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Preliminary communication

SYNTHESES OF POLYTHIA[*n*] RUTHENOCENOPHANES

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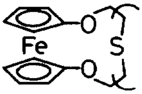
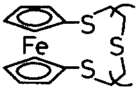
Summary

Thiacrown ethers containing ruthenocene as a subunit were synthesized by the reaction of 1,1′-bis(3-chloropropyl-1-thia)ruthenocene with disodium dithiolates in THF/EtOH. In these reactions, some unexpected products were obtained.

A great number of macrocyclic compounds containing an oxygen, sulfur, nitrogen or phosphorus atom as an electron donor heteroatom have been synthesized [1]. Recently, ferrocenocrown ethers (for example, **1** and **2**) [2—5] have received considerable attention because the iron atom may play a role as a coordinatable heteroatom. However, to the best of the authors' knowledge, no mention has been made in the literature about the syntheses of ruthenocenocrown ethers except our previous paper [6]. In that paper, we have reported the preparation and physicochemical properties of 1,*n*-dithiaoxa[*n*] ruthenocenophanes and their transition metal complexes, and we now wish to report the syntheses of polythia[*n*] ruthenocenophanes.



(1)



(2)

Polythia[*n*] ruthenocenophanes (**6—10**) were obtained as follows. 1,1′-Bis-(3-chloropropyl-1-thia)ruthenocenophane (**5**) was readily synthesized by the reaction of the disodium salt of 1,1′-ruthenocenedithiol (**3**), which was prepared by the method of the previous paper [6], with a large excess of 1-bromo-2-chloroethane (Scheme 1). A solution of **5** in THF/EtOH was added

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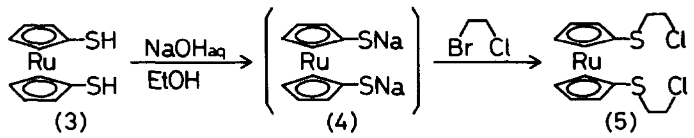
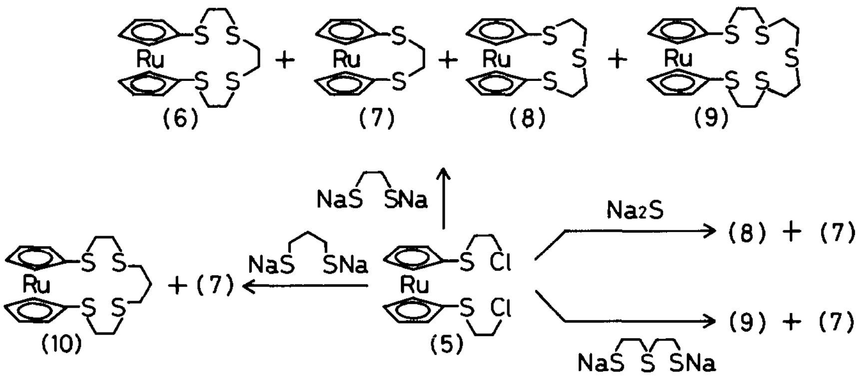


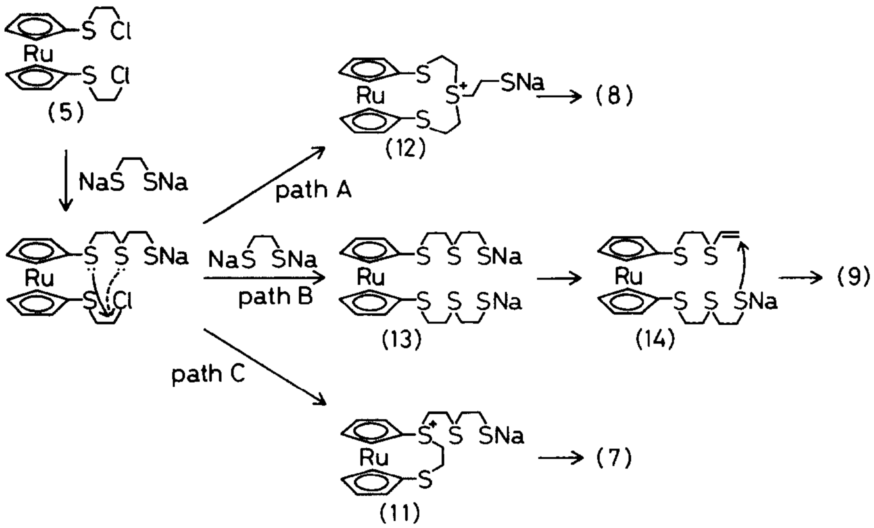
SCHEME 1

in one portion to a solution of an equimolar amount of disodium 1,2-ethanedithiolate in THF/EtOH mixture and the resulting mixture was separated by silica gel thin-layer chromatography. From the reaction mixture, 1,4,7,10-tetrathia[10]ruthenocenophane (**6**) (m.p. 138.0—139.0°C) was obtained in 9.8% yield. Besides this, the unexpected 1,4-dithia[4]ruthenocenophane (**7**) (m.p. 225.6—226.5°C), 1,4,7-trithia[7]ruthenocenophane (**8**) (m.p. 154.0—154.6°C), and 1,4,7,10,13-pentathia[13]ruthenocenophane (**9**) (m.p. 93.5—94.0°C) were obtained in trace amounts (Scheme 2). Similarly, **5** reacted with disodium propanedithiolate, the disodium salt of bis(2-mercaptoethyl)-sulfide, and sodium disulfide to give 1,4,8,11-tetrathia[11]ruthenocenophane (**10**) (m.p. 121.6—122.2°C, 15%), **9** (23%), and **8** (15%) as the main products.



SCHEME 2

Furthermore, in addition to the normal products, the unexpected product **7** was also isolated in all cases. The structures of these products were established by their spectral data and elemental analyses. For example, the molecular formula of **6** was deduced to be $C_{16}H_{20}S_4Ru$ by elemental analysis and mass spectrum (M^+ *m/e* 441). The ^{1}H NMR spectrum of **6** in $CDCl_3$ showed a pair of triplets corresponding to the α- and β-protons of a ruthenocene nucleus at δ 4.62 and 4.77 (J 1.8 Hz), in addition to a singlet at δ 3.10 (4H, CH_2) and a multiplet at δ 2.75—3.21. The structures of the other new compounds were also determined by a similar method. A possible mechanism for the unexpected formation of **7**, **8**, and **9** in the reaction of **5** with disodium 1,2-ethanedithiolate is proposed in Scheme 3. The formation of **7** may be rationalized in terms of the formation of the intermediate sulfonium ion **11** (path C) followed by dealkylation. The formation mechanisms of **8** and **9** were interpreted similarly as follows: dealkylation of **12** gives **8** and elimination of SH^- from **13** gives the vinylsulfide intermediate (**14**) followed by cyclization to give **9**. A similar reaction (path A and B) has been observed only in the reaction of 1,1'-



SCHEME 3

bis(3-chloropropyloxa)ferrocene [4] and 1,1′-bis(3-chloropropyl-1-thia)-ferrocene with disodium 1,2-ethanedithiolate [5].

Investigation about the isolation and physicochemical properties of the complexes of polythia[*n*]ruthenocenophanes with transition metal ions are in progress.

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