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PREPARATION OF 1,3-DITHIA[3]RUTHENOCENOPHANE DERIVATIVES AND THEIR BRIDGE REVERSAL ENERGY BARRIERS

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Summary

Several new ruthenocenophanes were prepared and their bridge reversal energy barriers were studied by a variable temperature NMR method. The bridge reversal energy barrier of 1,3-dithia-2,2-dimethyl[3]ruthenocenophane ($\Delta G^{\ddagger}$ 47.3 kJ mol^{-1}) is larger than that of the corresponding ferrocenophane ($\Delta G^{\ddagger}$ 42.8 kJ mol^{-1}). This is attributable mainly to the difference in inter-ring distance between the ruthenocene and ferrocene nuclei.

Introduction

It is well known that [3]ferrocenophanes are fluxional molecules and include bridge reversal processes. Variable temperature NMR (VTNMR) studies of these compounds were recently interpreted as indicating the nature of the medium-sized system [1–3]. Abel et al. reported that the free energies of activation ($\Delta G^{\ddagger}$) for the bridge reversal processes in 1,2,3-trithia[3]ferrocenophane and in [3]ferrocenophane were 80.1 [3] and 40.4 kJ mol^{-1} [2], respectively. Furthermore, they investigated a torsional barrier about the carbon–chalcogen and chalcogen–chalcogen bonds in [3]ferrocenophane derivatives. The structure of ruthenocenophane is quite similar to that of ferrocenophane, and the distance between the two cyclopentadienyl (Cp) rings in ruthenocene [4] is slightly longer than that in ferrocene [5]. So, it is interesting to determine whether such a difference has any influence on the bridge reversal processes of ruthenocenophanes. Therefore, we prepared 1,3-dithia[3]ruthenocenophane derivatives (**3–6**) and studied the bridge reversal barriers in these compounds.

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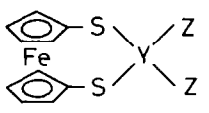
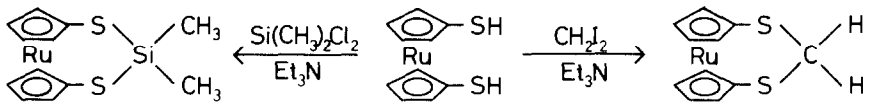
Results and discussion

It has been reported [1] that ferrocene-1,1′-dithiol reacts with diiodomethane, acetone, dichlorodimethylsilane, and benzophenone to give **1a**–**1d**, respectively. This



1a: Y=C , Z=H
1b: Y=C , Z=CH_3
1c: Y=Si , Z=CH_3
1d: Y=C , Z=Ph

method has been applied to the syntheses of the proposed compounds **3**–**6**. 1,3-Dithia[3]ruthenocenophane (**3**) and 1,3-dithia-2,2-dimethylsilyl[3]ruthenocenophane (**4**)



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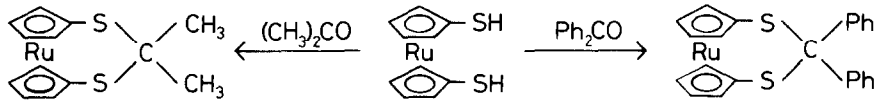
were obtained in moderate yields by the reaction of ruthenocene-1,1′-dithiol (**2**) with diiodomethane and dichlorodimethylsilane, respectively, in the presence of triethylamine. Also, 1,3-dithia-2,2-dimethyl[3]ruthenocenophane (**5**) and 1,3-dithia-2,2-diphenyl[3]ruthenocenophane (**6**) were prepared by the condensation of **2** with acetone



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and benzophenone in the presence of *p*-toluenesulfonic acid monohydrate, in 40 and 97% yields, respectively. The structures of the new compounds were determined on the basis of their elemental analyses, ^{1}H NMR and mass spectra.

In order to calculate the energy barrier in the bridge reversal process, VTNMR techniques were used. The rate constant k was calculated from the following equation [6]:

$$k = \pi\Delta\nu/\sqrt{2}$$

where $\Delta\nu$ is the frequency separation of resolved signals at the temperature at which the bridge reversal was stopped on the NMR time scale. The energy barrier $\Delta G^{\ddagger}$ was calculated from the following equation [7]:

$$\Delta G^{\ddagger} = 2.303RT_c(10.319 - \log_{10}k + \log_{10}T_c)$$

where $R = 8.314$ J mol^{-1} deg^{-1} and T_c is the coalescence temperature.

The 90 MHz ^{1}H NMR spectrum of 1,3-dithia-2,2-dimethyl[3]ruthenocenophane (**5**) in toluene-d_8/CS_2 (1/1) at -102°C showed singlets at δ1.16 and 1.80 ppm (6H, protons of two methyl groups), multiplets at δ 3.78 and 4.48 ppm (4H, α-ring protons), and multiplets at δ 4.48 and 4.41 ppm (4H, β-ring protons). With an increase in the temperature of the sample solution, the individual signals of the two methyl groups collapsed to a broad signal at -40°C, as shown in Fig. 1. Above this temperature the broad line became a sharp singlet. The temperature dependence of

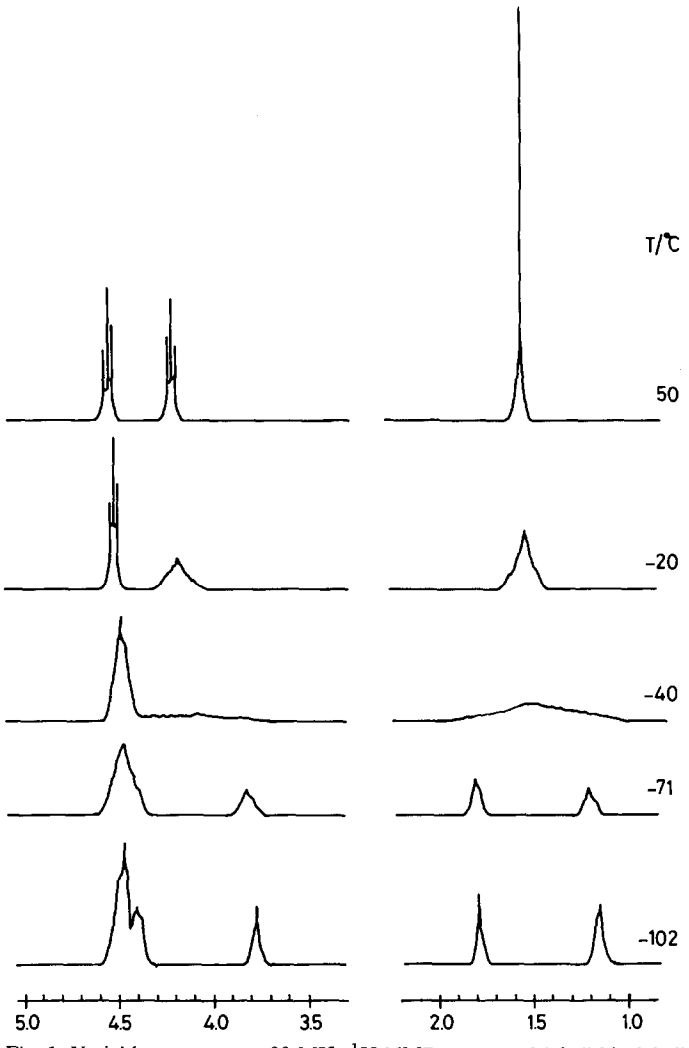

Fig. 1. Variable temperature 90 MHz ^{1}H NMR spectra of 1,3-dithia-2,2-dimethyl[3]ruthenocenophane in toluene-d_8/CS_2.

the signals of the methyl groups is well elucidated by the change in the environment of the two methyl groups resulting from ring inversion between conformations A and B (see Fig. 2). On the basis of the chemical shift at -102°C ($\Delta\nu$ 63.0 Hz) and

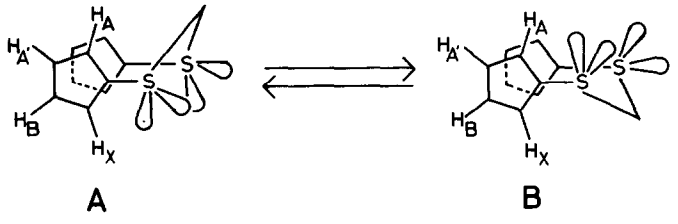

Fig. 2. Bridge reversal mechanism of [3]ruthenocenophane.

the coalescence temerature (T_c 233 K), the bridge reversal energy barrier for the interconversion is calculated to be $\Delta G^{\ddagger}$ 47.0 kJ mol^{-1}. The bridge reversal energy barrier was also calculated from the VTNMR study of the Cp-ring protons. The ^{1}H NMR signals of the α-ring protons of **5** showed multiplet resonance at δ3.78 and 4.48. The signals of the Cp-ring protons displayed a transition from the AA'BX pattern at -102°C to an AA'XX' pattern (each triplet (J 1.8 Hz) at δ 4.23 and 4.57 ppm) at 50°C. As the temperature of the solution was raised, the AX part due to the H_A and H_X protons of the AA'BX pattern of the CP-ring protons collapsed and coalesced into a broad peak at -40°C, as shown in Fig. 1. The bridge reversal barrier was calculated to be $\Delta G^{\ddagger}$ 47.3 kJ mol^{-1} ($\Delta\nu$ 56.7 Hz, T_c 233 K, k 126) from the behavior of the Cp-ring proton signals. The bridge reversal energy barrier of **5** which was obtained from the Cp-ring proton signals of the VTNMR spectra is in fair agreement with the results obtained from the spectral change of the methyl group part.

The ^{1}H NMR spectrum of 1,3-dithia-2,2-dimethylsilyl[3]ruthenocenophane (**4**) in toluene-d_8/CS_2 (1/1) at room temperature consisted of two singlets at δ 4.34 and 0.41 ppm attributed to the Cp-ring protons and the methyl protons, respectively. With decreasing temperature of the sample solution, the signal of the methyl groups broadened and coalesced to give one broad peak at δ 0.30 (T_c 176 K). At -101°C, the peak of the methyl groups separated into two peaks, although the latter remained broad. Therefore, we could not obtain an accurate value of the bridge reversal energy barrier for **4**. However, the T_c (176 K) and $\Delta\nu$ (> 14.4 Hz) data show that the energy barrier for the bridge reversal process of **4** is less than 37.3 kJ mol^{-1}. A similar tendency for the temperature dependence of the ^{1}H NMR spectrum of **4** was observed in the spectral changes in the Cp-ring proton region. The AA'BX pattern of the Cp region failed to "a freeze out" bridge reversal process at -101°C, due to the low temperature limit of the NMR instrument used. Therefore, the bridge reversal barrier was calculated to be < 36.6 kJ mol^{-1} ($\Delta\nu$ > 51.3 Hz, T_c 182 K). As shown in Fig. 3, the ^{1}H NMR spectrum of 1,3-dithia[3]ruthenocenophane (**3**) at temperatures below -59°C consisted of an AB-type quartet at δ 3.31 and 4.48 ppm for the methylene protons and signals of a poorly separated AA'BX-type quartet at δ 4.18 and 4.73–4.91 ppm for the Cp-ring protons. The maximum separation of the two inner peaks for the methylene protons was 90 Hz, and the coupling constant was 14.3 Hz. When the temperature was raised above -30°C, the peaks of the quartet due to the methylene protons started to converge and became one single broad peak at -10°C. When the temperature was increased above 27°C, the peak sharpened and remained constant up to the highest temperature studied (90°C). The bridge reversal energy barrier of **3** was calculated only from the change of the signals of the methylene protons because the peaks of the Cp-ring protons were poorly separated.

As shown in Fig. 4, the ^{1}H NMR spectrum of 1,3-dithia-2,2-diphenyl[3]-ruthenocenophane (**6**) at -90°C gave the expected signals of an AA'BX pattern for the Cp-ring protons in an intensity ratio of 1 (δ 3.54 ppm)/1 (δ 4.61 ppm)/2 (δ 4.79 ppm). When the temperature was raised to ambient, the signals at δ 3.54 and 4.79 ppm broadened and coalesced to give one triplet peak. As shown in Table 1, the bridge reversal energy barrier of **6** was calculated from the spectral changes of its Cp-ring protons. At low temperatures, the anisotropic effect of the phenyl group on the α-proton of the Cp-ring on the same side as the phenyl group will be larger than that on the α-ring protons on the other side and that on the β-ring protons because

the bridge reversal process of the ruthenocenophane is stopped on the NMR time scale. However, at high temperatures, the bridge reversal was speeded up and the signals due to the α-ring protons on the same side as the phenyl group could not be distinguished from the other α-ring protons. Indeed, upon raising the temperature, the peaks at δ 3.54 and 4.79 ppm broadened and coalesced to give one triplet peak at δ 4.15 ppm. When the temperature was raised further, the two peaks at δ 4.61 and 4.79 ppm became a sharp triplet at δ 4.70 ppm. Therefore, it is clear that the triplet signal at the higher field in the Cp-region corresponds to the α-protons of the Cp-ring of **6**.

It is interesting to compare the bridge reversal energy barriers determined for 1,3-dithia[3]ruthenocenophane derivatives with those of the analogous ferrocenophanes. For example, the energy barrier (52.3 kJ mol^{-1}) for the conformational inversion of 1,3-dithia[3]ruthenocenophane is considerably greater than that reported for 1,3-dithia[3]ferrocenophane (47.2 kJ mol^{-1}) [3]. Similar results were also obtained in the case of 1,3-dithia-2,2-dimethyl[3]ruthenocenophane (47.3 kJ mol^{-1}) and the corresponding ferrocenophane (42.8 kJ mol^{-1}) [3]. The results were expected

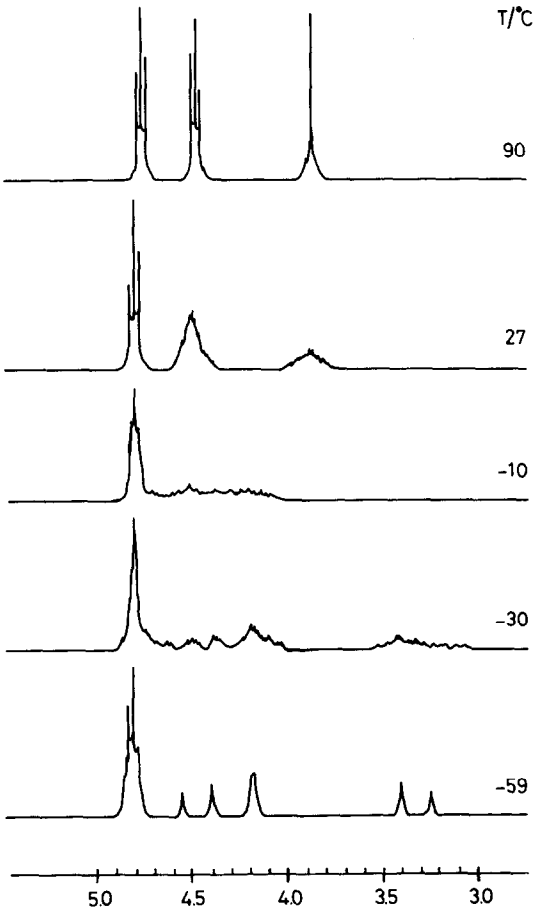

Fig. 3. Variable temperature 90 MHz ^{1}H NMR spectra of 1,3-dithia[3]ruthenocenophane in $CDCl_3$.

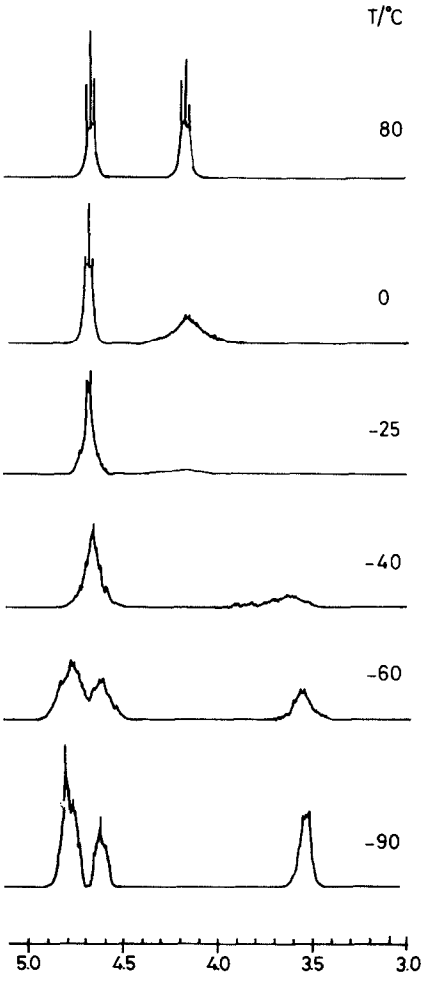

Fig. 4. Variable temperature 90 MHz ^{1}H NMR spectra of 1,3-dithia-2,2-diphenyl[3]ruthenocenophane in CD_2Cl_2 (Cp-ring region).

TABLE 1

ENERGY BARRIERS OF THE BRIDGE REVERSAL PROCESSES IN 1,3-DITHIA[3]RUTHENOCENOPHANES [a]

Compound	Solvent	T_c(K)	ν(Hz)	k	$\Delta G^{\ddagger}$(kJ mol^{-1})
$Cp_2RuS_2CH_2$	$CDCl_3$	263	105.3	234	52.3
(3)		(263)	(58.5)	(130)	(53.5)
$Cp_2RuS_2Si(Me)_2$	$C_6D_5CD_3/CS_2$	176	> 14.4	> 32.0	< 37.3
(4)	(1/1)	(182)	(> 51.3)	(> 114.0)	(< 36.6)
$Cp_2RuS_2C(Me)_2$	$C_6D_5CD_3$-CS_2	233	63.0	140	47.0
(5)	(1/1)	(233)	(56.7)	(126)	(47.3)
$Cp_2RuS_2C(Ph)_2$	CD_2Cl_2	(248)	(110.0)	(244)	(49.0)
(6)					

[a] The values in parentheses are the results obtained from the Cp-ring protons. The coalescence observed in the Cp-ring protons is complex (see Figs. 1,3 and 4) and the calculated values are approximate.

in view of the obviously longer distance between the two Cp-rings in the ruthenocenophane nucleus compared with that in the ferrocene nucleus [4,5]. This explanation is also supported by the following evidence: the 1,3-dithia-2,2-dimethylsilyl[3]ruthenocenophane shows a lower bridge reversal energy barrier (37.3 kJ mol^{-1}) than that of 1,3-dithia-2,2-dimethyl[3]ruthenocenophane (47.3 kJ mol^{-1}) because the length of the C–S bond (1.82 Å) is shorter than that of the S–Si bond (2.15 Å) [8]. Finally, the coalescence temperature (T_c) of 1,2,3-trithia[3]-ruthenocenophane (443 K in DMSO-d_6) was higher than that of 1,2,3-trithia[3]ferrocenophane (394 K in $C_6D_5NO_2$) [3]. This observation is in good agreement with the above discussion.

Experimental

All reactions were carried out in an atmosphere of nitrogen. Ruthenocene-1,1′-dithiol (**2**) was prepared according to the method reported previously [9]. The other reagents and solvents employed were commercially available. All melting points are uncorrected. The ^1H NMR spectra were obtained on a JEOL FX-90 spectrometer, TMS being chosen as the internal standard, and the VTNMR spectra were recorded on a JEOL NM-PVTS1 unit. Mass spectra were taken on a Hitachi M-80 spectrometer.

*1,3-Dithia[3]ruthenocenophane (**3**)*

Diiodomethane (0.5 g, 1.87 mmol) and triethylamine (0.5 ml, 3.66 mol) were added to a solution of **2** (0.218 g, 0.734 mmol) in 30 ml of anhydrous benzene. The solution was heated to reflux for 6 h. Precipitates of triethylammonium iodide were filtered off and the filtrate was concentrated in vacuo. The residue was recrystallized from benzene/hexane to give 0.102 g (45%) of yellow-brown crystals, m.p. 217.0–218.0°C. Anal.: Found: C, 43.29; H, 3.31. $C_{11}H_{10}S_2{}^{101}Ru$ calcd.: C, 42.98; H, 3.29%. MS (70 eV): *m/z* 308 (M^+, 100%). ^1H NMR ($CDCl_3$): δ 3.62–4.04 (2H, m), 4.48 (4H, broad peak), 4.78 (4H, t, *J* 1.8 Hz).

*1,3-Dithia-2,2-dimethylsilyl[3]ruthenocenophane (**4**)*

Dichlorodimethylsilane (0.25 ml, 2.06 mmol) was added by syringe to a solution of **2** (0.203 g, 0.687 mmol) in 30 ml of anhydrous benzene, followed by the slow addition of a solution of triethylamine (0.5 ml, 3.61 mmol) in 5 ml of anhydrous benzene. The solution was stirred for 45 min at room temperature. The precipitated triethylammonium chloride was filtered off and the filtrate was concentrated in vacuo. The residue was recrystalized from hexane to give 0.233 g (97%) of white-yellow crystals, m.p. 218.0–219.0°C. Anal.: Found: C, 40.96; H, 4.03. $C_{12}H_{14}S_2Si^{102}Ru$ calcd.: C, 41.00; H, 4.01%. MS (70 eV): *m/z* 352 (M^+, 100%). ^1H NMR (toluene-d_8/CS_2): δ 0.41 (6H, s) and 4.34 (8H, s) ppm.

*1,3-Dithia-2,2-dimethyl[3]ruthenocenophane (**5**)*

Acetone (0.8 ml, 10.9 mmol) and a few crystals of *p*-toluenesulfonic acid monohydrate were added to a solution of **2** (0.296 g, 0.996 mmol) in 50 ml of anhydrous benzene. The solution was heated to reflux for 5 h. Excess acetone and water were removed by distillation until a total volume of ca. 10 ml was attained and the remaining solvent was removed in vacuo. Recrystallization from benzene gave

0.214 g (64%) of yellow crystals, m.p. 179.0–180.0°C. Anal.: Found: C, 46.63; H, 4.12. $C_{13}H_{14}S_2{}^{101}Ru$ calcd.: C, 46.55; H, 4.22%. MS (70 eV): m/z 336 (M^+, 100%). ^1H NMR ($CDCl_3$): δ 1.76 (6H, s), 4.46 (4H, t, J 1.8 Hz), 4.84 (4H, t, J 1.8 Hz).

*1,3-Dithia-2,2-diphenyl[3]ruthenocenophane (**6**)*

Benzophenone (1.28 g, 7.30 mmol) and a few crystals of *p*-toluenesulfonic acid monohydrate were added to a solution of **2** (0.197 g, 0.668 mmol) in 35 ml of anhydrous benzene. The solution was heated to reflux for 6 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel using toluene/hexane (2/1 v/v) as the eluent. Recrystallization from benzene/hexane gave 0.123 g (40%) of yellow-green crystals, m.p. 230.0–243.0°C (dec).

Anal.: Found: C, 59.88; H, 4.00. $C_{23}H_{18}S_2{}^{101}Ru$ calcd.: C, 60.11; H, 3.95%. MS (70 eV): m/z 460 (M^+, 100%). ^1H NMR ($CDCl_3$): δ 4.19 (4H, broad peak), 4.68 (4H, t, J 1.8 Hz), and 7.18–7.60 (m, 10H).

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