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Synthesis and Cation-Complexing Ability of Oxo Crown Ethers Containing a Ferrocene Nucleus

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Fifteen new oxo crown ethers having a ferrocene unit as an integral part of the ring member are reported. These oxo crown ethers were synthesized by the reaction of 1,1′-bis(chloroformyl)ferrocene with oligoethylene glycols or heterocyclic dialcohol compounds such as 2,6-bis(hydroxymethyl)pyridine by the high dilution method. Complexing ability of these compounds with alkali, alkaline earth, and transition metal cations was measured by the solvent extraction method.

Since Pedersen's pioneering work,[1] the synthesis of a great number of macrocyclic polyethers has been reported. Among them, several groups of workers[2] have described the preparation of a new type of crown ethers containing a ferrocene unit as a ring member, in which iron atom plays the role of a coordinating atom. In connection with crown ethers, attention has recently been paid to the oxo crown compounds, because some of them showed a different complexing tendency towards cations from normal crown ethers. In this report we describe the synthesis and study the complexing behavior of these ferrocenophanes with alkali, alkaline earth and transition metal picrates.

Results and Discussion

Synthesis. A large number of oxo crown compounds have been synthesized, and their properties were investigated by Bradshaw,[3-11] Vögtle,[12-14] and Kellogg.[15-18] Most of these compounds have been prepared through either the reaction between diacids and dihalides (ditosylates) of oligoethylene glycols (**1**), or the reaction between diacyl chlorides and oligoethylene glycols. Oepen and Vögtle[2a] reported that in the presence of pyridine the reaction between 1,1′-bis(chloroformyl)ferrocene (**2**) and **1** (n=1, 2, 3) in benzene led to the formation of oxo crown ethers (**3**) (n=1, 2, 3) in 29—36% yields, but no detailed spectral data were published (elemental analyses only), and 1,1′-ferrocenediyl dialcohol derivative (**4**) was not mentioned as the coproduct. They also did not refer to the formation of binuclear ferrocenophanes (**5**). In the present study, the syntheses of **3** and **5** were carried out without bases by the modification of Bradshaw's method.[9] For example, the reaction of **1** (n=1) with **2** in dry benzene led to the formation of 1,1′-bis(5-hydroxy-3-oxapentyloxycarbonyl)ferrocene (**4b**) as the main product, and 2,5,8-trioxa[9](1,1′)ferrocenophane-1,9-dione (**3b**) as the minor one. Furthermore, the reaction of **4b** with **2** afforded 2,5,8,22,25,28-hexaoxa[9.9](1,1′)-ferrocenophane-1,9,21,29-tetrone (**5b**). The results of the reactions are summarized in Tables 1 and 2.

The oxo crown ethers containing both a heteroatom such as N, O, or S and the ferrocene unit were synthesized in order to examine the influence of the electron donating heteroatoms on complexing ability of the cation. For example, the reaction of **2** with diols **6** such as 2,6-bis(hydroxymethyl)pyridine (**6a**) was carried out in the presence of the base and resulted in the formation of mononuclear ferrocenophane (**7**) and 1,1′-

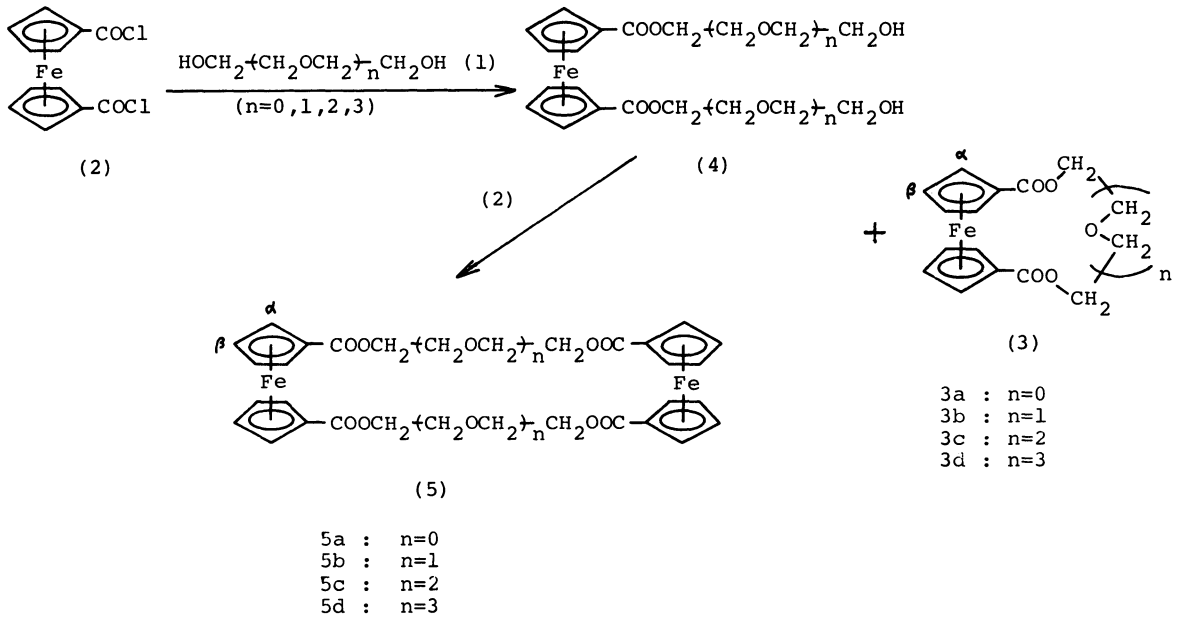

Fig. 1.

ferrocenediyl dialcohol derivative (**9**) (main product). Furthermore, the reaction of diol **9** with **2** led to the formation of **8**, but different results were obtained in the following two cases: 1,1′-Ferrocenediyl dialcohol (**9b**) was not obtained in the reaction of 2,5-bis(hydroxymethyl)furan (**6b**) with **2**, whereas, mononuclear ferrocenophane (**7b**) and binuclear ferrocenophane (**8b**) formed by the one-pot reaction. In addition, the reaction of 2,5-bis(hydroxymethyl)benzene (**6d**) with **2** gave mononuclear ferrocenophane (**7d**) and binuclear ferrocenophane (**8d**) together with 1,1′-ferrocenediyl dialcohol (**9d**). These results indicate that in most cases binuclear ferrocenophane is probably formed by the competitive reaction in the first reaction step, although the yield is extremely low ex-

Table 1. Reaction of 1,1′-bis(chloroformyl)ferrocene with oligoethylene glycol

Oligoethylene glycol	Product	Yield/%	Mp θ_m/°C (lit,)	Color
Ethyleoe glycol $n=0$	**3a**	28	187—188	red
	4a	51	oil	red
Diethylene glycol $n=1$	**3b**	26	134—135 (85)[2a]	red orange
	4b	59	oil	red
Triethylene glycol $n=2$	**3c**	23	129—130 (127)[2a]	orange
	4c	53	oil	red
Tetraethylene glycol $n=3$	**3d**	22	78—79 (60—62)[2a]	orange
	4d	55	oil	red

Table 2. Reaction of 1,1′-bis(chloroformyl)ferrocene with ferrocenyl dialcohol (**4a—d**)

Ferrocenyl dialcohol	Product	Yield/%	Mp θ_m/°C	Color
4a	**5a**	23	245—246	red orange
4b	**5b**	34	121—122	orange
4c	**5c**	36	106—107	yellow orange
4d	**5d**	35	oil	red

Table 3. Reaction of 1,1′-bis(chloroformyl)ferrocene with dialcohol (**6a—e**)

Dialcohol	Product	Yield/%	Mp θ_m/°C	Color
6a	**7a**	9	240—242 (decomp)	red
	9a	19	oil	red
6b	**7b**	1	145—146	orange
	8b	9	260—262 (decomp)	yellow
6c	**7c**	2	214—215	orange
	9c	49	123—124	orange
6d	**7d**	2	208—209	red
	8d	4	223—224	yellow
	9d	58	oil	red
6e	**7e**	2	134—135	orange
	9e	67	oil	red

Table 4. Reaction of 1,1′-bis(chloroformyl)ferrocene with ferrocenediyl dialcohol (**9a,c,d,e**)

Ferrocenediyl dialcohol	Product	Yield/%	Mp θ_m/°C	Color
9a	**8a**	5	231—232	yellow
9c	**8c**	5	245—246 (decomp)	yellow
9d	**8d**	39	223—224	yellow
9e	**8e**	5	214—215 (decomp)	yellow

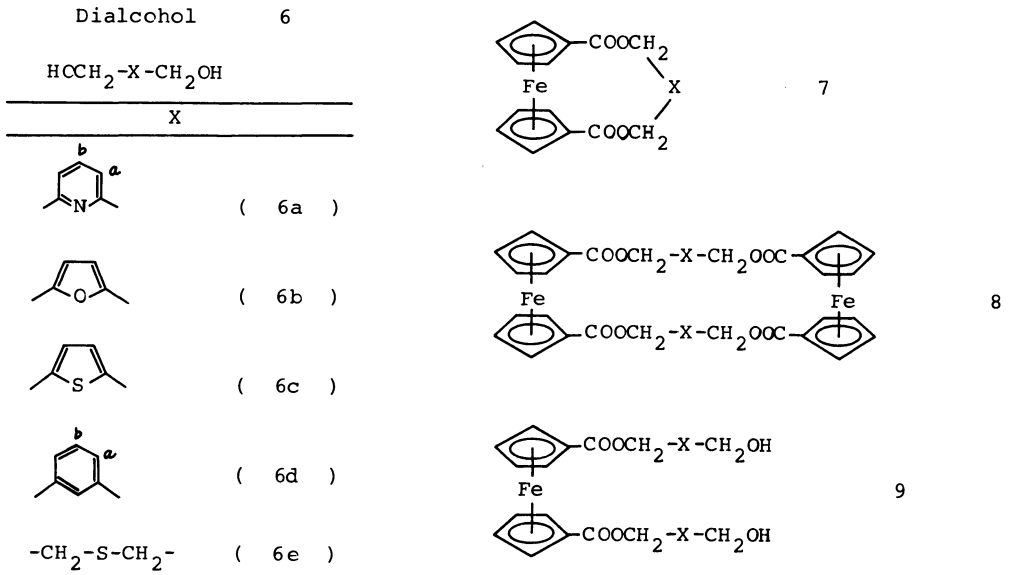

Fig. 2.

cept the above two cases. The results are summarized in Tables 3 and 4.

The structure of all ferrocenophanes thus prepared were determined on the basis of their IR, ^{1}H-NMR, and mass spectra and elemental analyses. The IR spectra of all the crown products showed the presence of an ester (1700—1720 cm^{-1}), a methylene (1460—1470 cm^{-1}), and a 1,1′-disubstituted ferrocene ring (815—840 cm^{-1}). In the ^{1}H-NMR spectra, the resonance for the α and β ring protons of the ferrocene nucleus appeared as the A_2B_2 pattern (triplet, J=4 Hz). In the ^{1}H-NMR spectra of ferrocenophane compounds, **7a—d** and **8a—d** possessing a heterocycle as a ring unit, the methylene protons are shifted to downfield by about 0.80—0.57 ppm as compared with those of **3a** and **5a**. This result was explained by the deshielding effect of the heteroaromatic (**7a—c** and **8a—c**) and aromatic rings (**7d** and **8d**).

Extraction Ability. The complexing ability of these ferrocenophanes toward alkali, alkaline earth, and transition metal cations was examined by Pedersen's extraction method.[19] The results are summarized in Table 5. As is known an increase in the number of the ester group leads to a drastic decrease of the electron donating ability of coordination sites,[20] and the presence of an ester group increases the selectivity toward alkali metal cations.[21] This tendency, however, was not observed clearly in the complexing ability of the ferrocenophanes as compared with that of polyoxaferrocenophanes.[2h,22] The ferrocenophanes (**3a—d** and **5a—d**) showed low complexing ability with alkali, alkaline earth, and transition metal cations without any difference in the extractability. Akabori *et al.*[2h,22] also reported a similar tendency in the extractability of alkali metal cations with polyoxa[*n*]ferrocenophanes prepared from 1,1′-dihydroxyferrocene and 1,1′-bis(hydroxymethyl)ferrocene. In ferrocenophanes **7e** and **8e**, it is anticipated that the incorporation of a sulfur atom (a soft atom) into the macrocycle has a strong influence on the complexing ability with transition metal ions (a soft atom) on the basis of the HSAB principle.[23] It should be emphasized that compound **8e** has a high complexing ability toward silver cation. Comparison of compound **7e** with **8e** suggests that complexing ability is influenced not only by the affinity of sulfur to a metal cation but also by the increase in the ring size. In order to know the influence of heteroatoms, extractability data of new ferrocenophanes (**7a—e** and **8a—e**) containing ferrocene and heterocyclic compound as a ring unit are listed in Table 5. These ferrocenophanes showed a poor extraction efficiency with alkali, alkaline earth, and transition metal cations, and only a small difference is found among their extractability. Compound **8a** is an exception and shows high preference toward silver ion. These results suggest that nitrogen atom has a higher affinity toward metal cations than sulfur atom (**7a** and **8a**). In Table 5, it is noteworthy that all ferrocenophanes are able to form stable complexes with silver, whereas ferrocene itself and many polyoxaferrocenophanes[2h,2j] prepared from 1,1′-dihydroxyferrocene were decomposed oxidatively by the complexed silver cation. Under acidic conditions ferrocenophanes **8a** and **8e** showed high complexing ability with mercury ion without decomposition of ferrocene nucleus. Poor complexing ability of all ferrocenophanes toward thallium ion as a transition metal cation is probably due to the nonfitness between the guest ion and the hole size of the host molecule.

Table 5. Extraction data (water-dichloromethane)[a]

Compound	Extracted/%					
	Na^+	K^+	Ba^{2+}	Tl^+	Ag^+	Hg^{+} [b]
3a	2.7	1.3	2.0	0	2.9	—
3b	3.0	1.4	2.1	2.1	5.1	—
3c	3.0	1.5	2.8	2.6	6.9	—
3d	3.0	3.0	3.6	0.7	6.8	—
5a	2.4	2.6	3.6	1.4	3.3	24.3
5b	3.0	3.7	3.6	3.3	6.5	—
5c	3.7	4.4	4.3	0.2	6.9	—
5d	4.4	6.5	4.3	6.4	7.9	—
7a	10.1	11.4	5.7	2.1	14.3	—
8a	16.4	11.4	2.9	2.9	71.5	69.7
7b	0	0	0	0	0	—
8b	0.3	0	0	0	0	—
7c	2.4	2.6	3.6	1.4	3.3	—
8c	9.0	6.4	2.1	1.4	5.0	—
7d	0.7	2.0	0	0	2.1	—
8d	5.1	5.3	1.9	1.8	3.6	—
7e	4.3	5.4	0.4	1.4	2.6	—
8e	4.1	5.4	1.1	1.4	47.1	79.3

a) Equal volumes of water and dichloromethane are mixed, and the concentration of picric acid is 7.0×10^{-5} M(1M=1 mol dm^{-3}). Concentration of ferrocenophane: 7.0×10^{-4} M. Concentration of metal nitrate: 0.1 M. b) Concentration of $HgNO_3\cdot H_2O$: 0.1 M in 0.6 N HNO_3.

Experimental

Materials and Measurements. All melting points are uncorrected. 1,1′-Bis(chloroformyl)ferrocene (**2**),[24] 2,5-bis(hydroxymethyl)furan,[25] and 2,5-bis(hydroxymethyl)thiophene[26] were prepared as described in the literature. The other reagents employed were commercial materials or were prepared by the usual method. All inorganic compounds were of the reagent grade. The IR, ^{1}H-NMR, mass, and electronic spectra were recorded on Hitachi 260-10, Hitachi R-22 (CW), Hitachi R-90H (FT), Hitachi RMU-6M, and Hitachi 200-10 spectrometers, respectively.

Syntheses of 3a—d. General Procedure: Under nitrogen atmosphere a solution of **2** (8.1 g, 0.026 mol) in dry benzene (200 ml) was added dropwise over 20 h to a refluxing solution of oligoethylene glycols (n=0—3) (0.052 mol) in dry benzene (200 ml). An additional 48 h period of gentle refluxing followed. After the reaction mixture was cooled to room temperature and evaporated to dryness under reduced pressure, the residue was purified by silica-gel column chromatography. The first fraction eluted with benzene gave mononuclear ferrocenophanes **3a—d**, and the second fraction eluted with chloroform gave 1,1′-ferrocene dialcohols **4a—d**. These results are summarized in Table 1.

*2,5-Dioxa[6](1,1')ferrocenophane-1,6-dione (**3a**).* ^{1}H-NMR ($CDCl_3$) δ=4.46 (t, 4H, Fc-Hβ, J=4 Hz), 4.64 (s, 4H, -C$\underline{H_2}$C$\underline{H_2}$-), 4.48 (t, 4H, Fc-Hα, J=4 Hz). IR (KBr): 3100, 2900, 1710, 1470, 1280, 820 cm^{-1}. MS (70 ev): m/z 300 (M^+). λ_{max} (CH_3OH): 455 nm (ε 290). Found: C, 55.98; H, 4.10 %. Calcd for $C_{14}H_{12}FeO_4$: C, 56.03; H, 4.03%; M, 300.09.

*2,5,8-Trioxa[9](1,1')ferrocenophane-1,9-dione (**3b**).* ^{1}H-NMR ($CDCl_3$) δ=3.83 (m, 4H, -C$\underline{H_2}$O-), 4.38 (m, 4H, -COOC$\underline{H_2}$-), 4.46 (t, 4H, Fc-Hβ, J=4 Hz), 4.71 (t, 4H, Fc-Hα, J=4 Hz). IR (KBr): 3100, 2950, 1720, 1470, 1280, 825 cm^{-1}. MS (70 eV): m/z 344 (M^+). λ_{max} (CH_3OH): 450 nm (ε 281). Found: C, 55.72; H, 4.73%. Calcd for $C_{16}H_{16}FeO_5$: C, 55.84; H, 4.69 %; M, 344.15.

*2,5,8,11-Tetraoxa[12](1,1')ferrocenophane-1,12-dione (**3c**).* ^{1}H-NMR ($CDCl_3$) δ=3.76 (s, 4H, -OC$\underline{H_2}$C$\underline{H_2}$-), 3.90 (m, 4H, -COOC$\underline{H_2}$C$\underline{H_2}$O-), 4.40 (m, 4H, -COOC$\underline{H_2}$CH$_2$O-), 4.48 (t, 4H, Fc-Hβ, J=4 Hz), 4.75 (t, 4H, Fc-Hα, J=4 Hz). IR (KBr): 3100, 2950, 1720, 1470, 1280, 825 cm^{-1}. MS (70 eV): m/z 388 (M^+). λ_{max} (CH_3OH): 452 nm (ε 339). Found: C, 55.61; H, 5.10%. Calcd for $C_{18}H_{20}FeO_6$: C, 55.69; H, 5.19%; M, 388.20.

*2,5,8,11,14-Pentaoxa[15](1,1')ferrocenophane-1,15-dione (**3d**).* ^{1}H-NMR ($CDCl_3$) δ=3.69 (s, 8H, -OC$\underline{H_2}$C$\underline{H_2}$OC$\underline{H_2}$C$\underline{H_2}$O-), 3.79 (m, 4H, -COOCH$_2$C$\underline{H_2}$-), 4.39 (m, 4H, -COOC$\underline{H_2}$CH$_2$-), 4.39 (t, 4H, Fc-Hβ, J=4 Hz), 4.78 (t, 4H, Fc-Hα, J=4 Hz). IR (KBr): 3100, 2950, 1710, 1460, 1280, 825 cm^{-1}. MS (70 eV): m/z 432 (M^+). λ_{max} (CH_3OH): 452 nm (ε 355). Found: C, 55.62; H, 5.51%. Calcd for $C_{20}H_{24}FeO_7$: C, 55.57; H, 5.60%; M, 432.25.

*Syntheses of **5a—d**.* *General Procedure*: Under nitrogen atmosphere, **2** (3.1 g, 0.01 mol) diluted with 200 ml of dry benzene was added dropwise over 20 h to the solution of 1,1'-ferrocene dialcohols **4a—d** (0.01 mol) in 200 ml of dry benzene. Additional 48 h period of gentle refluxing followed. After the removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography. The first fraction eluted with chloroform-acetone (10:1) gave binuclear ferrocenophanes **5a—d**. The second fraction eluted with chloroform-acetone (1:1) gave an oligomer as a reddish oil. These results are summarized in Table 2.

*2,5,19,22-Tetraoxa[6.6](1,1')ferrocenophane-1,9,21,29-tetrone (**5a**).* ^{1}H-NMR (FT) ($CDCl_3$) δ=4.46 (t, 8H, Fc-Hβ, J=3.96 Hz), 4.63 (s, 8H, -C$\underline{H_2}$C$\underline{H_2}$-), 4.89 (t, 8H, Fc-Hα, J=3.96 Hz). IR (KBr): 3100, 2950, 1720, 1460, 1270, 825 cm^{-1}. MS (70 eV): m/z 600 (M^+). λ_{max} (dioxane): 448 nm (ε 510). Found: C, 55.95; H, 4.11%. Calcd for $C_{28}H_{24}Fe_2O_8$: C, 56.03; H, 4.03%; M, 600.19.

*2,5,8,22,25,28,-Hexaoxa[9.9](1,1')ferrocenophane-1,9,21,29-tetraone (**5b**).* ^{1}H-NMR (FT) ($CDCl_3$) δ=3.83—3.94 (m, 8H, -CH$_2$C$\underline{H_2}$OC$\underline{H_2}$CH$_2$-), 4.41 (t, 8H, Fc-Hβ, J=3.95 Hz), 4.39—4.48 (m, 8H, -COOC$\underline{H_2}$-), 4.82 (t, 8H, Fc-Hα, J=3.95 Hz). IR (KBr): 3100, 2950, 1715, 1470, 1280, 815 cm^{-1}. MS (70 eV): m/z 688 (M^+). λ_{max} (dioxane): 448 nm (ε 580). Found: C, 55.78; H, 4.72%. Calcd for $C_{32}H_{32}Fe_2O_{10}$: C, 55.84; H, 4.69%; M, 688.29.

*2,5,8,11,25,28,31,34-Octaoxa[12.12](1,1')ferrocenophane-1,12,24,35-tetraone (**5c**).* ^{1}H-NMR ($CDCl_3$) δ=3.69 (s, 8H, -OC$\underline{H_2}$C$\underline{H_2}$O-), 3.76—3.81 (m, 8H, -COOCH$_2$C$\underline{H_2}$O-), 4.30—4.35 (m, 8H, -COOC$\underline{H_2}$CH$_2$O-), 4.38 (t, 8H, Fc-Hβ, J=4 Hz), 4.78 (t, 8H, Fc-Hα, J=4 Hz). IR (KBr): 3100, 2950, 1710, 1470, 1280, 820 cm^{-1}. MS (70 eV): m/z 776 (M^+). λ_{max} (dioxane): 449 nm (ε 532). Found: C, 55.61; H, 5.12%. Calcd for $C_{36}H_{40}Fe_2O_{12}$: C, 55.69; H, 5.19%; M, 776.40.

*2,5,8,11,14,28,31,34,37,40-Decaoxa[15.15](1,1')-ferrocenophane-1,15,27,41-tetrone (**5d**).* ^{1}H-NMR ($CDCl_3$) δ=3.62 (s, 16H, -OC$\underline{H_2}$C$\underline{H_2}$OC$\underline{H_2}$C$\underline{H_2}$O-), 3.71—3.76 (m, 8H, -COOCH$_2$-C$\underline{H_2}$O), 4.31—4.36 (m, 8H, -COOC$\underline{H_2}$CH$_2$O-), 4.37 (t, 8H, Fc-Hβ, J=4 Hz), 4.48 (t, 8H, Fc-Hα, J=4 Hz). IR (neat): 3100, 2950, 1710, 1465, 1280, 825 cm^{-1}. MS (70 eV): m/z 864 (M^+). λ_{max} (dioxane): 447 nm (ε 514). Found: C, 55.48; H. 5.66%. Calcd for $C_{40}H_{48}Fe_2O_{14}$: C, 55.57; H, 5.60%; M, 864.51.

*Syntheses of **7a—e**, **8b**, **d**, and **9a**, **c**, **d**, **e**.* A solution of **2** (5.9 g, 0.019 mol) in 200 ml of dry benzene was added dropwise to a solution of **6** (0.038 mol) and triethylamine (3.8 g, 0.038 mol) in acetonitrile (250 ml) for 20 h under nitrogen atmosphere. Additional 20 h period of gentle refluxing followed. After usual work-up, the products were separated by silica-gel column chromatography. The first fraction eluted with chloroform gave mononuclear ferrocenophanes **7a—e**. The second fraction eluted with chloroform-diethyl ether (9:1) gave **8b** or **8d** from **6b** and **6d**, respectively. The third fraction eluted with chloroform-methanol (9:1) gave ferrocene dialcohols **9a**, **c**, **d**, **e**. These results are summarized in Table 3.

*Syntheses of **8a**, **c**, **d**, **e**.* Under nitrogen atmosphere, reaction of **2** (9.6 g, 0.03 mol) with ferrocene dialcohols **9a**, **c**, **d**, **e** (0.03 mol) and triethylamine (3.0 g, 0.03 mol) in dry benzene (300 ml) gave compounds **8a**, **c**, **d**, **e**, respectively.

*2,11-Dioxa[3](2,6)pyridino[3](1,1')ferrocenophane-1,12-dione (**7a**).* ^{1}H-NMR ($CDCl_3$) δ=4.42 (t, 4H, Fc-Hβ, J=4 Hz), 4.92 (t, 4H, Fc-Hα, J=4 Hz), 5.36 (s, 4H, methylene), 7.06 (d, 2H, 2,6-disubstituted pyridine-H$_a$, J=8 Hz), 7.63 (d-d, 1H, 2,6-disubstituted pyridine-H$_b$, J=8 Hz). IR (KBr): 3100, 2950, 1710, 1600, 1460, 1280, 820 cm^{-1}. MS (70 eV): m/z 377 (M^+). λ_{max} (dioxane): 467 nm (ε 197). Found: C, 60.39; H, 3.92%. Calcd for $C_{19}H_{15}FeNO_4$: C, 60.50; H, 4.01%; M, 377.18.

*2,11,25,34,-Tetraoxa[3](2,6)pyridino[3](1,1')ferroceno-[3](2,6)-pyridino[3](1,1')ferrocenophane-1,12,24,35-tetrone (**8a**).* ^{1}H-NMR ($CDCl_3$) δ=4.39 (t, 8H, Fc-Hβ, J=4 Hz), 4.85 (t, 8H, Fc-Hα, J=4 Hz), 5.33 (s, 8H, methylene), 7.36 (d, 4H, 2,6-disubstituted pyridine-H$_a$, J=8 Hz), 7.70 (d-d, 2H, 2,6-disubstituted pyridine-H$_b$, J=8 Hz). IR (KBr): 3100, 2925, 1710, 1580, 1470 1280, 815 cm^{-1}. MS (70 eV): m/z 754 (M^+). λ_{max} (dioxane): 450 nm (ε 564). Found: C, 60.53, H, 3.94%. Calcd for $C_{38}H_{30}Fe_2N_2O_8$: C, 60.50; H, 4.01%; M, 754.36.

*2,10-Dioxa[3](2,5)furano[3](1,1')ferrocenophane-1,11-dione (**7b**).* ^{1}H-NMR ($CDCl_3$) δ=4.27 (t, 4H, Fc-Hβ, J=4 Hz), 4.71 (t, 4H, Fc-Hα, J=4 Hz), 5.21 (s, 4H, methylene), 6.49 (s, 2H, 2,5-disubstituted furan). IR (KBr): 3100, 2960, 1720, 1560, 1470, 1280, 840 cm^{-1}. MS (70 eV): m/z 366 (M^+). λ_{max} (dioxane): 450 nm (ε 329). Found: C, 59.11; H, 3.74%. Calcd for $C_{18}H_{14}FeO_5$: C, 59.05; H, 3.85%; M, 366.15.

*2,10,24,32-Tetraoxa[3](2,5)furano[3](1,1')ferroceno[3](2,5)furano-[3](1,1')ferrocenophane-1,11,23,33-tetrone (**8b**).* ^{1}H-NMR ($CDCl_3$) δ=4.16 (t, 8H, Fc-Hβ, J=4 Hz), 4.63 (t, 8H, Fc-Hα, J=4 Hz), 5.23 (t, 8H, methylene), 6.48 (t, 4H, 2,5-disubstituted furan). IR (KBr): 3100, 1720, 1560, 1280, 840, 770 cm^{-1}. MS (70 eV): m/z 732 (M^+). λ_{max} (dioxane): 450 nm (ε 630). Found: C, 59.12; H, 3.78%. Calcd for $C_{36}H_{28}Fe_2O_{10}$: C, 59.05; H, 3.85%; M, 732.31.

*2,10-Dioxa[3](2,5)thiopheno[3](1,1')ferrocenophane-1,11-dione (**7c**).* ^{1}H-NMR ($CDCl_3$) δ=4.39 (t, 4H, Fc-Hβ, J=4 Hz), 4.89 (t, 4H, Fc-Hα, J=4 Hz), 5.27 (s, 4H, methylene), 7.16 (s, 2H, 2,5-disubstituted thiophene). IR (KBr): 3100, 1700, 1280, 820, 770 cm^{-1}. MS (70 eV): m/z 382 (M^+). λ_{max} (dioxane): 450 nm (ε 205). Found: C, 56.47; H, 3.58%. Calcd for $C_{18}H_{14}FeO_4S$: C, 56.56; H, 3.69%; M, 382.21.

*2,10,24,32-Tetraoxa[3](2,5)thiopheno[3](1,1')ferrocenophane-1,11,23,33-tetrone (**8c**).* ^{1}H-NMR (FT) ($CDCl_3$) δ=4.07 (t, 8H, Fc-Hβ, J=3.95 Hz), 4.59 (t, 8H, Fc-Hα, J=3.95 Hz), 5.36 (s, 4H, methylene), 7.06 (s, 4H, 2,5-disubstituted thiophene). IR (KBr): 3100, 1700, 1280, 820, 770 cm^{-1}. MS (70 eV): m/z 764 (M^+). λ_{max} (dioxane): 450 nm (ε 690). Found: C, 56.64; H, 3.60%. Calcd for $C_{36}H_{28}Fe_2O_8S_2$: C, 56.56; H, 3.69%; M, 764.43.

*2,11-Dioxa[3]methacyclo[3](1,1')ferrocenophane-1,12-dione (**7d**).* ^{1}H-NMR ($CDCl_3$) δ=4.56 (t, 4H, Fc-H$_\beta$, J=4 Hz), 4.90 (t, 4H, Fc-H$_\alpha$, J=4 Hz), 5.44 (s, 4H, methylene), 7.10—7.45 (m, 4H, 1,3-disubstituted benzene). IR (KBr): 3100, 1720, 1500, 1290, 820, 780 cm^{-1}. MS (70 eV): 376 (M^+). λ_{max} (dioxane): 450 nm (ε 343). Found: C, 63.95; H, 4.34%. Calcd for $C_{20}H_{16}FeO_4$: C, 63.86; H, 4.29%; M, 376.19.

*2,11,25,34-Tetraoxa[3]methacyclo[3](1,1')ferrocenophane-1,12,24,35-tetrone (**8d**).* ^{1}H-NMR (FT) ($CDCl_3$) δ=4.29 (t, 8H, Fc-H$_\beta$, J=4.06 Hz), 4.77 (t, 8H, Fc-H$_\alpha$, J=4.06 Hz), 5.24 (s, 8H, methylene), 7.40 (d, 6H, 1,3-disubstituted benzene-H$_a$, J=1.3 Hz), 7.60 (br-s, 2H, 1,3-disubstituted benzene-H$_b$). IR (KBr): 3100, 1720, 1500, 1280, 840, 780 cm^{-1}. MS (70 eV): m/z 752 (M^+). λ_{max} (dioxane): 450 nm (ε 580). Found: C, 63.79; H, 4.23%. Calcd for $C_{40}H_{32}Fe_2O_8$: C, 63.86; H, 4.29%; M, 752.38.

*2,8-Dioxa-5-thia[9](1,1')ferrocenophane-1,9-dione (**7e**).* ^{1}H-NMR ($CDCl_3$) δ=3.00 (t, 4H, -COOCH$_2$C$\underline{H}_2$S-, J=10 Hz), 4.51 (t, 4H, Fc-H$_\beta$, J=4 Hz), 4.52 (t, 4H, -COOC$\underline{H}_2$-CH$_2$S-, J=10 Hz), 4.75 (t, 4H, Fc-H$_\alpha$, J=4 Hz). IR (KBr): 3100, 2950, 1710, 1460, 1275, 835 cm^{-1}. MS (70 eV): m/z 360 (M^+). λ_{max} (dioxane): 448 nm (ε 231). Found: C, 53.26; H, 4.43%. Calcd for $C_{16}H_{16}FeO_4S$: C, 53.35; H, 4.48%; M, 360.21.

*2,8,22,28-Tetraoxa-5,25-dithia[9.9](1,1')ferrocenophane-1,9,21,29-tetrone (**8e**).* ^{1}H-NMR (FT) ($CDCl_3$) δ=3.03 (t, 8H, -COOCH$_2$C$\underline{H}_2$S-, J=13.6 Hz), 4.46 (t, 8H, Fc-H$_\beta$, J=3.96 Hz), 4.48 (t, 8H, -COOC$\underline{H}_2$CH$_2$S-, J=13.6 Hz), 4.83 (t, 8H, Fc-H$_\alpha$, J=3.96 Hz). IR (KBr): 3100, 2950, 1720, 1465, 1280, 820 cm^{-1}. MS (70 eV): m/z 720 (M^+). λ_{max} (dioxane): 448 nm (ε 583). Found: C, 53.42; H, 4.53%. Calcd for $C_{32}H_{32}Fe_2O_8S_2$: C, 53.35; H, 4.48%; M, 720.42.

Solvent Extraction. Solvent extraction was carried out by the similar method as described by Pedersen.[19] The dichloromethane solution contained 7×10^{-4} M (1 M=1 mol dm^{-3}) of ferrocenophane, and 1×10^{-1} M of MNO_3 (M: metal cation). Equal volumes (10 ml) of the organic and the aqueous solutions were agitated thoroughly for 10 min at room temperature (20—23 °C). After setting the solution, upper aqueous layer was withdrawn, and its electronic spectrum was measured (picrate λ_{max}: 360 nm). A similar extraction was performed with pure dichloromethane. The concentration of the picrate was determined by using the calibration curve. The extractability was calculated by the following equation:

$$\text{Extractability} = \frac{C_0 - C}{C_0} \times 100$$

C_0: Initial concentration of the picrate.
C: Concentration of the picrate after extraction.

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