Conformational Changes of 1,2,3-Triselena- and 1,2,3-Trithia-[3](1,1′)ruthenocenophane

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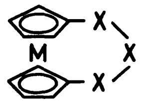
Synopsis. 1,2,3-Triselena[3](1,1′)ruthenocenophane was obtained by the reaction of 1,1′-dilithioruthenocene with selenium powder in 22% yield. The energy barriers of the bridge reversal inversion of 1,2,3-triselena- and 1,2,3-trithia[3](1,1′)ruthenocenophane are 78.8 and 91.5 kJ mol^{-1}, respectively.

It is well-known that [3](1,1′)metallocenophanes are fluxional molecules and include bridge reversal processes. The high-temperature NMR spectra of 1,2,3-tricalcogena[3](1,1′)ferrocenophanes and their derivatives were recently interpreted as indicating the rigid nature of their medium-sized ring system.$^{1)}$ For example, the activation energies required for the interconversion of 1,2,3-trithia[3](1,1′)ferrocenophane (**1**) and 1,2,3-triselena[3](1,1′)ferrocenophane (**2**) were estimated to be 80.3 and 68.4 kJ mol^{-1}, respectively. The difference in the activation energy between the two compounds is mainly attributable to the bond length of their bridge rings. In this connection, we have previously reported on the bridge reversal energy barriers of [3](1,1′)ruthenocenophane derivatives$^{2)}$ containing calcogen atoms in the bridge. However, the bridge reversal energy barriers of 1,2,3-trithia[3](1,1′)ruthenocenophane (**3**) and 1,2,3-triselena[3](1,1′)ruthenocenophane (**4**) have not previously been reported. It seemed interesting to compare the bridge reversal energy barriers of the metallocenophanes **1**, **2**, **3**, and **4**. Therefore, we prepared compound **3** and **4** and investigated the bridge reversal barriers in these ruthenocenophanes.



1: M=Fe, X=S
2: M=Fe, X=Se
3: M=Ru, X=S
4: M=Ru, X=Se

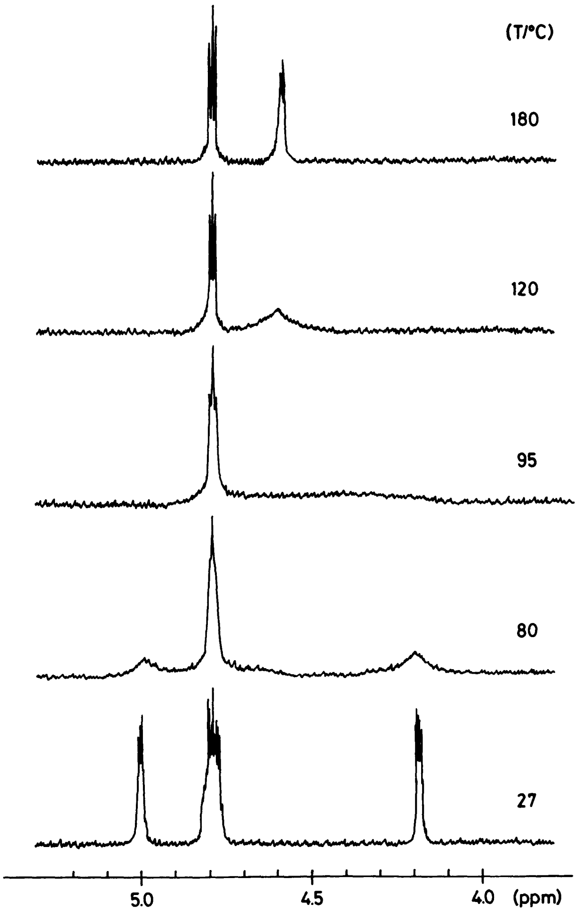


Fig. 1. Variable temperature 90 MHz ^{1}H NMR spectra of 1,2,3,-triselena[3](1,1′)ruthenocenophane in DMSO-d_6.

The reaction of 1,1′-dilithioruthenocene, which was prepared from ruthenocene and butyllithium in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), with selenium gave 1,2,3-triselena[3](1,1′)ruthenocenophane (**4**) in 22% yield. The ^{1}H NMR spectrum of **4** in DMSO-d_6 showed the cyclopentadienyl (Cp) ring protons as an AMM′X pattern at δ 4.19, 4.79 and 5.00 as shown in Fig. 1, supporting the assigned structure. The multiplet at the highest field was assigned for H_X, due to the shielding effect of the lone pair electrons of the sulfur atoms located at the 1- and 3-positions in the bridge. Similarly, the lowest one was assigned for H_A. When the temperature was raised, these two multiplet peaks were broadened and coalesced at 95.2 °C. Above this temperature (180 °C) the broad peak due to H_α becomes sharp triplet. Also, the multiplet peak due to H_M at δ 4.79 was sharpened. The temperature dependence of the AMM′X pattern is in line with the exchange between the two α-ring protons, environments resulting from the bridge reversal inversion among conformer A and B (Fig 2). The rate of exchange k^1 at the temperature of coalescence T_c was calculated according to Gutowsky and Holm's method, from the Eq. 1,$^{3)}$ where $\Delta\nu$ is the frequency separation of the resolved signals at room temperature.

$$k^1 = \pi\Delta\nu/\sqrt{2}, \tag{1}$$

$$k^1 = \kappa\frac{kT}{h}\exp\left(\frac{-\Delta G^{\neq}}{RT}\right). \tag{2}$$

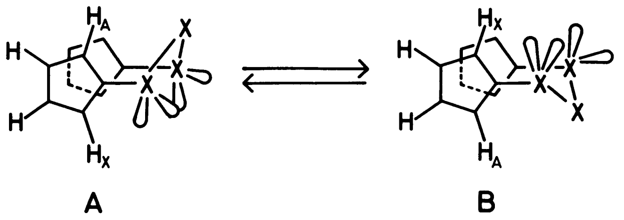
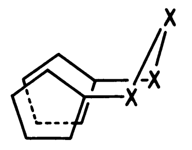


Fig. 2. Bridge reversal mechanism of [3](1,1′)metallocenophane.

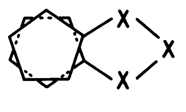
The values of $\Delta G^{\neq}$ were derived from the Eyring Eq. 2,[4] a unit transmission coefficient (k^1) being assumed. Equation 2 was transformed to Eq. 3 for the purpose of calculation.

$$\Delta G^{\neq} = 2.303RT_c(10.319 - \log_{10} k^1 + \log_{10} T_c) \qquad (3)$$

When T_c=368 K, $k^1(\mathrm{s}^{-1})$=161, and $\Delta\nu$(Hz)=72.6, the energy barrier for **4** was calculated to be about 75.2± 0.3 kJ mol^{-1}. This value is considerably greater than that of the bridge reversal barrier (67.2 kJ mol^{-1}) of corresponding ferrocenophane (**2**). This result is explainable by the fact that the distance between the two Cp rings of the ruthenocene nucleus was slightly longer than that of the ferrocene nucleus.[5,6] That is to say, the greater the angle of the bridge (X–X–X), the harder the bridge reversal. As shown in Fig. 3, the ^{1}H NMR spectra of 1,2,3-trithia[3](1,1′)ruthenocenophane (**3**) in DMSO-d_6 at room temperature also showed an AMM′X pattern at δ 4.28, 5.00, and 5.12. When the temperature was raised, the two multiplets of the H_A and H_X were broadened to ultimately coalesce at 170 °C. The bridge reversal barrier of **3** was calculated to be 91.5 kJ mol^{-1} ($\Delta\nu$=68.1 Hz, T_c=443 K, k^1=151 s^{-1}). The energy barrier was considerably greater than that of **4**. This result was in good agreement with the study previously reported by Abel et al. (1981).[1] They suggested that the bridge reversal barriers of [3](1,1′)-metallocenophane were correlated with the bridge length (Cp–X–X–X–Cp) determined from the covalent radii. That is, the longer the bridge length, the easier the inversion of the bridge. As the bridge length (8.56 Å) of **4** is longer than that (7.78 Å) of **3**, the value of the bridge reversal barrier of **4** is lower than that of **3**.



I



II

Conformations I and II were possible as the low temperature limited conformation. For example, the structure of 1,2,3-trithia[3](1,1′)ferrocenophane took an eclipsed conformation I in a solid state and the energy of the staggered conformation II had to be higher than that of the eclipsed conformation I. Furthermore, in the [3](1,1′)ferrocenophanes, it has been proved and reported that the conformation I is the low temperature limiting conformation.[1] The conformation II is rather regarded as the transition state in the fluxional process. Accordingly, the 1,2,3-tricalcogena[3](1,1′)ruthenocenophanes (**3** and **4**) must take an eclipsed conformation as the low temperature limiting conformation.

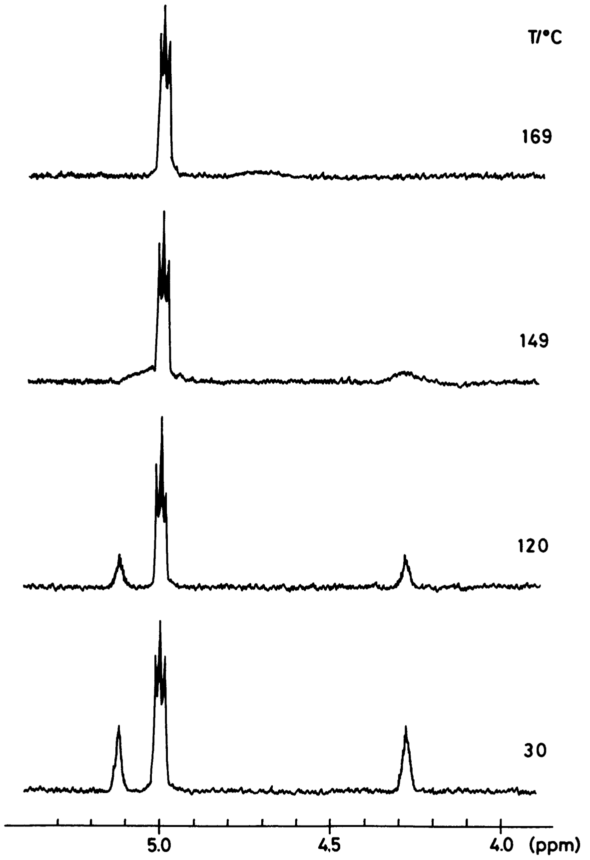


Fig. 3. Variable temperature 90 MHz ^{1}H NMR spectra of 1,2,3,-trithia[3](1,1′)ruthenocenophane in DMSO-d_6.

Experimental

1,2,3-Trithia[3](1,1′)ruthenocenophane (**3**) was prepared according to the previously reported method.[7] The variable temperature 90 MHz ^{1}H NMR of **3** and **4** were recorded in DMSO-d_6, on a JEOL FX-90 spectrometer, TMS being chosen as the internal standard. Mass spectra were taken on a Hitachi M-80 spectrometer. The melting point was not corrected.

1,2,3-Triselena[3](1,1′)ruthenocenophane (4). To a solution of ruthenocene (3.5 g, 15.2 mmol) in hexane (200 ml) was added a solution of TMEDA (5.6 ml, 37.7 mmol) and butyllithium (78.1 mmol) in hexane (50 ml) under nitrogen at a refluxing temperature. After the mixture was refluxed for 2 h, 1,2-dimethoxyethane (150 ml) and selenium powder (7.0 g, 88.6 mmol) were added to the mixture, and then refluxed for 16 h. After the mixture was cooled to room temperature, 10 ml of water was added. The supernatants were decanted and the residue was extracted with hot hexane until the extracts became colorless. The supernatants and the extracts were combined and concentrated in vacuo and the residue was chromatographed on activated alumina using a benzene : hexane (2:5) solution as the eluant. The yellow third fraction was collected and concentrated in vacuo. The residue was recrystallized from hexane to give **4** as yellow plates in 22% yield, mp, 219.5—220.5 °C. Found: C, 25.96; H, 1.86%. Calcd for $C_{10}H_8RuSe_3$: C, 25.77; H, 1.73%. MS (70 eV), *m/z* 466 (M^+).

References

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