Journal of Organometallic Chemistry, *446* (1993) 177–181

JOM 22980

^{1}H, ^{13}C NMR spectroscopic studies of iodoferrocenylruthenocenium$^+$ salts *

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(Received April 17, 1992)

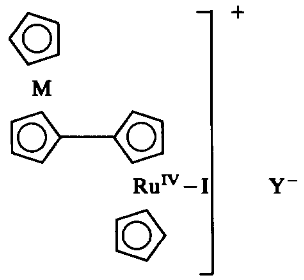
Abstract

Ferrocenylruthenocene is oxidized by iodine giving iodoferrocenylruthenocenium$^+$ I_3^- salt and by iodoruthenocenium(IV)$^+$Y$^-$ (Y = PF_6, BF_4) giving iodoferrocenylruthenocenium$^+$Y$^-$ (Y = PF_6, BF_4) salts. The cation in the solid state is concluded to be $[Fe^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}I]^+$ on the results of ^{57}Fe-Mössbauer and ^{13}C-CP-MAS NMR spectroscopies. The salts are highly soluble in organic solvents giving the green colour characteristic of ferrocenium cations. As the ^{1}H, ^{13}C NMR spectra of the salts in acetone or acetonitrile are temperature-dependent, a strong interaction was inferred between the Ru and Fe atoms in the mixed metal (Ru/Fe) binuclear metallocene system. In acetone the cation is considered to be $[Fe^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}I]^+$ at 183 K and $[Fe^{III}Cp(C_5H_4)(C_5H_4)CpRu^{II}]^+$ at room temperature.

1. Introduction

Recent studies [1–4] of halobiruthenocenium(II,IV)$^+$Y$^-$ salts, $[RcRcX]^+Y^-$ (Rc; ruthenocenyl $C_5H_5RuC_5H_4$, X; Cl, Br, I, Y; PF_6, I_3), in acetone or acetonitrile have revealed a remarkable temperature dependence of ^{1}H, ^{13}C NMR spectra which has been ascribed to their mixed-valence state; *i.e.*, a trapped-valence state, $[Ru^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}X]^+$ at low temperature and an averaged-valence state, $[Ru^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}X]^+ \Leftrightarrow [XRu^{IV}Cp(C_5H_4)(C_5H_4)CpRu^{II}]^+$ or $[Cp(C_5H_4)\text{-}Ru^{III}\text{-}X\text{-}Ru^{III}\text{-}(C_5H_4)Cp]^+$, at higher temperature. A strong interaction is indicated between the Ru^{II}-$(C_5H_4)Cp$ and $[XRu^{IV}(C_5H_4)Cp]^+$ moieties in solution.

Ferrocenylruthenocene, FcRc (Fc; ferrocenyl C_5H_5-FeC_5H_4), first prepared by Neuse and Loonat in 1981 [5], reacts with I_2 giving $FcRcI_4$ as a black salt (**1**, see Scheme 1). Most ferrocenium and biferrocenium salts are paramagnetic, but **1** is diamagnetic from 78 to 300



	M	Y
1	Fe^{II}	I_3
2	Fe^{II}	PF_6
3	Fe^{II}	BF_4
4	Ru^{II}	I_3

Scheme 1.

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* Dedicated to Professor M.G. Voronkov in recognition of his important contributions to organometallic chemistry.

0022-328X/93/$6.00

K in the solid state. Salt **1** is soluble in organic solvents such as acetone or acetonitrile, giving the green colour characteristic of ferrocenium cations (*e.g.*, λ_{max} 640 nm, in acetonitrile) at room temperature. The ferrocene moiety of **1** is evidently rapidly oxidized in solution and the cation can apparently cause some interaction between Ru^{IV} and Fe^{II} in solution by changing the ionic structure from that found in the solid state. This communication reports an investigation by temperature dependent ^1H and ^{13}C NMR spectroscopy in acetone and acetonitrile of the electron transfer phenomena in mixed metal (Ru/Fe) binuclear systems such as **1**, iodoferrocenylruthenocenium$^+PF_6^-$ (**2**) and iodoferrocenylruthenocenium$^+BF_4^-$ (**3**).

2. Experimental details

The compound FcRc, its salt **1** and iodobiruthenocenium$^+I_3^-$ ($[RcRcI]^+I_3^-$, **4**) were obtained by the literature method [4–6]. Salt **2** was prepared by adding FcRc (100 mg; 0.24 mmol in 30 ml of CH_2Cl_2) to a stoichiometric amount of iodoruthenocenium$^+PF_6^-$, $[RcHI]^+PF_6^-$, in 100 ml of CH_2Cl_2. The reaction mixture was stirred for 30 min and the solvent removed. Ruthenocene was extracted in a benzene–hexane mixture. The remaining solid was recrystallized from a CH_2Cl_2–C_6H_{14} mixture to give dark green crystals of **2**. Found: C, 35.10; H, 2.83. $C_{20}H_{18}FeRuIPF_6$ calc.: C, 34.96; H 2.64%. Salt **3** was obtained in a similar manner by using $[RcHI]^+BF_4^-$ in place of $[RcHI]^+PF_6^-$. Found: C, 38.00; H, 2.78. $C_{20}H_{18}FeRuIBF_4$ calc.: C, 38.19; H, 2.88%.

3. NMR spectroscopy

^1H- and ^{13}C-NMR spectra in solution were determined 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 at ±1°C. ^{13}C CP-MAS NMR spectra were recorded under conditions similar to those reported previously [1–3].

4. Results and discussion

Figure 1 shows the temperature-dependence of ^1H NMR spectra of **1**. Chemical shifts are in Table 1. Compound FcRc gives sharp six lines, 4.85 (2H), 4.51 (2H), 4.41 (5H), 4.08 (2H), 4.29 (2H), and 4.04 (5H) ppm. The main peak at higher field (4.41 ppm) has been ascribed to a Cp-ring of the ruthenocene moiety and that at lower field (4.04 ppm) to that of the ferrocene moiety [6]. Although no temperature dependence of ^1H-NMR is found for FcRc or the $[RcHI]^+I_3^-$ salt, strong temperature dependence of the spectra is found for **1** (Fig. 1), with six sharp lines at 6.58 (2H), 6.10 (5H), 5.97 (2H), 5.13 (2H), 5.05 (2H), and 4.29 (5H) ppm at 183 K. Based on the data of the Cp-ring of $[RcHI]^+I_3^-$ (6.43 ppm, at 183 K) salt and **4**, the main signal at 6.10 ppm is ascribed to the Cp-ring of $[Cp(C_5H_4)Ru^{IV}I]^+$ and the other main peak (4.29 ppm) to that of $Cp(C_5H_4)Fe^{II}$. Two kinds of low-field shift ($\Delta\delta_H$) of the main peak in comparison with δ_H values of FcRc (4.41 and 4.04 ppm) are observed for **1**; *i.e.*, one small ($\Delta\delta_H$; 0.25 ppm for ferrocene) and one large ($\Delta\delta_H$; 1.69 ppm for ruthenocene). This means that in acetone at 183 K, only the Ru atom in FcRc is bound with the I atom in **1**, because the Ru atoms in ruthenocene have softer e_{2g} electrons (4d) than those of the Fe atoms (3d) in ferrocene. The slightly increased chemical shift in $[Cp(C_5H_4)Ru^{IV}I]^+$ and the decreased shift in $Cp(C_5H_4)Fe^{II}$ in the salt (compared respectively to those of ruthenoceniumI$^+I_3^-$ and the ferrocene moiety of FcRc) are explained by proposing a weak interaction between the $[Cp(C_5H_4)Ru^{IV}I]^+$ and $Cp(C_5H_4)Fe^{II}$ moieties through the $(C_5H_4)(C_5H_4)$ system in the salt. Upon heating **1** to 255 K in acetone,

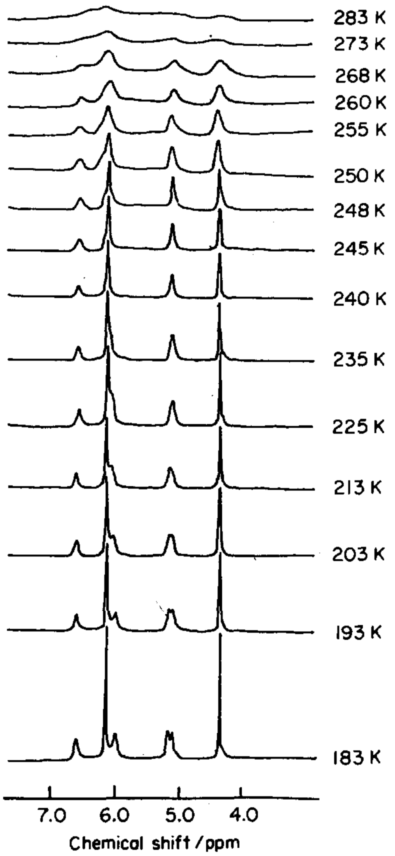

Fig. 1. Temperature-dependent ^1H-NMR spectra of **1** in acetone at indicated temperatures.

TABLE 1. ^{1}H-chemical shifts of FcRc, its salts and related compounds in acetone

Compound	T (K)	Chemical shift (δ_H)	
FcRc	298	4.85, 4.51 ($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Ru^{II}$
		4.41 (C_5H_5)	
		4.08, 4.29 ($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Fe^{II}$
		4.04 (C_5H_5)	
1	183	6.58, 5.97 ($H_{2,5}$, $H_{3,4}$)	$[Cp(C_5H_4)Ru^{IV}I]^+$
		6.10 (C_5H_5)	
		5.05, 5.13 ($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Fe^{II}$
		4.29 (C_5H_5)	
2	183	6.55, 6.00 ($H_{2,5}$, $H_{3,4}$)	$[Cp(C_5H_4)Ru^{IV}I]^+$
		6.08 (C_5H_5)	
		5.06, 5.11 ($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Fe^{II}$
		4.31 (C_5H_5)	
3	183	6.54, 5.95 ($H_{2,5}$, $H_{3,4}$)	$[Cp(C_5H_4)Ru^{IV}I]^+$
		6.06 (C_5H_5)	
		5.06, 5.12 ($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Fe^{II}$
		4.31 (C_5H_5)	
4	183	6.41, 5.76 ($H_{2,5}$, $H_{3,4}$)	$[Cp(C_5H_4)Ru^{IV}I]^+$
		6.05 (C_5H_5)	
		5.33, 5.19 ($H_{2,5}$, $H_{3,4}$)	$Cp(C_5H_4)Ru^{II}$
		4.61 (C_5H_5)	
Ruthenocene	298	4.51 (C_5H_5)	
	183	4.51 (C_5H_5)	
RcRc	298	4.68, 4.44 ($H_{2,5}$, $H_{3,4}$)	
		4.48 (C_5H_5)	
	183	4.69, 4.43 ($H_{2,5}$, $H_{3,4}$)	
		4.46 (C_5H_5)	
$[RcHI]^+I_3$	298	6.38 (C_5H_5)	
	183	6.43 (C_5H_5)	

the peaks are broadened and finally they all disappear at 283 K. The same flattened ^{1}H NMR spectra are also obtained for 1 in acetonitrile at 298 K. Upon cooling to 183 K, sharp ^{1}H NMR lines reappear; *i.e.*, this phenomenon is to be expected for a reversible reaction.

Similar spectral features are also observed in the ^{13}C NMR spectroscopy of 1 (Fig. 2). Chemical shifts are listed in Table 2. Although no temperature dependence of ^{13}C-NMR spectra is found for FcRc (there are sharp seven lines, 87.17 (1C), 71.41 (5C), 70.66 (2C) and 70.20 (2C) for ruthenocene and 85.86 (1C), 69.78 (5C) and 68.10 (4C) for ferrocene), 1 gives a remarkably temperature-dependent ^{13}C-NMR spectrum. Spectra at temperatures above 283 K are almost flat, and six sharp lines are observed at 88.77 (5C), 86.97 (2C), 77.70 (2C), 77.05 (2C), 72.91 (5C) and 71.50 (2C) ppm at 183 K. The main signal at 88.77 ppm is ascribed to the carbon atoms of the Cp-ring in the $[Cp(C_5H_4)Ru^{IV}I]^+$ moiety; this corresponds well to that of 4 (88.64 ppm), and the other main peak at 72.91 ppm to those in $Cp(C_5H_4)Fe^{II}$. Although the C_1 sig-

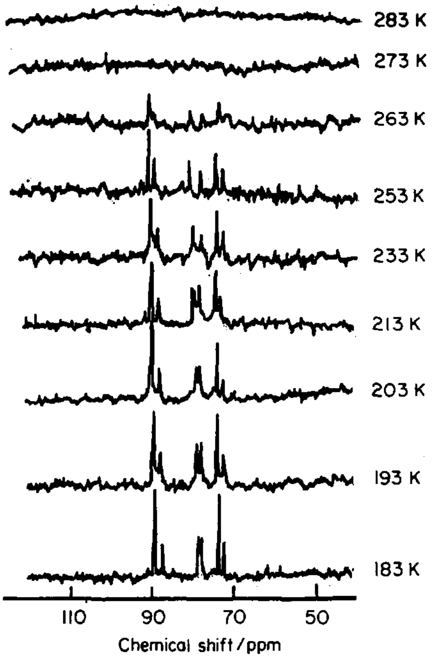

Fig. 2. Temperature-dependent ^{13}C-NMR spectra of 1 in acetone at indicated temperatures.

TABLE 2. ^{13}C-chemical shifts of FcRc, its salts and related compounds in acetone and acetonitrile *

Compound	T (K)	Chemical shift (δ_C)	
FcRc	298	87.17 (C_1)	$Cp(C_5H_4)Ru^{II}$
		71.41 (C_5H_5)	
		70.66, 70.20 ($C_{2,5}$, $C_{3,4}$)	
		85.86 (C_1)	$Cp(C_5H_4)Fe^{II}$
		69.78 (C_5H_5)	
		68.10 ($C_{2,5}$, $C_{3,4}$)	
1	183	86.97, 77.70 ($C_{2,5}$, $C_{3,4}$)	$[Cp(C_5H_4)Ru^{IV}I]^+$
		88.77 (C_5H_5)	
		77.05, 71.50 ($C_{2,5}$, $C_{3,4}$)	$Cp(C_5H_4)Fe^{II}$
		72.91 (C_5H_5)	
2	183	87.17, 78.00 ($C_{2,5}$, $C_{3,4}$)	$[Cp(C_5H_4)Ru^{IV}I]^+$
		88.96 (C_5H_5)	
		77.08, 71.57 ($C_{2,5}$, $C_{3,4}$)	$Cp(C_5H_4)Fe^{II}$
		72.96 (C_5H_5)	
2 *	223	86.55, 77.92 ($C_{2,5}$, $C_{3,4}$)	$[Cp(C_5H_4)Ru^{IV}I]^+$
		88.23 (C_5H_5)	
		76.06, 69.50 ($C_{2,5}$, $C_{3,4}$)	$Cp(C_5H_4)Fe^{II}$
		72.07 (C_5H_5)	
4	183	86.50, 77.01 ($C_{2,5}$, $C_{3,4}$)	$[Cp(C_5H_4)Ru^{IV}I]^+$
		88.64 (C_5H_5)	
		77.45, 72.92 ($C_{2,5}$, $C_{3,4}$)	$Cp(C_5H_4)Ru^{II}$
		74.87 (C_5H_5)	
	308	82.41, 76.28 ($C_{2,5}$, $C_{3,4}$)	$[Cp(C_5H_4)Ru^{III}I]^+$
		83.58 (C_5H_5)	

nals of $[Cp(C_5H_4)Ru^{IV}I]^+$ and $Cp(C_5H_4)Fe^{II}$ are hardly observable because of low intensities, a formula $[Fe^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}I]^+I_3^-$ can be given to **1** in acetone at 183 K.

Comparative studies were carried out for **2** (as shown in Fig. 3) and **3**. Both are very soluble in acetone and acetonitrile giving the same green-coloured solutions. Although neither solution gave ^{1}H-NMR signals at room temperature, sharp six lines were observed in the ^{1}H-NMR spectra of both at 183 K in acetone, and the chemical shifts of the salts corresponded well to those of **1**, *i.e.*, under these conditions the **2** and **3** are $[Fe^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}I]^+Y^-$ (Y; PF_6 and BF_4). These reversible spectral features therefore suggest the chemical reaction takes place on the cation, $[Fe^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}I]^+$, only.

The structures of **1**–**3** in solution at lower temperatures correspond well to the salts in a solid. Figure 4 shows the ^{13}C CP-MAS NMR spectra of **1** and FcRc. In the latter, four sharp lines (88.5, 72.9 ppm for ruthenocene and 84.6, 71.3 ppm for ferrocene) and one shoulder (67.9 ppm) are observed. These signals agree well with the ^{13}C-NMR spectra of FcRc in CD_3COCD_3. Salt **1** gives two broad main peaks (93.6 for ruthenocene and 76.5 ppm for ferrocene) and one shoulder (78.6 ppm). These signals correspond well to the ^{13}C NMR spectra of **1** in acetone at 183 K. *i.e.* the main signal of the lower field (93.6 ppm) is ascribed to the carbon atoms of the Cp-ring in $[Cp(C_5H_4)Ru^{IV}I]^+$ and the other main peak at 76.5 ppm to those in $Cp(C_5H_4)Fe^{II}$. The areal intensity of the higher field signal (76.5 ppm) is larger than that of the lower field one (93.6 ppm) because of overlapping by part of the signal of $[Cp(C_5H_4)Ru^{IV}I]^+$ (77.7 ppm in acetone at 183 K) to that of $Cp(C_5H_4)Fe^{II}$. **1** is concluded to be $[Fe^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}I]^+I_3^-$ when in the solid state.

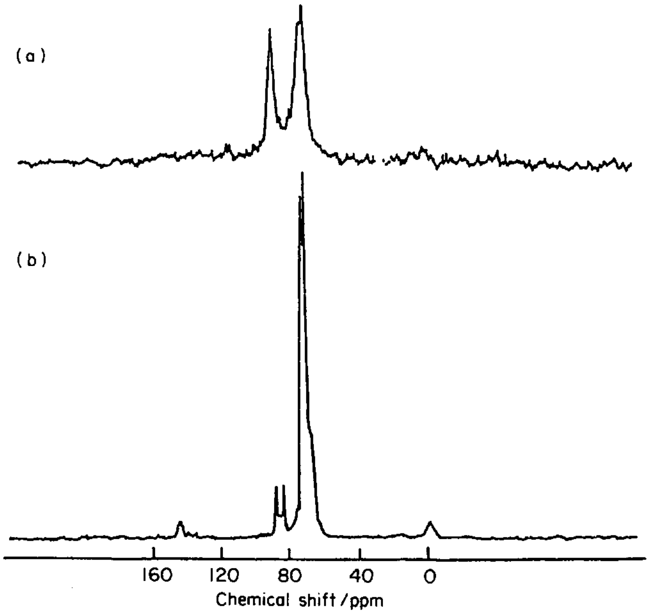

Fig. 4. ^{13}C-CP-MAS NMR spectra of **1** (a) and FcRc (b).

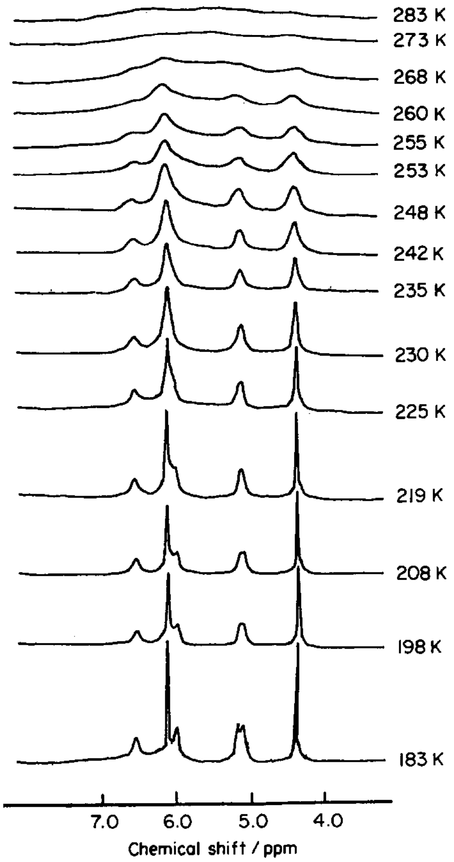

Fig. 3. Temperature-dependent ^{1}H-NMR spectra of **2** at indicated temperatures.

^{57}Fe-Mössbauer spectroscopy of **1** also supports this conclusion. The quadrupole splitting value of **1** was found to be 2.16 mm s^{-1} at both 78 and 300 K, which is smaller than the value of the original FcRc (2.36 mm s^{-1} at 78 K and 2.29 mm s^{-1} at 300 K), because of some interaction between $[(C_5H_4)CpRu^{IV}I]^+$ and $(C_5H_4)CpFe^{II}$ [6]. The absence of both a broad ferrocenium-like singlet line and of an anomalously larger quadrupole split line shows that the Fe atom is neither oxidized by iodine nor bonded to an I atom like iodo[2]ferrocenophanium(IV)$^+I_3^-$ salt [7]. The salt in the solid state is clearly indicated to be $[Fe^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}I]^+$.

As described previously, **1** is soluble in acetonitrile and acetone, giving a green colour characteristic of a ferrocenium salt. Cyclic voltammetry in acetonitrile at room temperature has indicated too that the Fe atom in ferrocene is oxidized more easily than the Ru atom in ruthenocene in FcRc [8]. Because of the paramagnetism of the ferrocenium moiety in **1–3**, no ^{1}H or ^{13}C NMR peaks are observed at room temperature in acetone or acetonitrile.

It has been established that there is a rapid intramolecular electron transfer between the Ru^{II} and Ru^{IV} atoms in **4** in acetone and in other solvents at room temperature, accompanied by the intramolecular exchange of iodine atoms between the Ru^{II} and Ru^{IV} atoms [1,3]. It can be concluded that the Ru atom in **1–3** is easily reduced to $(C_5H_4)CpRu^{II}$, oxidizing $(C_5H_4)CpFe^{II}$ to $[(C_5H_4)CpFe^{III}]^+$. The salts may be concluded to be $[Fe^{III}Cp(C_5H_4)(C_5H_4)CpRu^{II}]^+Y^- \cdot 0.5I_2$ (Y; I_3, PF_6, BF_4) at room temperature. Direct evidence is needed to prove this conclusion, for example, determination of the valence state of Ru atoms using ^{99}Ru NMR spectroscopy.

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