Journal of Organometallic Chemistry, 289 (1985) 91–95
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESES OF FERROCENOPHANES CONTAINING AROMATIC OR HETEROAROMATIC RINGS IN THE BRIDGING CHAIN

MASARU SATO*, SHINSUKE TANAKA,

Chemical Analysis Center, Saitama University, Urawa, Saitama 338 (Japan)

SEIJI EBINE, KENICHI MORINAGA,

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338 (Japan)

and SADATOSHI AKABORI

Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274 (Japan)

(Received December 19th, 1984)

Summary

1,10-Dithia[2]-*o*-cyclo-, 1,10-dithia[2]-*m*-cyclo-, 1,10-dithia[2](2,6)pyridino-, and 1,9-dithia[2](2,5)furano-[2](1,1′)ferrocenophanes were synthesized. The structural features are discussed on the basis of spectral data and redox potentials.

Much attention has recently been focussed on the chemistry of ferrocenophanes [1,2]. Many [*n*]ferrocenophanes have been prepared to examine their structure and character, but only a few studies report ferrocenophanes containing aromatic and heteroaromatic rings in the bridging chain [3–5]. Also crown and thiacrown analogs containing a ferrocene nucleus in the ring, i.e., oxathia- and polythia-[*n*]ferrocenophanes have been prepared [6,7] and a novel interaction between the sulfur atom and the ferrocene nucleus was found in 1,*n*-dithia[*n*]ferrocenophanes [8]. We now report the synthesis of dithiaferrocenophanes containing either an aromatic or a heteroaromatic ring in the bridging chain.

Results and discussion

Disodium 1,1′-ferrocenedithiolate (**1**), prepared from the reaction of 1,1′-ferrocenedithiol with 40% aqueous sodium hydroxide in ethanol, reacted with *o*-xylene dibromide in ethanol under highly diluted conditions to give 1,10-dithia[2]-*o*-cyclo[2](1,1′)ferrocenophane (**2**) in 38% yield. Similarly, the reaction of **1** with *m*-xylene dibromide in ethanol gave 1,10-dithia[2]-*m*-cyclo[2](1,1′)ferrocenophane (**3**) in 8.1% yield, along with its dimer **4** in 17.3% yield. However, the reaction of **1** with *p*-xylene dibromide gave only polymeric materials (Scheme 1).

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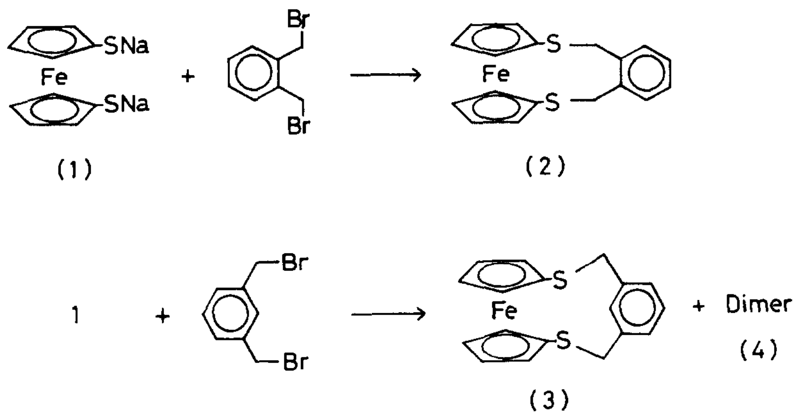


SCHEME 1

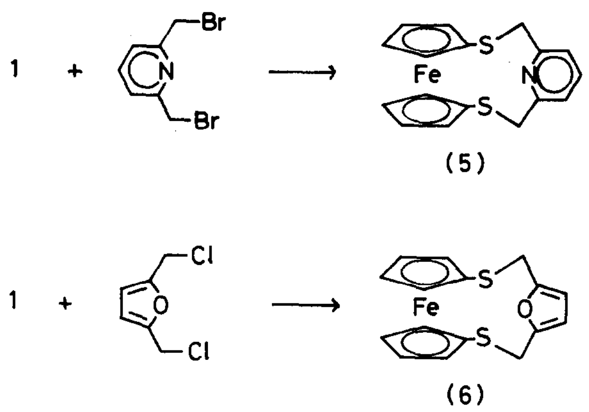
In the ^{1}H NMR spectrum of **3** (Table 1), the signals of the cyclopentadienyl rings of the ferrocene nucleus appeared as two well-split triplets. The signals of the α-protons were considerably shifted to higher field (0.3 ppm) compared to those of 1,7-dithia[7]ferrocenophane (**7**) [8], suggesting that the α-protons were located in the shielding zone of the benzene ring in the bridging chain. The proton signals of the 8-position of the benzene moiety resonated at δ 8.92 ppm, whose position was

TABLE 1

ELECTRONIC, ^{1}H and ^{13}C NMR SPECTRAL DATA AND REDOX POTENTIALS

Compound	λ_{max} (CH_3CN, nm)	^{1}H NMR ($CDCl_3$, 90 MHz)	^{13}C NMR [b] ($CDCl_3$, 22.5 MHz)	$E^{\ominus a}$ (V)
2	470	4.19(t, 4H, J 2.7 Hz) 4.13 (t, 4H, J 2.7 Hz) 4.70 (s, 4H) 7.19 (s, 4H)	95.5 (C_b), 68.5 (C_α), 67.5 (C_β) 137.2 (CH), 130.1 (CH), 127.7 (CH) 36.3 (CH_2)	+0.08
3	467	3.86 (t, 4H, J 1.8 Hz) 4.17 (t, 4H, J 1.8 Hz) 4.04 (s, 4H) 7.0–7.5 (m, 3H) 8.92 (s, 1H)	91.3 (C_b), 67.8 (C_α), 66.4 (C_β) 138.7 (CH), 131.4 (CH), 128.4 (CH) 125.6 (CH), 36.4 (CH_2)	−0.04
5	452	3.93 (t, 4H, J 1.8 Hz) 4.12 (t, 4H, J 1.8 Hz) 4.16 (s, 4H) 7.08 (d, 2H, J 7.2 Hz) 7.56 (t, 1H, J 7.2 Hz)	90.5 (C_b), 69.5 (C_α), 66.6 (C_β) 157.9 (CH), 137.1 (CH), 120.2 (CH) 38.8 (CH_2)	−0.02
6	458	3.88 (t, 4H, J 1.8 Hz) 3.98 (s, 4H) 4.14 (t, 4H, J 1.8 Hz) 5.13 (s, 2H)	90.4 (C_b), 68.3 (C_α), 66.7 (C_β) 107.4 (CH), 151.2 (CH) 28.4 (CH_2)	+0.05
7	468	4.16 (m, 4H), 4.12 (m, 4H) 3.01 (t, 4H, J 6.3 Hz) 1.90 (m, 6H)	91.8 (C_b), 67.2 (C_α), 66.4 (C_β) 32.8, 26.9, 23.8 (CH_2)	−0.04

[a] Ag/$AgNO_3$, CH_3CN. [b] C_b denotes a bridge-head carbon.



SCHEME 2

shifted to lower field by about 1.8 ppm more than the other benzenoid protons. This is probably because the proton at the 8-position is located deeply in the deshielding zone of the ferrocene nucleus [9]. These facts are supported by the stereo-molecular model of **3**. [2]-*m*-cyclo[2](1,1′)ferrocenophane which was recently prepared has very similar structural features to **3** [5].

Disodium 1,1′-ferrocenedithiolate (**1**) reacted with 2,6-bis(bromomethyl)pyridine under highly diluted conditions to give 1,10-dithia[2](2,6)pyridino[2](1,1′)ferrocenophane (**5**) in moderate yield. When **1** was similarly treated with 2,5-bis(chloromethyl)furan, 1,9-dithia[2](2,5)furano[2](1,1′)ferrocenophane (**6**) was obtained although in low yield. However, a similar reaction of **1** with 2,5-bis(chloromethyl)thiophene gave no definite product. The ^{1}H NMR spectra of **5** and **6** also showed large highfield shifts of the α-ring protons, indicating that **5** and **6** have similar conformations to **3** (Scheme 2).

The absorption at 440 nm due to the *d–d* transition in the ferrocene nucleus [11] showed a large bathochromic shift in **2**, **3**, **5**, and **6**, which are derivatives of 1,6-dithia[6]- and 1,7-dithia[7]-ferrocenophanes containing an aromatic or a heteroaromatic ring in the bridging chain. As shown in Table 1, the trend of the bathochromic shift is rather similar to that observed in 1,6-dithia[6]- and 1,7-dithia[7]-ferrocenophanes, suggesting also the presence of a certain interaction between the sulfur atom and the ferrocene nucleus in these compounds [8]. According to the molecular model for **3**, introduction of a benzene ring into the bridging chain of 1,7-dithia[7]ferrocenophane causes only a slight tilting deformation of the two cyclopentadienyl rings in the ferrocene nucleus. This seems to be supported by the presence of the 9° tilting angle in the [2]-*m*-cyclo[2](1,1′)ferrocenophane as shown in its X-ray analysis data [5]. However, the bathochromic shift in **5** and **6** was somewhat small compared with that in **2** and **3**. The molecular model for **6** indicates that the tilting of the cyclopentadienyl rings in the ferrocene ring is larger than that of **3** due to the large external CCO angle of the furan nucleus. The smaller bathochromic shift of **6** compared with **3** may be partly due to the decrease of the interaction between a sulfur atom and the ferrocene ring by the change in the rotation angle of the C–S bond, since an increasingly tilted angle in a ferrocene ring brings a bathochromic shift [10]. Alternatively, the interaction between the hetero atom lone pair in the heteroaromatic ring of **5** or **6** and the sulfur atom lone pair or the iron atom may also influence the absorption at 440 nm of the ferrocenophanes. In the ^{13}C NMR spectrum of 1,*n*-dithia[*n*]ferrocenophanes, the bridge-head carbon shifts to lower field and the α- and β-carbons shift to higher field compared to the corresponding carbon atoms in 1,1'-bis(methylthio)ferrocene [8]. A similar shift was also obtained in **2**, **3**, **5**, and **6** (Table 1), except that the β-carbon atom in **5** shifted only a little to higher field. The result of electronic and ^{13}C NMR spectra of **2**, **3**, **5**, and **6** suggests that stereoelectronic interaction between the sulfur atom and the ferrocene nucleus also takes place in these compounds similar to 1,7-dithia[7]ferrocenephane itself, in spite of the condensation of an aromatic or a heteroaromatic ring in the bridging chain. In order to confirm further the above suggestion, the redox potentials of **2**, **3**, **5**, and **6** were measured by cyclic voltammetry. The results are summarized in Table 1. These compounds showed an extremely low redox potential similar to 1,6-dithia[6]- and 1,7-dithia[7]-ferrocenophanes [8] in comparison to 1,1'-bis(methylthio)ferrocene and other 1,*n*-dithia[*n*]ferrocenophanes. The results indicate that the HOMO level elevation seems to be caused by the d_π–p_π interaction between the HOMO level (nonbonding e_{2g}) of the ferrocene nucleus and the occupied *p*-orbital of the sulfur lone pair. Therefore, some stereoelectronic phenomena here observed may be fully due to the d_π–p_π interaction, although other possibilities should not be ruled out.

Experimental

Materials

o-, *m*- and *p*-Xylene dibromides are commercially available. 2,6-Bis(bromomethyl)pyridine [12] and 2,5-bis(chloromethyl)furan [13] were prepared according to literature methods.

All experiments were carried out using N_2-saturated ethanol under nitrogen.

General procedure

A solution of disodium 1,1'-ferrocenedithiolate, prepared from 1,1'-ferrocenedithiol (0.50 g, 2 mmol) and 20% aqueous sodium hydroxide (2 ml) in ethanol (100 ml), and a solution of the dibromide (2 mmol) in ethanol (100 ml) were added dropwise with stirring for over 5 h to ethanol (500 ml). The mixture was stirred overnight, the solvent was then evaporated under reduced pressure and water (200 ml) was added to the residue. Ether (200 ml) was used to extract the resulting mixture and another 200 ml were used to remove the aqueous layer. The ethereal extracts were combined and dried over anhydrous magnesium sulfate. After evaporation, the yellow crystalline residue was chromatographed on silica gel by elution with a hexane/benzene mixture to give the corresponding ferrocenophane described below.

1,10-Dithia[2]-o-cyclo[2](1,1')ferrocenophane (2). Red crystals, m.p. 243–244°C. Yield: 38%. Found: C, 61.51; H, 4.64. $C_{18}H_{16}S_2Fe$ calcd.: C, 61.36; H, 4.59%. MS (75 eV): *m/z* 416 (M^+, 100%). IR (KBr): 3110, 2910, 1158, 1026, 886, 808, 772, and 704 cm^{-1}.

1,10-Dithia[2]-m-cyclo[2](1,1')ferrocenophane (3). Red cubes, m.p. 166–167°C. Yield: 8.1%. Found: C, 61.22; H, 4.69. $C_{18}H_{16}S_2Fe$ calcd.: C, 61.36; H, 4.59%. MS

(75 eV): m/z 416 (M^+, 100%). IR (KBr): 3090, 2910, 1606, 1445, 1415, 1366, 1030, 1015, 812, and 700 cm^{-1}.

1,10,22,31-Tetrathia[2]-m-cyclo[2](1,1')ferroceno[2]methacyclo[2](1,1')ferrocenophane (4). Yellow needles, m.p. 204–205°C (dec.). Yield: 17.3%. Found: C, 61.19; H, 4.73. $C_{36}H_{32}S_4Fe_2$ calcd.: C, 61.36; H, 4.59%. MS (75 eV): m/z 832 (M^+). IR (KBr): 3070, 2910, 1436, 1412, 1225, 1158, 1025, 1015, 812, 800, 792, and 702 cm^{-1}.

1,10-Dithia[2](2,6)pyridino[2](1,1')ferrocenophane (5). Red crystals, m.p. 162–163°C. Yield: 24.7%. Found: C, 57.66; H, 4.25; N, 3.97. $C_{17}H_{15}NS_2Fe$ calcd.: C, 57.79; H, 4.29; N, 3.97%. MS (75 eV): m/z 353 (M^+, 100%). IR (KBr): 3080, 2910, 1585, 1570, 1453, 1416, 1395, 1030, 873, 806, 797, and 742 cm^{-1}.

1,9-Dithia[2](2,5)furano[2](1,1')ferrocenophane (6). Red crystals, m.p. 99–102°C. Yield: 4.0%. Found: C, 56.52; H, 4.37. $C_{16}H_{14}OS_2Fe$ calcd.: C, 56.14; H, 4.13%. MS (75 eV): m/z 342 (M^+, 100%). IR (KBr): 3090, 2950, 1416, 1402, 1260, 1156, 1032, 1012, 968, 804, and 793 cm^{-1}.

The electronic, ^{1}H NMR, and ^{13}C NMR spectral data are summarized in Table 1.

Measurement of cyclic voltammetry

Redox potentials were determined by the cyclic voltammetry in a solution of 0.05 *M* tetrabutylammonium perchlorate in acetonitrile (dried over phosphorus pentoxide and distilled from calcium hydride) under nitrogen at 25°C, using a standard three-electrode cell. All potentials were measured vs. a $Ag/AgNO_3$ (0.05 *M*) electrode and the scan rate was 100 mV/s. The voltammograms show that the redox reaction proceeds reversibly at a platinum electrode.

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