectral features is the presence of a signal at the lower field (δ_H = 7.85–8.00), although no signal is observed for the original FcCH$_2$Rc in this region.

Similar results are obtained for ^{13}C NMR spectra for 1, as shown in Fig. 4. Two main peaks at δ_C = 83.9 and 71.2 are observed at 183 K and they are assigned to the non-substituted Cp ring of the Ru^{II} and Fe^{II} sides, respectively. A large low field shift in the Ru^{II} side ($\Delta\delta_c$ = 12.5) and the smaller shift in the Fe^{II} side ($\Delta\delta_c$ = 1.4) are obtained as compared with the corresponding value of FcCH$_2$Rc, as shown in Table 2. In spite of the absence of the temperature dependence of the two C$_1$ (δ_c = 97.5 and 79.6 for the Ru^{II} and Fe^{II} sides, respectively) and two non-substituted Cp signals,

TABLE 2. ^{13}C-NMR chemical shifts of FcCH$_2$Rc and of salt 1 in acetone

Compound	Temperature (K)	Chemical shift δ_c		
FcCH$_2$Rc	298	87.2	(C$_1$)	Cp(C$_5$H$_4$)Ru^{II}
		71.4	(C$_5$H$_5$)	
		70.7, 70.2	(C$_{2,5}$, C$_{3,4}$)	
		85.9	(C$_1$)	Cp(C$_5$H$_4$)Fe^{II}
		69.8	(C$_5$H$_5$)	
		68.1	(C$_{2,5}$, C$_{3,4}$)	
		29.5	(CH$_2$)	
1	183	97.5	(C$_1$)	Cp(C$_5$H$_4$)Ru^{II}
		83.9	(C$_5$H$_5$)	
		90.2, 89.7, 83.0	(C$_{2,5}$, C$_{3,4}$)	
		79.6	(C$_1$)	Cp(C$_5$H$_4$)Fe^{II}
		71.2	(C$_5$H$_5$)	
		75.1, 74.1, 66.7	(C$_{2,5}$, C$_{3,4}$)	
		111.3	(–CH$^+$–)	
	323	97.5	(C$_1$)	Cp(C$_5$H$_4$)Ru^{II}
		83.7	(C$_5$H$_5$)	
		89.7, 83.7	(C$_{2,5}$, C$_{3,4}$)	
		79.6	(C$_1$)	Cp(C$_5$H$_4$)Fe^{II}
		72.8	(C$_5$H$_5$)	
		76.8, 71.8	(C$_{2,5}$, C$_{3,4}$)	
		117.8	(–CH$^+$–)	
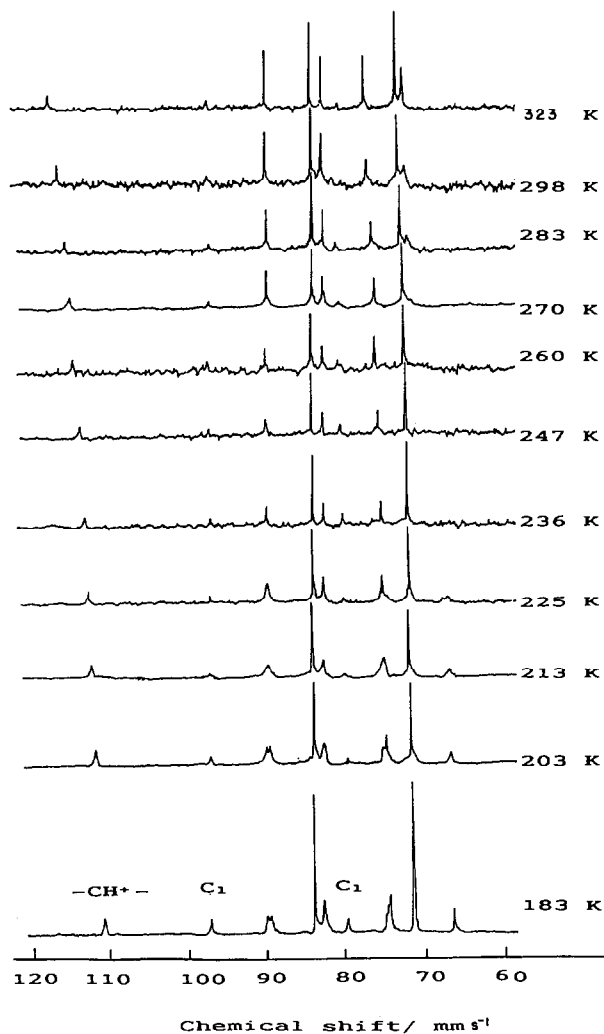
Fig. 4. Temperature-dependent ^{13}C NMR spectra of 1 at indicated temperatures.

The extraordinary stability of the α-carbonium ion, $Cp(C_5H_4)CH_2^+M^{II}$ (M = Fe, Ru and Os), has been reported [10–13]. In the ^{13}C NMR spectroscopic study of α-carbonium $FcCH_2^+$ and $FcCH^+CH_3$ by Koridze et al. [14] and Olah [15], the $-CH_2^+$ and $-CH^+CH_3$ carbon atoms in $FcCH_2^+$ and $FcCH^+CH_3$, respectively, resonated at lower field ($\delta_c = 110.6$ and 117.9, respectively). Therefore, the signal at lower field of 1 can be assigned to the carbonium carbon and the salt can be formulated as $[Fe^{II}Cp(C_5H_4CH^+C_5H_4)CpRu^{II}]PF_6^-$ in solid and in acetone, that should result in the ^{1}H- and ^{13}C-NMR and electronic spectra features.

The temperature dependent ^{1}H and ^{13}C NMR spectra for 1 can be due to the rotation of exocyclic carbon atom based on the results of the temperature dependent ^{1}H-NMR studies of the α,α-diferrocenylmethylium salt formulated as $[Fe^{II}Cp(C_5H_4CH^+C_5H_4)CpFe^{II}]$ reported by Lupan et al. [10].

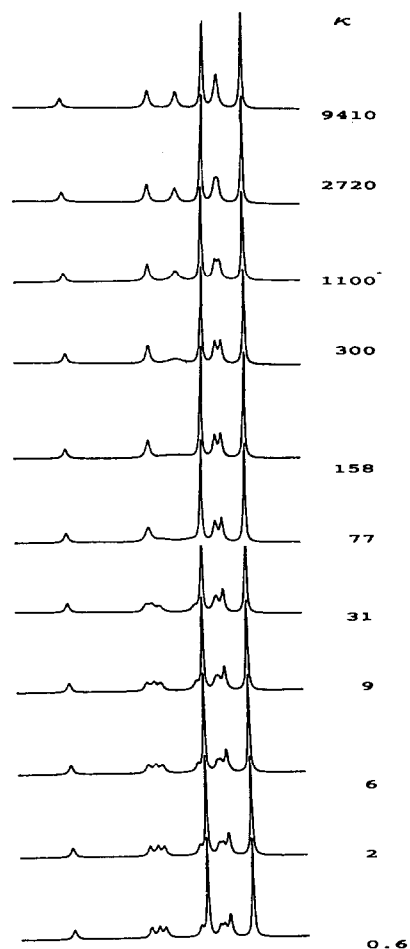To estimate the energy barrier of the rotation, ^{1}H-NMR spectral simulation was carried out, as shown in

considerable temperature dependence of ^{13}C NMR spectra on the $C_{2,5}$ and $C_{3,4}$ signals is observed.

Moreover, a weak signal ($\delta_c = 111.3$ and 117.8 at 183 and 323 K, respectively) is observed, whereas the original $FcCH_2Rc$ gives no peaks in this region. The bridged methylene signal is observed at δ_c 29.5 for $FcCH_2Rc$, but the corresponding signal disappears in the spectrum of 1. In order to assign the peak ($\delta_c = 111.3–117.8$), an off-resonance ^{13}C NMR spectroscopic study was carried out on 1. The Cp ring signals, except for C_1 signals, ($\delta_c = 97.5$ and 79.6) split into two due to the bonding proton (–CH). The peak at the low frequency side ($\delta_c = 111.3–117.8$) also splits into two, probably due to the methine proton not the methylene one. Moreover, from the results of a selective proton-decoupling experiment on 1 at 298 K, the lower shielded carbon peak ($\delta_c = 116.8$) showed good correlation to the lower shielded proton signal ($\delta_H = 8.00$).
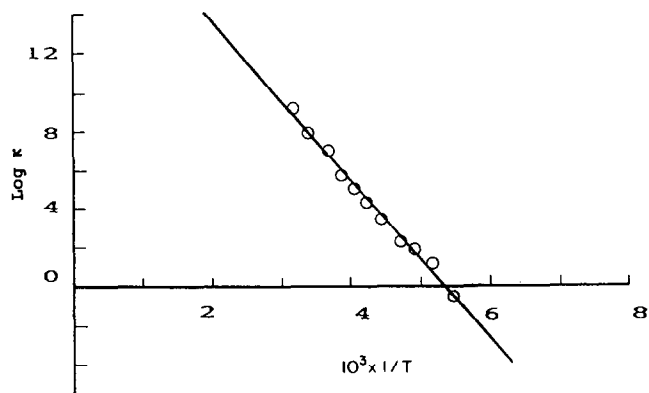

Fig. 5. The calculated ^{1}H NMR spectra of 1.

Fig. 6. The Arrhenius plot of log κ versus $1/T$ for 1.

Fig. 5. The simulation was calculated using the model of chemical exchange between two equivalent sites proposed by Abragam [16]. The activation energy, E_a, was obtained from plots of T^{-1} versus log κ (see Fig. 6) (κ is defined as τ^{-1}; τ is a mean lifetime). Good linear plots of log κ versus T^{-1} were obtained. From the plots, the values of E_a, $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ can be estimated to be 34.0 ± 0.6, 53.1 ± 0.2, 31.5 ± 0.6 kJ mol and -17.3 ± 0.6 e.u., respectively. From the temperature dependent ^{13}C NMR spectra for 1, the corresponding values are obtained; i.e., E_a, $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are estimated to be 35.7 ± 1.0, 52.7 ± 0.3, 33.2 ± 1.0 kJ/mol and -15.6 ± 1.1 e.u., respectively, in good agreement with the results above.

As already reported, $FcCH_2Rc$ was oxidized by I_2, giving a dicationic and paramagnetic ferrocenium salt 2, estimated as $[IRu^{IV}Cp(C_5H_4CH_2C_5H_4)Cp\text{-}Fe^{III}]^{2+}(I_3^-)_2$ on the basis of ^{57}Fe-Mössbauer and elemental analysis data [4]. $FcCH_2Rc$ was oxidized by $RcHI^+PF_6^-$ in CH_2Cl_2, giving a paramagnetic salt 3. The salt dissolves well in acetone, giving a grey solution, but no ^1H NMR line was obtained over a range of temperatures, the facts are quite different from those of salt 1. Only a broad singlet ^{57}Fe-Mössbauer line (IS; 0.42 mm s^{-1}) was obtained at 300 K, as shown in Fig. 2(b). Because the results obtained for 3 correspond well to those for 2, the formula of 3 was estimated as $[IRu^{IV}Cp(C_5H_4CH_2C_5H_4)CpFe^{III}]^{2+}(PF_6^-)_2$ on the basis of elemental analysis. The same cation was prepared by the reaction of $FcCH_2Rc$ with $RcHI^+BF_4^-$ in the same conditions as those used for 3, giving dicationic 4. A broad single ^{57}Fe-Mössbauer line (IS; 0.42 mm s^{-1}) was obtained and 4 was formulated as $[IRu^{IV}Cp(C_5H_4CH_2C_5H_4)CpFe^{III}]^{2+}(BF_4^-)_2$.

From the results obtained in the present studies, it can be concluded that $FcCH_2Rc$ reacts with $RcHX^+PF_6^-$ (X = Cl, Br), giving a diamagnetic α-carbonium $[Ru^{II}Cp(C_5H_4CH^+C_5H_4)CpFe^{II}]$ and with either $RcHI^+Y^-$ (Y = PF_6^-, BF_4^-) or I_2, giving a

paramagnetic $[IRu^{IV}Cp(C_5H_4CH_2C_5H_4)Fe^{III}]^{2+}$ dication not giving an α-carbonium salt. The difference in the mechanism of the two oxidations in $FcCH_2Rc$ may be considered as follows.

Based on the results of cyclic voltammogrammetry of $FcCH_2Rc$, the Fe should be oxidized first with the above reagents. Thus, oxidation in various molar ratios ($c = 0.01–1.00$) of $RcHX^+PF_6^-/FcCH_2Rc$ (X = Cl and I) were examined by ^1H NMR spectroscopy in acetone at room temperature. When a small amount of oxidizing reagent such as $RcHX^+PF_6^-$ (X = Cl, I) added to $FcCH_2Rc$ ($c = 0.01–0.03$), the same spectral features were observed in the former oxidation and in the latter; i.e., ^1H NMR lines for the Fe^{II} side and $-CH_2$ of $FcCH_2Rc$ start broadening and then disappear owing to the paramagnetism of ferrocenium ion. With increasing amount of the oxidizing reagent ($c = 0.80–1.00$), different spectral features were observed for the two cases. In the case of the $RcHI^+PF_6^-/FcCH_2Rc$ system, all the signals of $FcCH_2Rc$ disappeared soon except only an increasing RcH signal ($\delta = 4.51$) formed by reduction of $RcHI^+PF_6^-$ with $FcCH_2Rc$. On the other hand, in the case of $RcHCl^+PF_6^-/FcCH_2Rc$ system, new signals of 1 and RcH reappeared accompanied with colour change of the system from yellow–green to deep purple.

In general, the stability of the $Ru^{IV}-X$ (X = Cl, Br, I) bond in the haloruthenocenium cation increases in the order Cl < Br < I. The reason for the stability of the Ru–I bond has been rationalized by the HSAB principle, i.e., Ru as a soft acid in the $Ru^{IV}-X$ bond has an increasing affinity to soft base (I) rather than to hard base atoms (Cl, Br). Therefore, monocation $[Fe^{III}Cp(C_5H_4CH_2C_5H_4)CpRu^{II}]^+$ is oxidized by $RcHI^+Y^-$ (Y = PF_6^-, BF_4^-) or I_2, giving the dication expressed as $[Fe^{III}Cp(C_5H_4CH_2C_5H_4)CpRu^{IV}I]^{2+}$ with stable $Ru^{IV}-I$ bond and the bond prevents the formation of the α-carbonium ion $[Ru^{II}Cp(C_5H_4CH^+\text{-}C_5H_4)CpFe^{II}]$.

Because of the lesser stability of $Ru^{IV}-Cl$ or $Ru^{IV}-Br$ bonds, monocation $[Fe^{III}Cp(C_5H_4CH_2C_5H_4)Cp\text{-}Ru^{II}]^+$ will change easily to $[Fe^{II}Cp(C_5H_4CH^+C_5H_4)\text{-}CpRu^{II}]$ cation on using $RcHCl^+PF_6^-$ or $RcHBr^+PF_6^-$ as an oxidizing reagent because the cation is stabilized by the softer e_{2g} electrons of the Ru^{II} atom ($Ru^{II} \cdots -CH^+-$).

In general, an α-carbonium ion is obtained on treating the metallocenylcarbinol (such as $FcCH_2OH$ and $RcCH_2OH$) in acetic acid with an aqueous solution of an acid such as HBF_4. In the present studies, the $FcCH^+Rc$ cation was prepared easily by oxidation of $FcCH_2Rc$ with $RcHX^+PF_6^-$ (X = Cl and Br), and the stability of the cation is due to the 4d e_{2g} electrons of Ru^{II} rather than to the 3d e_{2g} electrons of Fe^{II}; this

should result in large lower field shifts of ^1H and ^{13}C NMR signals in the Ru^{II} side. Further studies by X-ray diffraction will be necessary to obtain direct evidence for the structure of salt 1.

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