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A novel method for the synthesis of biruthenocene and an NMR spectroscopic study of the products of the reaction of biruthenocene with Lewis acids

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Abstract

Biruthenocene was prepared in a high yield by a radical reaction of ruthenocene in sulfuric acid at 80 °C. Biruthenocene reacts with Fe^{III} salts, HX (X; Br, Cl), and NH₄PF₆, giving diamagnetic biruthenoceniumX⁺PF₆⁻ salts. Based on the ¹³C-CP-MAS, ¹³C-, and ¹H-NMR spectroscopic studies of the salts, it was found that the structure is expressed as [Ru^{II}Cp(C₅H₄)(C₅H₄)CpRu^{IV}X]⁺PF₆⁻ in solid, and there is a rapid intramolecular electron transfer transition between the two Ru atoms, [Ru^{II}Cp^{*}(C₅H₄)(C₅H₄)CpRu^{IV}X]⁺ ⇌ [XRu^{IV}Cp^{*}(C₅H₄)(C₅H₄)CpRu^{II}]⁺, in acetonitrile.

Introduction

Biruthenocene was first prepared from ruthenocene in 1981 by using Ullmann coupling of monoiodoruthenocene by Neuse and Loonat [1]. The yield was too low (≤ 3%) for detailed studies like those of biferrocene and ferrocenylruthenocene [2–6] to the made on the chemistry of its derivatives. Biruthenocene has a structure favorable to studies of the interaction between the two Ru atoms, because the intramolecular distance between the two Ru atoms leaves a possibility of direct interaction between the two Ru atoms in the salts. The present study was planned to find a high-yield synthetic route of biruthenocene in order to provide information on the chemical state of Ru atoms in [biruthenoceniumX]⁺PF₆⁻ (X = Br, Cl) salts by means of ¹³C-CP-MAS, ¹³C-NMR, and ¹H-NMR spectroscopies.

Results and discussion

Ruthenocene is soluble in sulphuric acid, giving a colourless solution. No ESR peak is observed for this solution. On heating, a brown solution results for which a

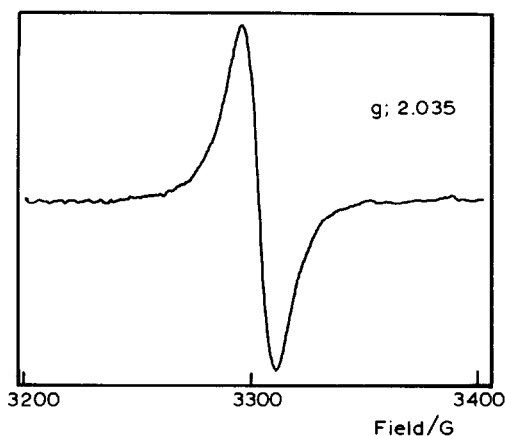
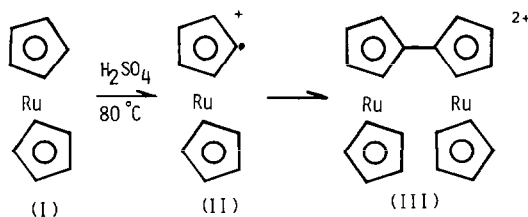


Fig. 1. ESR spectrum of ruthenocene in concentrated sulphuric acid at 80 °C.

broad ESR spectrum is observed (as shown in Fig. 1). This brown solution gives biruthenocene by reduction with TiCl_3 , suggesting that ruthenocene does not give the ruthenocenium cation, $\text{Cp}_2\text{Ru}^{\text{III}+}$, because of instability of this cation [7]. Instead it gives a ruthenocenyl radical cation, $[\text{Cp}(\text{C}_5\text{H}_4)\text{Ru}^{\text{II}}]^+$ (II), which shows a broad ESR line in sulphuric acid. The radical finally gives a biruthenocene dication, $[\text{CpRu}(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_4)\text{RuCp}]^{2+}$ (III), as shown in Scheme 1.

Figure 2 shows the ^{13}C -CP-MAS NMR spectra of biruthenocene (a), biruthenocenium Br^+PF_6^- (b), biruthenocenium Cl^+PF_6^- (c), ruthenocene (d), ruthenocenium Br^+PF_6^- (e), and ruthenocenium Cl^+PF_6^- (f) salts. The chemical shifts of the cyclopentadienyl rings (Cp) carbon atoms in the compounds are listed in Table 1. As mentioned in our previous reports [3,4], anomalously large low-field shifts ($\Delta\delta_{\text{C}}$) of the Cp-ring carbon atoms compared to that of ruthenocene itself ($\Delta\delta_{\text{C}}$; 21.8 and 23.1 ppm, as found in Table 1) are observed for the ruthenocenium X^+ cation ($\text{X} = \text{Br}, \text{Cl}$, respectively). The salts are expressed as $[\text{C}_5\text{H}_5)_2\text{Ru}^{\text{IV}}-\text{X}]^+\text{PF}_6^-$, and typical ^{13}C -CP-MAS NMR spectra are in Fig. 2 (d-f).

On the other hand, two kinds of broad signals were observed for biruthenocenium Br^+PF_6^- ($\delta_{\text{C}} = 91.9, 76.8$ ppm) and biruthenocenium Cl^+PF_6^- ($\delta_{\text{C}} = 92.6$ and 76.1 ppm) salts. Based on the ^{13}C -CP-MAS NMR spectroscopic studies of ruthenocenium X^+PF_6^- salts and the dipolar dephasing ^{13}C -CP-MAS NMR spectroscopic studies of biruthenocenium X^+PF_6^- salts, the smaller values ($\delta_{\text{C}} = 76.8$ and 76.1 ppm) are assigned to the $(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{Ru}$ moiety and the larger one ($\delta_{\text{C}} = 91.9$



Scheme 1

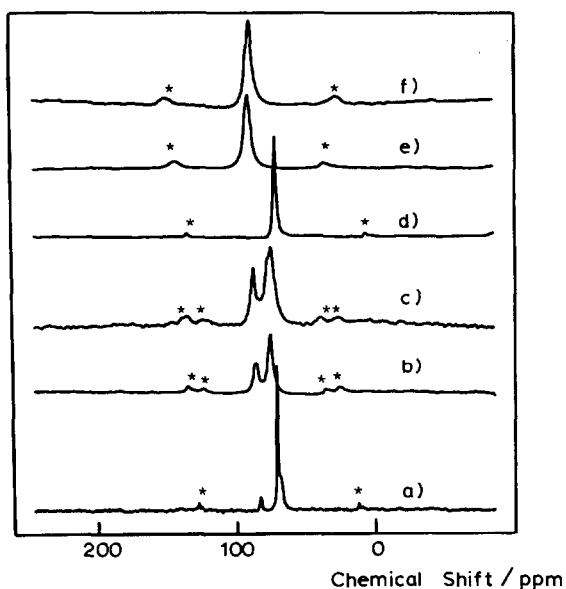


Fig. 2. ^{13}C -CP-MAS NMR spectra of biruthenocene (a), biruthenocenium Br^+PF_6^- (b), biruthenocenium Cl^+PF_6^- (c), ruthenocene (d), ruthenocenium Br^+PF_6^- (e) and ruthenocenium Cl^+PF_6^- (f). Star mark (*) indicates spinning side bands.

and 92.6 ppm) to the $(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{Ru}-\text{X}$ moiety ($\text{X} = \text{Br}$ and Cl), respectively. These facts indicate that the biruthenocenium X^+PF_6^- salts may be expressed as $[\text{Ru}^{\text{II}}\text{Cp}(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_4)\text{CpRu}^{\text{IV}}-\text{X}]^+\text{PF}_6^-$ in solid state. The explanation for the

Table 1

^{13}C - and ^1H -chemical shifts of biruthenocene, ruthenocene and their salts in a solid and in acetonitrile

Compound	^{13}C -Chemical shift				^1H -Chemical shift in CD_3CN	
	Solid		in CD_3CN			
	$\delta_{\text{C}}/\text{ppm}$	$\Delta\delta_{\text{C}}/\text{ppm}$	$\delta_{\text{C}}/\text{ppm}$	$\Delta\delta_{\text{C}}/\text{ppm}$	$\delta_{\text{H}}/\text{ppm}$	$\Delta\delta_{\text{H}}/\text{ppm}$
Biruthenocene ^a	87.5(C_1) 7.23($\text{C}_5\text{H}_5, \text{C}_{2,5}$) 69.1($\text{C}_{3,4}$)	-	86.9(C_1)vw 70.7($\text{C}_{2,5}$) 70.3(C_5H_5) 68.9($\text{C}_{3,4}$)	-	5.53($\text{H}_{2,5}$) 5.32(C_5H_5) 5.30($\text{H}_{3,4}$)	-
Biruthenocenium Br^+PF_6^-	91.9(C_5H_5) 80.6sh 76.8(C_5H_5)	19.6 4.5	92.3(C_1)vw 82.6($\text{C}_{2,5}$) 82.0(C_5H_5) 75.5($\text{C}_{3,4}$)	11.7	6.45($\text{H}_{2,5}$) 6.04(C_5H_5) 5.96($\text{H}_{3,4}$)	0.72
Biruthenocenium Cl^+PF_6^-	92.6(C_5H_5) 80.2sh 76.1(C_5H_5)	20.3 3.8	92.3(C_1)vw 83.1($\text{C}_{2,5}$) 82.0(C_5H_5) 75.8($\text{C}_{3,4}$)	11.7	6.43($\text{H}_{2,5}$) 6.02(C_5H_5) 5.96($\text{H}_{3,4}$)	0.70
Ruthenocene ^a	73.2(C_5H_5)	-	70.2(C_5H_5)	-	5.37(C_5H_5)	-
Ruthenocenium Br^+PF_6^- ^b	95.3(C_5H_5)	22.1	93.9(C_5H_5)	23.7	6.79(C_5H_5)	1.42
Ruthenocenium Cl^+PF_6^- ^b	97.1(C_5H_5)	23.9	95.7(C_5H_5)	25.5	6.79(C_5H_5)	1.42

^a From ref. 3. ^b From ref. 9.

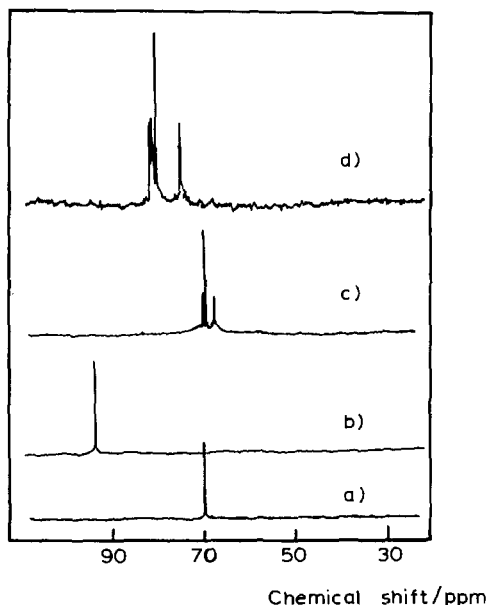


Fig. 3. ^{13}C NMR spectra of ruthenocene (a), ruthenocenium Br^+PF_6^- (b), biruthenocene (c) and biruthenocenium Br^+PF_6^- (d) compounds in acetonitrile solution.

slightly increased chemical shifts (3–5 ppm) in the $(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{Ru}$ moiety and for decreased one (3–5 ppm) in the $[(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{Ru}-\text{X}]^+$ moiety in the biruthenocenium $^+\text{PF}_6^-$ salts compared to those of biruthenocene and ruthenocenium X^+PF_6^- salts, is that there is some intramolecular electron transfer from $(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{Ru}$ to $[(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{Ru}-\text{X}]^+$ moieties through the fulvenide system, $(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_4)$.

The biruthenocenium X^+PF_6^- salts dissolves well in acetonitrile giving a deep red-purple solution. Figures 3 and 4 show the ^{13}C and ^1H NMR spectra of ruthenocene (a), ruthenocenium Br^+PF_6^- (b), biruthenocene (c), and biruthenocenium Br^+PF_6^- (d) compounds, respectively, while their chemical shift values are summarized in Table 1. As in the case of ^{13}C -CP-MAS NMR spectrum, low-field of the ^{13}C - and ^1H -chemical shifts in Cp-ring of the salts are observed. The facts that chemical shift values of Cp-ring carbon and proton atoms in $(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{Ru}$ moiety are equivalent to those values of $[(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{Ru}-\text{X}]^+$ moiety in the PF_6^- salts and the low-field shift values of the biruthenocenium X^+PF_6^- ($\Delta\delta_{\text{C}} = 11.7$ and $\Delta\delta_{\text{H}} = 0.72$ ppm for the biruthenocenium Br^+PF_6^-) are about half those of ruthenocenium X^+PF_6^- ($\Delta\delta_{\text{C}} = 25.5$ and $\Delta\delta_{\text{H}} = 1.42$ ppm for carbon and proton in Cp-ring for the ruthenocenium Br^+PF_6^-), respectively, suggest that possibility of a rapid electron transfer between the two ruthenocenium atoms in acetonitrile; $[\text{Ru}^{\text{II}}\text{Cp}^*(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_4)\text{CpRu}^{\text{IV}}\text{X}]^+\text{PF}_6^- \rightleftharpoons [\text{X}-\text{Ru}^{\text{IV}}\text{Cp}^*(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_4)\text{CpRu}^{\text{II}}]^+\text{PF}_6^-$.

All the results obtained in the study lead us to the conclusion that the structure of the biruthenocenium X^+PF_6^- salts is expressed as $[\text{Ru}^{\text{II}}\text{Cp}(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_4)\text{Cp}-\text{Ru}^{\text{IV}}\text{X}]^+\text{PF}_6^-$ in solid, and there is a rapid intramolecular electron transfer transi-

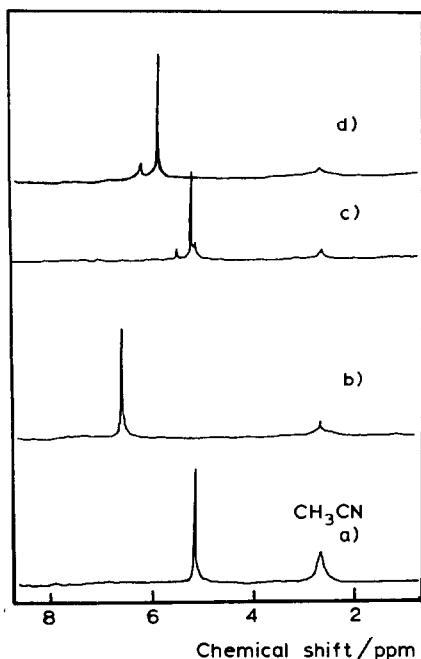


Fig. 4. ^1H NMR spectra of ruthenocene (a), ruthenocenium Br^+PF_6^- (b), biferrocene (c) and biruthenocenium Br^+PF_6^- (d) compounds in acetonitrile solution.

tion with exchange of X atoms between the Ru^{II} and Ru^{IV} atoms in the salts in acetonitrile solution.

Experimental

Preparation of biruthenocene

Ruthenocene (2.0 g, 0.087 mol) was dissolved in concentrated sulphuric acid (10 ml) at room temperature. The resulting colourless solution turns deep brown on heating at ca. 80°C . After allowing the solution to stand for 30 min. the solution was poured into ice-water with a large excess of TiCl_3 , losing its colour. Crude biruthenocene was extracted from the colourless solution with benzene. Biruthenocene was purified by column chromatography on alumina. Ruthenocene was first eluted by a mixture of hexane and benzene (3:1). Biruthenocene was eluted by a mixture of hexane and benzene (1:1). Light yellow biruthenocene was recrystallized in the same solution (1.3 g, 0.028 mol; yield 64%). Found: C, 52.11; H, 3.94. $\text{C}_{20}\text{H}_{18}\text{Ru}_2$ calcd.: C, 52.16; H, 3.94%. ^1H -NMR (CDCl_3): 4.51(s), 4.67(t), 4.47 (t)ppm. (lit (CDCl_3): 4.50(s), 4.68 (t), 4.48 (t)ppm.) ^{13}C -NMR(CDCl_3): 70.9, 71.3, 69.6, 87.5 ppm.

Preparation of biruthenocenium X^+PF_6^- salts

Biruthenocenium Cl^+PF_6^- salt was prepared by a similar method as that used to prepare ruthenocenium Cl^+PF_6^- [8]. Biruthenocene (1.0 g) was added to 25 ml of 4 mol/l HCl containing FeCl_3 (4.0 g). The mixture was stirred vigorously for 4 h. The water layer was separated and washed with benzene. A concentrated NH_4PF_6

solution was added to the deep brown water solution. The crude PF_6^- salt was filtered. A diamagnetic biruthenocenium Cl^+PF_6^- salt was obtained by recrystallization from a mixture of acetonitrile and ether as deep red-purple precipitates. Found: C, 37.22; H, 2.88. $\text{C}_{20}\text{H}_{18}\text{Ru}_2\text{ClPF}_6$ calcd.: C, 37.48; H, 2.83%. A deep red-purple biruthenocenium Br^+PF_6^- salt was obtained by a similar method to that used for biruthenocenium Cl^+PF_6^- salt except for the use of FeBr_3 and HBr instead of FeCl_3 and HCl , respectively. Found: C, 35.89; H, 2.92. $\text{C}_{20}\text{H}_{18}\text{Ru}_2\text{BrPF}_6$ calcd.: C, 35.05; H, 2.65%.

NMR spectroscopy

The ^{13}C -CP-MAS NMR spectra were obtained under the same conditions as those reported previously [2–5]. Chemical shift values were measured with respect to external adamantane and then converted to the shift values from TMS. Both the ^1H - and ^{13}C -NMR spectra in solution were determined using a Jeol FX-200 spectrometer at 200.0 and 50.1 MHz, respectively, using TMS as a standard. The assignment of the ^{13}C signals in ^{13}C -CP-MAS NMR spectroscopy of the compounds was carried out using ^{13}C -NMR and dipolar dephasing techniques.

ESR spectroscopy

X-band ESR spectra of ruthenocene in concentrated sulphuric acid were observed using a Jeol JES-PE-3X ESR spectrometer at room temperature.

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