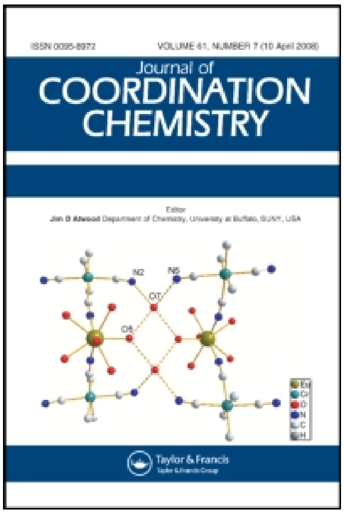

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Preparation of 1',1'''-Diethylbiruthenocene and a Study of the Mixed Valence State of Iodo-1',1'''-Diethylbiruthenocenium(II,IV)+I$^-_3$ by ^{1}H-NMR Spectroscopy

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PREPARATION OF 1′,1‴-DIETHYLBIRUTHENOCENE AND A STUDY OF THE MIXED VALENCE STATE OF IODO-1′,1‴-DIETHYLBIRUTHENOCENIUM(II,IV)$^+$I$_3^-$ BY ^{1}H-NMR SPECTROSCOPY

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1′,1‴-Diethylbiruthenocene(II), prepared from biruthenocene *via* diacetylbiruthenocene(II), is oxidized by iodine to give the iodo-1′.1‴-diethylbiruthenocenium(II,IV)$^+$I$_3^-$ salt. The temperature dependence of the ^{1}H-NMR spectra observed for the salt in acetone suggests the rate of electron transfer between the Ru^{II} and Ru^{IV} decreases as compared with that in iodo-1,1″-biruthenocenium(II,IV)$^+$I$_3^-$ owing to steric hindrance caused by the ethyl groups.

Keywords: Ruthenocene, 1′,1‴-diethylbiruthenocene, mixed-valence states, nmr

INTRODUCTION

We have recently reported novel syntheses of 1,1″-biruthenocene, RcRc, and its oxidation products in the mixed-valence state halobiruthenocenium(II,IV) hexafluorophosphate salts, $[\mathrm{RcRcX}]^+\mathrm{PF}_6^-$ for X = Br, Cl.[1–3] Although the salts hold trapped valence states at lower temperatures, the remarkable temperature dependencies of ^{1}H-NMR spectra observed for their acetone solutions support the suggestion that the valence states are averaged between the formal Ru^{II} and Ru^{IV} centres at higher temperatures. Electron transfer between Fe^{II} and Fe^{III} in mixed-valence biferrocenium systems is affected much by dialkyl substitution on the cyclopentadienyl (Cp) ring.[4–7] This communication reports the effect of diethyl substitution on the electron transfer between Ru^{II} and Ru^{IV} in iodo-1′,1‴-diethylbiruthenocenium(II,IV) triiodide, $[\mathrm{RcRcEt_2I}]^+\mathrm{I}_3^-$, 1, investigated by 90 MHz ^{1}H-NMR spectroscopy in acetone-d_6 solution.

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EXPERIMENTAL

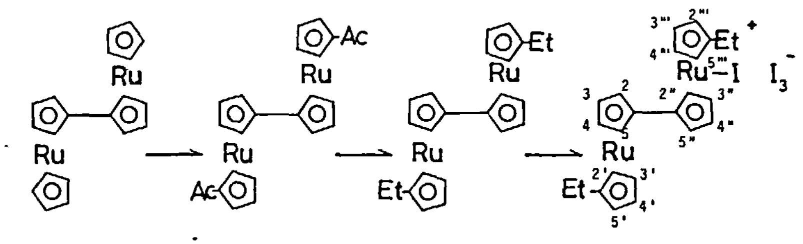
The preparations of 1′,1‴-diethylbiruthenocene, $RcRcEt_2$, and related compounds are illustrated in Scheme 1.

Preparation of 1′,1‴-diacetylbiruthenocene

1,1″-Biruthenocene, RcRc, (2.0 g) dissolved in methylene chloride (200 cm^3) was placed in a 3-necked flask. Acetic chloride (0.7 cm^3) and borontrifluoride-diethyl ether (5.0 cm^3) in methylene chloride (100 cm^3) were dropped into the solution from a stoppered funnel at 0°C over a period of 1 h. The resulting solution was refluxed for 10 h under a nitrogen atmosphere. The reaction mixture was poured into an aqueous solution of sodium carbonate. The organic phase extracted with benzene was washed with dilute hydrochloric acid, then water, dried, and the solvent evaporated. The residues were dissolved in methylene chloride and transferred to an alumina column for chromatography. The first fraction of a pale yellow band eluted with benzene contained RcRc. After this band, monoacetylbiruthenocene was obtained by using a benzene-diethyl ether (2:1) mixture as eluant. The crude product was recrystallized from hexane-benzene (1:2) mixture to give yellow crystals (1.2 g, Yield: 55%). Anal.: Calcd. for $C_{22}H_{20}ORu_2$: C, 52.58; H, 4.01%. Found: C, 52.38; H, 4.16%. ^{1}H-NMR($CDCl_3$): $\delta = 5.01$ (2H, t), 4.73 (2H, t). 4.70 (2H, t), 4.68 (2H, t), 4.50 (4H, t), 4.47 (5H, s), 2.08 (3H, s) ppm. ^{13}C-NMR($CDCl_3$): $\delta = 201.49$, 91.66, 87.17, 76.24, 73.84, 73.64, 73.32, 73.12, 72.02, 71.88, 28.83 ppm. The third fraction eluted with a benzene-diethyl ether-methanol (5:5:1) mixture gave 1′,1‴-diacetylbiruthenocene, which was recrystallized from a benzene-hexane (1:1) mixture as yellow crystals (0.6 g, Yield: 25%). Anal.: Calcd. for $C_{24}H_{22}O_2Ru_2$: C, 52.93; H, 4.07%. Found: C, 53.09; H, 4.02%. ^{1}H-NMR($CDCl_3$): $\delta = 5.01$ (4H, t), 4.72 (4H, t), 4.69 (4H, t), 4.55 (4H, t), 2.03 (6H, s) ppm. ^{13}C-NMR($CDCl_3$): $\delta = 201.24$, 89.32, 87.17, 76.32, 73.98, 73.65, 72.74, 28.92 ppm.

Preparation of $RcRcEt_2$

1′,1‴-Diacetylbiruthenocene (2.0 g) was added to a dry ether solution (100 cm^3) of anhydrous aluminum chloride (5.0 g) and lithium aluminum hydride (2.0 g); the yellow colour of the solution immediately faded. After water was added to the solution, the organic phase extracted with benzene was washed with water, dried, and the solvent evaporated. The residues were dissolved in methylene chloride and transferred to an alumina column for chromatography. The first fraction of a pale yellow band eluted



Scheme 1

with hexane-benzene (1:1) mixture contained 1',1'''-diethylbiruthenocene. The crude product was recrystallized from benzene-hexane (1:2) mixture to give pale yellow crystals (1.5 g, Yield: 79%). Anal.: Calcd. for $C_{24}H_{26}Ru_2$: C, 55.80; H. 5.07%. Found: C, 55.87; H, 5.09%. ^{1}H-NMR($CDCl_3$): $\delta = 4.64$ (4H, t), 4.45 (4H, t), 4.41 (4H, t), 4.36 (4H, t), 2.07 (4H, q), 1.00 (6H, t) ppm. ^{13}C-NMR($CDCl_3$): $\delta = 97.13$, 88.94, 73.16, 72.08, 72.03, 71.68, 23.49, 17.12 ppm.

Preparation of 1

Compound **1** was prepared by the following method. $RcRcEt_2$ (100 mg) was dissolved in dry hexane (100 cm^3). To this solution a solution of hexane-benzene (1:1; 200 cm^3) with iodine (114 mg) was added. The solution was stirred for 1 h, and the solvent then evaporated. Compound **1** was obtained by recrystallization of the residues from acetonitrile-ether (1:2) mixture to give brown crystals (136 mg, Yield: 65%). Anal.: Calcd for $C_{24}H_{26}Ru_2I_4$: C, 28.14; H, 2.56%. Found: C, 27.95; H, 2.60%. Optical spectrum in CH_3CN: 291 nm ($\varepsilon = 20900\,M^{-1}\,cm^{-1}$), 362 (12900), 490^{sh} (2400).

Measurements

^{1}H-NMR spectra of $[RcRcEt_2I]^+I_3^-$ and $[RcRcI]^+I_3^-$ salts in acetone-d_6 were recorded on a JEOL FX-90 spectrometer at 90 MHz using TMS as standard. An NM-VTS unit was used to control the probe temperatures in the range 183 K to 333 K with an accuracy of at least ±1°C.

RESULTS AND DISCUSSION

In order to investigate the effect of the ethyl groups in **1**, temperature-dependent 90 MHz ^{1}H-NMR spectroscopy of **1** was carried out in CD_3COCD_3; spectra are shown in Figure 1a along with those observed for $[RcRcI]^+I_3^-$, **2**, (Figure 1b). ^{1}H chemical shift values (δ) are listed in Table I. Although those of **1** are more complicated due to the ethyl groups than those of **2**, both series of the spectra exhibit remarkable temperature dependencies, supporting the suggestion that the Ru^{II}–Ru^{IV} trapped valence state at 183 K is averaged with increasing temperature as in the case of $[RcRcX]^+PF_6^-$ (X = Cl, Br) systems.[1]

The imbalanced trapped valence state of **1** is reflected in the spectrum observed at 183 K. In comparison with the spectrum observed for **2**,[3] the eight bands (4–7 ppm region) are assigned as follows: 6.41 (2H), 5.90 (2H) ppm to the Cp-ring protons $H_{2'',5''}$ and $H_{3'',4''}$; 6.11 (2H) and 5.95 (2H) ppm to $H_{2''',5'''}$ and $H_{3''',4'''}$; 5.39 (2H) and 5.21 (2H) to $H_{2,5}$ and $H_{3,4}$; 4.65 (2H) and 4.53 (2H) to $H_{2',5'}$ and $H_{3',4'}$. The methyl and methylene signals of the ethyl groups also suffer effects of imbalanced valence states of the Ru atoms. The signal centred at 2.56 ppm is assigned to the methylene protons on the Ru^{IV} side, whereas that of those on the Ru^{II} side is overlapped with the signals of acetone-d_6. The triplet at 1.00 ppm assigned to the methyl protons at Ru^{II} and Ru^{IV} sides is broadened. The broadening of the signal is due not only to the chemical shift difference of the methyl protons on the Ru^{II} and Ru^{IV} sides, but also to some dynamic behavior. Upon heating, the Cp bands broaden, and the coalescence temperature, Tc, for the $H_{2',5'}$, $H_{3',4'}$ and $H_{2''',5'''}$, $H_{3''',4'''}$ is 254 K.

At higher temperatures than Tc, the bands due to the Cp, methylene, and methyl

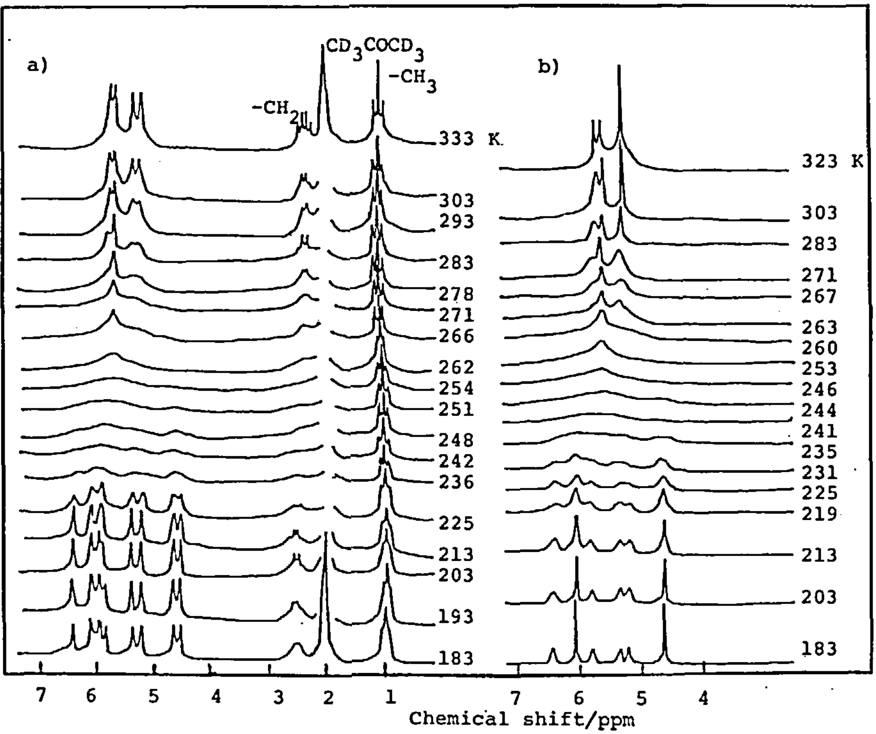


FIGURE 1 Temperature-dependent 90 MHz NMR spectra of **1**(a) and **2**(b) at indicated temperatures.

TABLE I
^{1}H-Chemical shifts of RcRcEt$_2$ and related compounds in acetone and chloroform[a] at indicated temperatures.

Compound	Temp./K	Chemical shifts δ/ppm	
RcRcEt$_2$[a]	298	4.64, 4.45, 4.41 4.36	
		2.07 ($-CH_2-$), 1.00 ($-CH_3$)	
1	183	6.41, 6.11, 5.95, 5.90	$[(C_5H_4)(C_5H_4C_2H_5)Ru^{IV}I]^+$
		5.39, 5.21, 4.65, 4.53	$(C_5H_4)(C_5H_4C_2H_5)Ru^{II}$
		2.56 ($-CH_2-$), 1.00 ($-CH_3$)	
	333	5.71, 5.67, 5.34, 5.21	
		2.30 ($-CH_2-$), 1.08 ($-CH_3$)	
RcRc[a]	298	4.68, 4.44, 4.48	
2	183	6.41, 5.76, 6.05	$[(C_5H_4)(C_5H_5)Ru^{IV}]^+$
		5.33, 5.19, 4.61	$(C_5H_4)(C_5H_5)Ru^{II}$
	323	5.72, 5.62, 5.30	

protons sharpen, with no chemical shift difference between the Ru^{II} and Ru^{IV} sides; the bands at 5.71 and 5.67 ppm are assigned to the Cp-ring protons of ($H_4C_5-C_5H_4$), at 5.34 and 5.21 ppm to those of $-(C_5H_4C_2H_5)(C_5H_4C_2H_5)-$, 2.33 ppm to $-CH_2-$ and 1.08 ppm to $-CH_3$ of the ethyl groups at 333 K. Hence, the iodo-1′,1‴-diethylbiruthenocenium cation takes an averaged valence state of $[(C_5H_4C_2H_5)(C_5H_4)Ru^{III}$-$I$-$Ru^{III}(C_5H_4)(C_5H_4C_2H_5)]^+$; *i.e.*, electrons transfer between the Ru^{II} and Ru^{IV} atoms in the salt. The lifetime, τ, for the $H_{2'-5'}$, $H_{2'''-5'''}$ signals is estimated to be 3.47 ms at Tc from the equation, $\tau = 2^{0.5}/\pi\Delta\delta$, where $\Delta\delta$ (1.44 ppm, 129.6 Hz) is the difference of the chemical shift for the signals at 183 K. The value of Gibbs free energy of activation at Tc, $\Delta G^\ddagger$(Tc) is $49.9 \pm 0.2\,kJ\,mol^{-1}$ from the calculation reported previously.[3,8]

In order to estimate the values of Tc, τ, and $\Delta G^\ddagger$(Tc) for **2**, temperature-dependent 90 MHz NMR spectroscopy was carried out, as shown in Figure 1b. As already shown in our previous report of ^1H-NMR spectra of **2** at 200 MHz, six and three sharp lines are observed at 183 K and 323 K, respectively.[3] The Tc of the main signals is at *ca* 246 K and the values of τ and $\Delta\ G^\ddagger$(Tc) are estimated to be 3.47 ms and $48.3 \pm 0.2\,kJ\,mol^{-1}$ (1.56 ms and $48.0 \pm 0.2\,kJ\,mol^{-1}$ at 200 MHz, respectively). The larger $\Delta G^\ddagger$(Tc) and higher Tc values are found for **1**.

Computer simulation spectra of the temperature-dependent spectra of **1** and **2** are shown in Figures 2a and b, respectively, by using the modified Bloch equation method to obtain the activation parameters. The activation energy, Ea, for **1** was obtained from the usual method from plots of log κ ($\kappa = 1/\tau$) *versus* T^{-1}, as shown in Figure 3a, and the value is found to be $39.2 \pm 0.6\,kJ\,mol^{-1}$. The values of $\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at 298 K are found to be $52.2 \pm 0.2\,kJ\,mol^{-1}$, $36.7 \pm 0.6\,kJ\,mol^{-1}$ and -12.4 ± 0.6 e.u. Although good linear plots are also obtained for **2**, the slope of the line is smaller than that for **1** (see Figure 3b), giving the smaller Ea ($36.5 \pm 0.6\,kJ\,mol^{-1}$), $\Delta G^\ddagger$

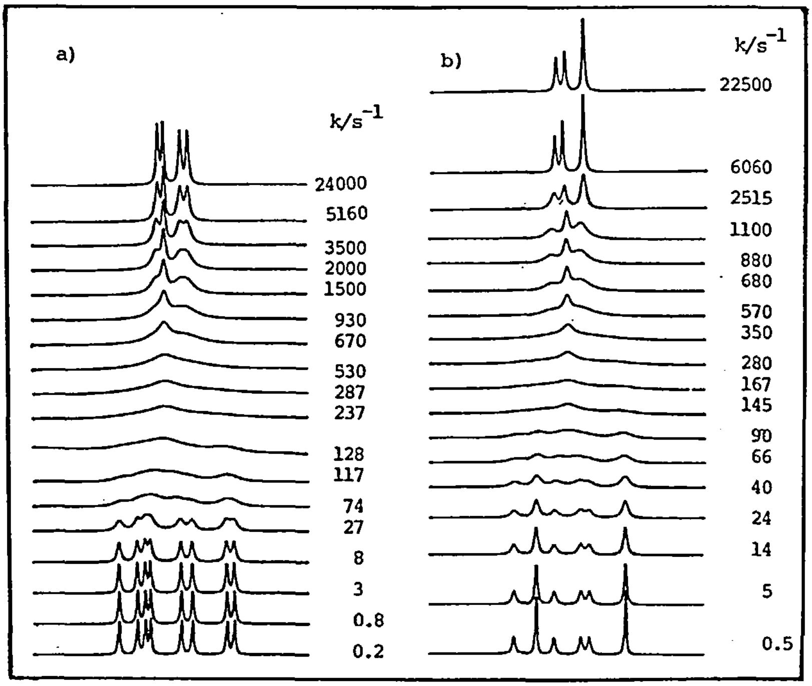


FIGURE 2 Calculated ^1H NMR spectra of **1**(a) and **2**(b).

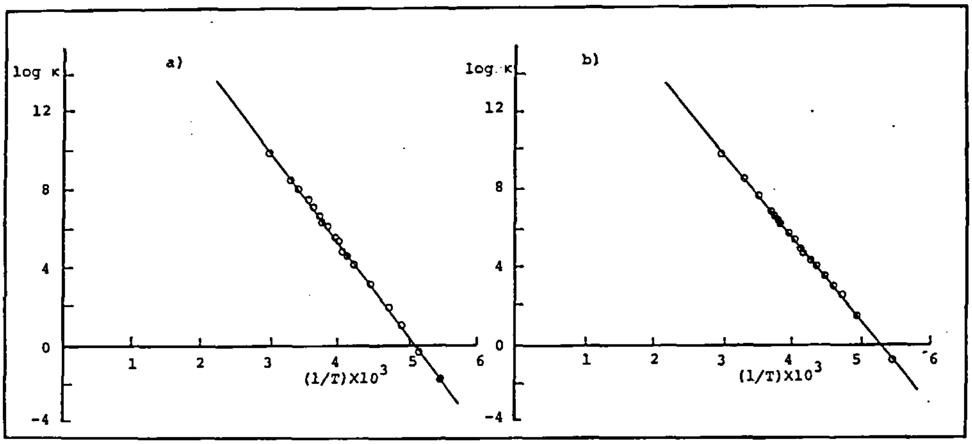


FIGURE 3 Arrhenius plots of log κ *versus* 1/T for 1(a) and 2(b).

(49.1 ± 0.2 kJ mol^{-1}) and $\Delta H^{\ddagger}$ (34.0 ± 0.6 kJ mol^{-1}) values as compared to **1**. No ^{1}H-NMR change *versus* concentration change of **1** and **2** (0.01–0.0001 mol dm^{-3}) was observed within the range 183–333 K. Therefore, there occurs an intramolecular electron exchange reaction between the Ru^{II} and Ru^{IV} atoms in **1** and **2** salts, and the rate for **1** is smaller than for **2**.

Compared with the case of the biferrocenium system, where the intramolecular electron transfer between the Fe^{II} and Fe^{III} is accelerated by the presence of ethyl groups on the Cp-ring, electron transfer between Ru^{II} and Ru^{IV} is retarded in the biruthenocenium system. This may be due to the difference in the electron transfer mechanism between the biferrocenium and the biruthenocenium systems. In the former, the electron transfer occurs through the conjugated (H_4C_5–C_5H_4) grouping, while the transfer should be accompanied by exchange of iodide between Ru^{II} and Ru^{IV} in the latter system; $[IRu^{IV}Cp'(H_4C_5{-}C_5H_4)Cp'Ru^{II}]^+ \rightleftharpoons [Ru^{II}Cp'(H_4C_5{-}C_5H_4)Cp'Ru^{IV}I]^+$. The precence of the ethyl groups on the terminal Cp groups may sterically hinder the iodide exchange.

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