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^{1}H-NMR Spectroscopic Studies on the BiruthenoceniumX$^+$PF$_6^-$ (X; Br, Cl) Salts

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BiruthenoceniumX$^+$PF$_6^-$ salts expressed as [Ru(II)Cp(C_5H_4)(C_5H_4)CpRu(IV)X]$^+$PF$_6^-$ were obtained by oxidizing biruthenocene with FeX$_3$ in HX-NH$_4$PF$_6$ (X; Br, Cl) solution. ^{1}H-NMR spectroscopic studies of the salts suggest the presence of rapid intramolecular electron transfer between the Ru(II) and Ru(IV) atoms at room temperature.

Although a large number of papers on the mixed-valence state of biferrocenium salts and related compounds has been reported,$^{1-4)}$ no report on the mixed-valence state has been reported for biruthenocenium salts, probably because of the practically low yield of biruthenocene. Recently, we have reported that ruthenocene reacts with concentrated sulfuric acid, giving biruthenocene in high yield (about 64%) by radical reaction.$^{5)}$ In the present study, biruthenocene was first oxidized by FeX$_3$, HX and NH$_4$PF$_6$ (X; Br, Cl), and mixed-valence biruthenoceniumX$^+$PF$_6^-$ salts expressed as [Ru(II)Cp(C_5H_4)(C_5H_4)CpRu(IV)X]$^+$PF$_6^-$ were obtained, and the chemical state of two Ru atoms in the salts was investigated by means of NMR spectroscopy.

Biruthenocene was prepared by the method described previously.$^{5)}$ BiruthenoceniumBr$^+$PF$_6^-$ salt was prepared by a similar method to that of ruthenoceniumBr$^+$PF$_6^-$.$^{6)}$ Biruthenocene (1.0 g) was added to 25 cm^3 of 4 mol dm^{-3} HBr containing FeBr$_3$ (4.0 g). The mixture was stirred vigorously for 4 h. The aqueous phase was separated and washed with benzene. A concentrated NH$_4$PF$_6$ solution was added to the deep brown aqueous solution. The crude PF$_6^-$ salt was filtered. Diamagnetic biruthenoceniumBr$^+$PF$_6^-$ salt was obtained as deep red-purple precipitates by the recrystallization from a mixture of acetonitrile and ether.$^{5)}$ Found: C, 35.89; H, 2.92%. Calcd for $C_{20}H_{18}Ru_2BrPF_6$: C, 35.05; H, 2.65%. Deep red-purple biruthenoceniumCl$^+$PF$_6^-$ salt was obtained by a similar method to that used for biruthenoceniumBr$^+$PF$_6^-$ salt except for the use of FeCl$_3$ and HCl instead of FeBr$_3$ and

HBr, respectively. Found: C, 37.22; H, 2.88%. Calcd for $C_{20}H_{18}Ru_2ClPF_6$: C, 37.48; H, 2.83%. ^{1}H-NMR spectra in acetone were measured using a JEOL FX-200 spectrometer at 199.56 Hz.

The ruthenoceniumX$^+PF_6^-$ and biruthenoceniumX$^+PF_6^-$ (X; Br and Cl) salts dissolve in acetone giving yellow-green and deep red-purple solutions, respectively. Large low-field shifts ($\Delta\delta$) of the ^{1}H-signals in Cp-rings are observed for both the ruthenoceniumX$^+PF_6^-$ salts in acetone (1.74-1.83 ppm, as shown in Table 1), as in the case of ^{13}C-CP-MAS NMR spectra of the ruthenoceniumX$^+PF_6^-$ salts in a solid,[7] suggesting bond formation between the Ru(IV) and X^- atoms. The structure of the salts are expressed as $[Cp_2RuX]^+PF_6^-$ (X; Br and Cl). Similar $\Delta\delta$ are observed for biruthenoceniumX$^+PF_6^-$ salts; i.e., the $\Delta\delta$ values for protons of Cp-rings in the salts are found to be 0.88 and 0.83 ppm for the biruthenoceniumBr$^+PF_6^-$ and -Cl$^+PF_6^-$ salts, respectively, suggesting bond formation between the Ru

Table 1. ^{1}H-chemical shifts of ruthenocene, biruthenocene, and their salts in solution

Compound	Temperature	^{1}H-Chemical shift	
	K	δ/ppm	$\Delta\delta$/ppm
Ruthenocene[a]	298	4.51 (C_5H_5)	-
	183	4.51 (C_5H_5)	-
RuthenoceniumBr$^+PF_6^-$[a]	298	6.29 (C_5H_5)	1.78
	183	6.34 (C_5H_5)	1.83
RuthenoceniumCl$^+PF_6^-$[a]	298	6.25 (C_5H_5)	1.74
	183	6.29 (C_5H_5)	1.78
Biruthenocene[a]	298	4.68, 4.44 ($H_{2,5}$, $H_{3,4}$)	
		4.47 (C_5H_5)	-
	183	4.69, 4.43 ($H_{2,5}$, $H_{3,4}$)	
		4.46 (C_5H_5)	-
BiruthenoceniumBr$^+PF_6^-$[a]	298	5.81, 5.48 ($H_{3,4}$, $H_{2,5}$)	
		5.35 (C_5H_5)	0.88
	183	6.38, 5.71 ($H_{3,4}$, $H_{2,5}$)	
		6.00 (C_5H_5)	1.54
		5.32 ($H_{3,4}$,$H_{2,5}$)	
		4.75 (C_5H_5)	0.29
BiruthenoceniumCl$^+PF_6^-$[a]	298	5.76, 5.40 ($H_{3,4}$, $H_{2,5}$)	
		5.30 (C_5H_5)	0.83
	183	6.31, 5.73 ($H_{3,4}$, $H_{2,5}$)	
		5.94 (C_5H_5)	1.48
		5.30, 5.27 ($H_{3,4}$,$H_{2,5}$)	
		4.75 (C_5H_5)	0.29
Ruthenocene[b]	298	5.37 (C_5H_5)	-
RuthenoceniumBr$^+PF_6^-$[b]	298	6.79 (C_5H_5)	1.42
RuthenoceniumCl$^+PF_6^-$[b]	298	6.79 (C_5H_5)	1.42
Biruthenocene[b]	298	5.53, 5.30 ($H_{3,4}$, $H_{2,5}$)	
		5.32 (C_5H_5)	-
BiruthenoceniumBr$^+PF_6^-$[b]	298	6.45, 5.96 ($H_{3,4}$, $H_{2,5}$)	
		6.04 (C_5H_5)	0.72
BiruthenoceniumCl$^+PF_6^-$[b]	298	6.43, 5.96 ($H_{3,4}$, $H_{2,5}$)	
		6.02 (C_5H_5)	0.70

a) Acetone. b) Acetonitrile.

and X atoms. The Δδ (1.42 and 0.70-0.72 ppm) are also found for the ruthenoceniumX$^+$PF$_6^-$ salts and for the biruthenoceniumX$^+$PF$_6^-$ salts in acetonitrile, respectively, although those values are a little smaller than the values in acetone.

The fact that Δδ of the biruthenoceniumX$^+$PF$_6^-$ are about a half of those of ruthenoceniumX$^+$PF$_6^-$ may be interpreted by assuming the possibility of a rapid electron transfer between the two Ru atoms in biruthenoceniumX$^+$PF$_6^-$ in acetone and acetonitrile, although the possibility of interchange in the bonding of X atoms to Ru atoms, as indicated in $\mathrm{Ru(II)^*Cp(C_5H_4)(C_5H_4)CpRu(IV)X]^+PF_6^- \rightleftharpoons [XRu(IV)^*Cp(C_5H_4)(C_5H_4)CpRu(II)]^+PF_6^-}$, cannot be ruled out either based on the temperature-dependence of ^{1}H-NMR spectrum obtained in the present studies.

In order to confirm the conclusion, temperature-dependence ^{1}H-NMR studies of the biruthenoceniumX$^+$PF$_6^-$ salts have been carried out.

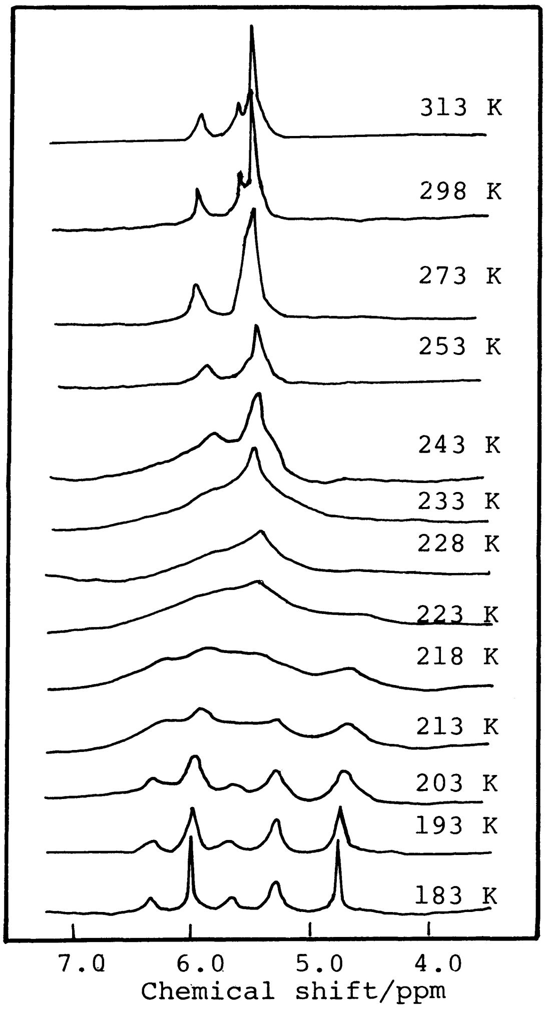

Fig. 1. ^{1}H-NMR spectra of biruthenoceniumBr$^+$PF$_6^-$ salt in acetone at indicated temperatures.

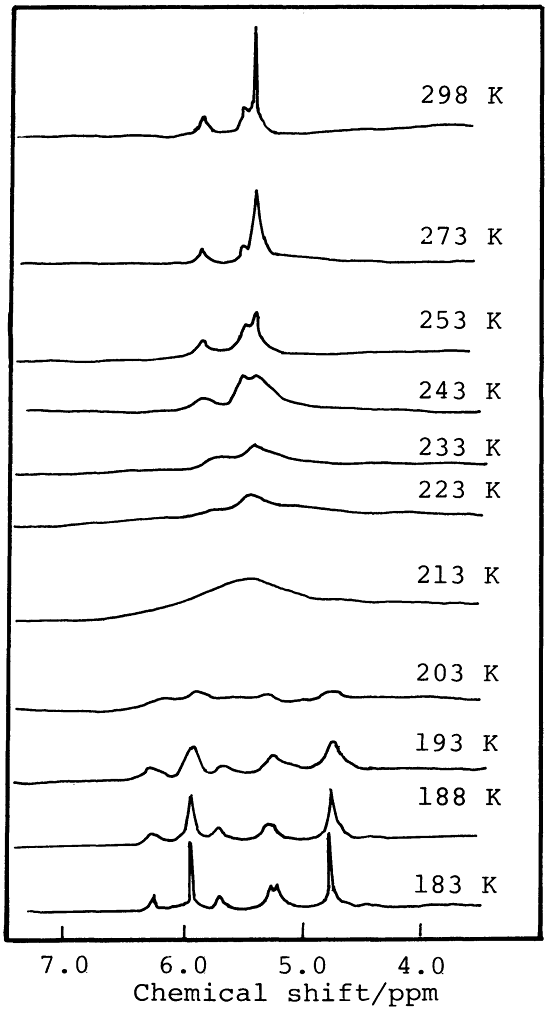

Fig. 2. ^{1}H-NMR spectra of biruthenoceniumCl$^+$PF$_6^-$ salt in acetone at indicated temperatures.

Figures 1 and 2 show the temperature dependent ^{1}H-NMR spectra of biruthenoceniumBr$^+$PF$_6^-$ and -Cl$^+$PF$_6^-$ salts in acetone, respectively. Large temperature dependence of the spectra are observed for both the salts, although no temperature dependence of the spectra is observed for the ruthenocene, biruthenocene and ruthenoceniumX$^+$PF$_6^-$ salts. Upon cooling to 228 K (as shown in Fig. 1), the peaks are broaden for the biruthenoceniumBr$^+$PF$_6^-$. The coalescence temperature (T_C) is found to be about 228 K. In a lower temperature than T_C, sharp lines are observed (at 183 K) and the chemical shift values are found to be 6.38 (2H), 6.00(5H), 5.71(2H), 5.32(4H), and 4.75(5H) ppm. Based on the results of the same study of biruthenocene and ruthenoceniumBr$^+$PF$_6^-$ salt, it may be reasonable to assign the lower field main peak (6.00 ppm) to the Cp-ring proton of [Cp(C_5H_4)Ru(IV)Br]$^+$ moiety and the higher one (4.75 ppm) to that of [Cp(C_5H_4)Ru(II)] moiety. The structure of the biruthenoceniumBr$^+$PF$_6^-$ salt is expressed as [Ru(II)Cp(C_5H_4)(C_5H_4)CpRu(IV)Br]$^+$PF$_6^-$ at 183 K. The life time (τ) at T_C can be estimated using the following equation $\tau = \sqrt{2}/\pi \cdot \Delta\delta_H$, where $\Delta\delta_H$(Hz) is the difference in the chemical shifts of Cp-ring of the [Cp(C_5H_4)Ru(II)] and [Cp(C_5H_4)Ru(IV)Br]$^+$ moieties (1.25 ppm, 249.45 Hz). By using the equation, τ is estimated to be 1.81×10^{-3} (s) for the biruthenoceniumBr$^+$PF$_6^-$ salt. The same observation was also found for the biruthenoceniumCl$^+$PF$_6^-$ salt, but the T_C (213 K) is a little lower and τ is a little longer (1.90×10^{-3} s) than those values of the biruthenoceniumBr$^+$PF$_6^-$, as found in Fig. 2. By using acetonitrile as a solvent, the same temperature dependent ^{1}H-NMR spectra (313-229 K) are also observed for the biruthenoceniumX$^+$PF$_6^-$ salts.

All the results obtained in the present studies indicate clearly that there is an intramolecular electron transfer between the Ru(II) and Ru(IV) atoms in the biruthenoceniumX$^+$PF$_6^-$ salts at room temperature in acetone and acetonitrile, while the exchange rate is gradually decreased at lower temperatures and finally the salts are expressed as a trapped-valence state, [Ru(II)Cp(C_5H_4)(C_5H_4)CpRu(IV)X]$^+$PF$_6^-$, at 183 K in the NMR time scale.

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