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MACROCYCLIC POLYFUNCTIONAL LEWIS BASES—VI[1] POLYOXAFERROCENOPHANES

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(*Received in UK*)

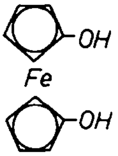
Abstract—1,1′-Dihydroxyferrocene reacts with chloroethers **7**–**11** forming the respective polyoxaferrocenophanes **2**–**6**. These compounds behave analogously to the "crown" ethers.

Macrocylic polyethers usually contain the $-O-CH_2CH_2-O-$ or the $-O-\overset{|}{C}=\overset{|}{C}-O-$ groupings, which differ in conformation and interatomic distances. These factors together with the number of electron donating atoms and dimension of the macrocycle mainly determine the complexation selectivity towards different cations.[2] Hence it may be expected that considerable changes in the geometry and the arrangement of the O atoms may significantly change the complexability of macrocyclic Lewis bases. Such a new situation is offered by introducing the ferrocenylene residue to the macrocycle.[3]

We have synthesised several polyoxaferrocenophanes **2**–**6** starting from 1,1′-bisacetoxyferrocene.[4] This ester was converted into the dihydroxyferrocene **1** by the action of sodium hydroxide[4] or better by the action of concentrated ammonia. Condensation of **1** with the chloroethers **7**–**11** was performed in *n*-butanol,[5] dimethylformamide[6] or in dimethylsulphoxide in the presence of sodium hydroxide. It was rather unexpected (*cf* the synthesis of dibenzo-18-crown-6[5]), that condensation of **1** with chloroethers **7** and **8** gave relatively high yields of compounds **2** and **3** respectively and not the dimeric compounds **12** and **13**, which were formed only as by-products and were not isolated in a pure state. The purities and molecular weights of compounds **2**–**6** were unequivocally determined by mass spectrometry using FD technique (Table 1).

The complexabilities of macrocyclic compounds **2**–**6** towards alkali metal cations were compared using the chromatographic method.[7] The results are presented in Table 2.

The higher the B % value, the greater the stability of the complex.[7] Hence compound **2** formed very stable



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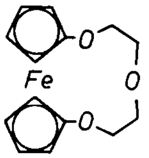

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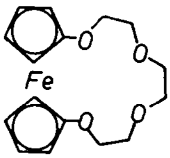

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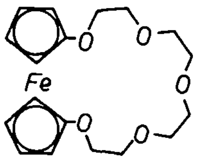

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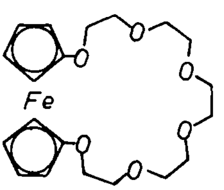

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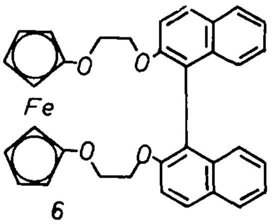

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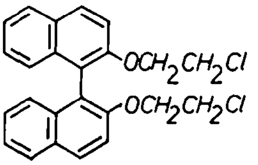
7 $ClCH_2CH_2OCH_2CH_2Cl$

8 $ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$

9 $ClCH_2CH_2O(CH_2CH_2O)_2CH_2CH_2Cl$

10 $ClCH_2CH_2O(CH_2CH_2O)_3CH_2CH_2Cl$



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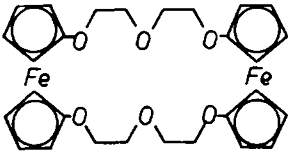

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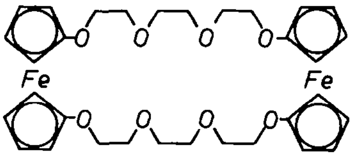

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Compound	Method	Yield %	M.p.°C	Formula m.w.	m/e MS/FD	^{1}HNMR spectra, δ ppm. Solvent $CDCl_3$, TMS as internal standard
2	a	17	119–120	$C_{14}H_{16}O_3Fe$ /288/	288	$-OC\underline{H}_2-$ and $C_5\underline{H}_4$ /16H, 3.70 - 4.40 m/
3	b	22	liquid	$C_{16}H_{20}O_4Fe$ /332/	332	$-OC\underline{H}_2-$ /12H, 3.50 - 3.65 m/, $C_5\underline{H}_4O-$ /8H, 3.35 - 3.40 2d, J=6.0 Hz/
4	b	36	59–60.5	$C_{18}H_{24}O_5Fe$ /376/	376	$-OC\underline{H}_2-$ /16H, 3.50 - 3.55 m/, $C_5\underline{H}_4O-$ /8H, 3.35 - 3.40 2d, J=6.0 Hz/
5	b	36	liquid	$C_{20}H_{28}O_6Fe$ /420/	420	$-OC\underline{H}_2-$ /20H, 3.50 - 3.60 m/, $C_5\underline{H}_4O-$ /8H, 3.35 - 3.45 2d, J=6.25 Hz
6	a	25	110–112	$C_{34}H_{28}O_4Fe$ /556/	556	$-C\underline{H}$/naphtalene/ /12H, 7.1 - 8.0 m/, $C_5\underline{H}_4O-$ and $-OC\underline{H}_2$ /16 H, 3.7 - 4.2 m

Table 1. Synthetic method, yields and properties of polyoxaferrocenophanes

Compound	Solvent system	R_F on Silufol	B % on a Silufol plate impregnated with 2 % solution of salt				
			LiCl	NaCl	KCl	RbCl	CsCl
2	Chloroform-acetone 4 : 1	0.80	15	5	25	5	15
3	chloroform-acetone 9 : 1	0.65	30	20	45	40	35
4	chloroform-acetone 4 : 1	0.65	20	70	75	80	70
5	chloroform-acetone 4 : 1	0.40	35	40	80	80	70
6	chloroform	0.35	25	25	30	35	40

$$B\ \% = \frac{R_F - R_F^x}{R_F} \cdot 100, \text{ where } R_F^x = R_F \text{ on a salt impregnated Silufol plate}$$

Table 2. Chromatographic behavior of polyoxaferrocenophanes

complexes with Li^+ (probably 1:1 complex) and K^+ (probably 2:1 complex). As the dimension of the hole increased, the stability of complexes with the cations of greater size increased. For the same number of O atoms, the differences in the stability of fairly-large cation complexes with polyoxaferrocenophanes are small, as compared with complexes of 12-crown-4, 15-crown-5 and 18-crown-6.[2]

The UV spectrum of compound **4** in ethanol does not change after addition of rubidium chloride indicating, that the Fe atom does not essentially take part in complexation.

EXPERIMENTAL

Tlc was performed on Silufol UV_{254} (Czechoslovakia) and the spots were detected with iodine. The salt impregnated plates were prepared as recorded. MN Kieselgel 60 (Macherey Nagel + Co) was used for column chromatography. ^{1}H NMR spectra were taken at 80 MHz on a Tesla BS 487 spectrometer. Molecular weights and purities of macrocyclic compounds were determined by mass spectrometry on a Varian MAT 711 apparatus using FD technique.

1,1'-Ferrocenediboronic acid was prepared according to Nesmeyanov[4] starting from dilitium ferrocene obtained as described[8] with the overall yield of about 60%. This compound was finally converted into bisacetoxyferrocene in usual way.[4]

Syntheses of macrocyclic polyoxaferrocenophanes

Method a. To a soln of 302 mg (1 mmole) of bisacetoxyferrocene in 2 ml toluene 1 ml conc ammonia was added and the mixture was stirred vigorously for 1 hr under N_2. The solvents were removed under vacuum and to the residue 5 ml dimethylsulfoxide or dimethylformamide, (0.12 ml; 1 mmole) chloroether **7** and 100 mg NaOH were added. The mixture was refluxed under N_2 for 1 hr and poured into 30 ml water. The product was extracted with $CHCl_3$ and concentrated to a small volume. The desired compound was isolated chromatographically using $CHCl_3$ as an eluent, yielding 50 mg (17%) of **2**, m.p. 119–120°.

Compound **6** (140 mg, 25%), m.p. 110–112° was eluted from the column with CCl_4-benzene (3:1 mixture).

Method b. A mixture of (1 g, 3.21 mmole) bisacetoxyferrocene, 10 ml *n*-BuOH and 500 mg NaOH dissolved in 2 ml water was refluxed under N_2 for 1 hr. The mixture was acidified with 0.5 ml conc. H_2SO_4 and the solvents were evaporated under vacuum. 10 ml n-BuOH was added to the residue and the evaporation repeated. Then 10 ml *n*-BuOH, (0.75 ml; 3.9 mmole) chloroether **9** and 0.6 g NaOH were added and the mixture was refluxed under N_2 for 20 hr. The solvent was removed and the residue extracted with $CHCl_3$ (50 ml). After evaporation the product was purified chromatographically using $CHCl_3$ as an eluent, yield 440 mg (36%) of compound **4**, m.p. 59.5–60.5°.

Similarly compounds **3** and **5** were obtained.

Racemic dichloroether **11**. A mixture of 2,2′-dihydroxybinaphtyl (5 g, 17.5 mmole), 100 ml water, 5 g KOH and 4.25 ml ethylene chlorohydrin was stirred at 70–90° for 1 hr. Then 4.25 ml chlorohydrin were added and heating and stirring was continued for a further 3 hr the pH being maintained at about 10 by dropwise addition of 10% KOHaq (*cf.* Ref. 9). The mixture was extracted with ethyl ether, the organic layer was washed to twice with 10% KOHaq, water and finally dried. After evaporation of the solvent the residue crystallised after addition of small amount of MeOH, yield 1.14 g (17%) of 2,2′-bis(2-hydroxyethoxy)-1,1′-binaphtyl, m.p. 112–114°. HNMR ($CDCl_3$), δ ppm: Ar$\underline{H}$ 7.0–7.9 m, 12 H, ArOC$\underline{H}_2$ 3.95 m, 4 H; C$\underline{H}_2$OH 3.4 m, 4 H; O$\underline{H}$ 2.4 s (broad), 2 H. R_F ($CHCl_3$) = 0.12.

To a mixture of (2 g, 5.34 mmole) of the diol and 2 ml pyridine, 2 ml thionyl chloride were added dropwise. The mixture was left for 2 hr at room temp and heated at 45° for 2 hr and poured into water. The product was extracted with benzene, the organic layer was washed with water, dil HCl, again with water and dried. The soln was concentrated and the crude product was purified by column chromatography using CCl_4 as an eluent. The desired product crystallised from diisopropyl ether, yield 1.41 g (64%), m.p. 100–103°. H NMR(CCl_4), δ ppm: Ar$\underline{H}$ 7.0–7.85 m, 12 H; OC$\underline{H}_2$ 4.0 t, 4 H; C$\underline{H}_2$Cl 3.2 t, 4 H; J = 6.25 Hz. R_F($CHCl_3$) = 0.65.

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