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Bis-crown ethers in which the benzo-15-crown-5 units were linked to 1,1'-positions of metallocene ($M = \text{Fe}$ or Ru) with amide, ester, or $-\text{C}-\text{C}-$ bonds were synthesized. Complexing ability of the compounds with alkali, alkali earth, and transition metal cations were measured by the solvent extraction method. The results showed that these crown ethers had high affinity toward alkali metal cations (Li^+ , Na^+ , K^+ , and Rb^+) and heavy-metal cations (Ag^+ and Tl^+). The difference of complexing ability for metal cations between ferrocene and ruthenocene derivatives could not be detected significantly. The extractability of metallocene-bis-crown ethers for metal cations was more larger than that of the corresponding mono-crown ethers, and irregular increments of extractability were explained by assuming the existence of a mixture of 1:1 and 2:1 complexes.

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A number of crown ethers with ferrocene and ruthenocene units incorporated have already been reported, and the interest in them has mainly been in the interaction between metal cations and iron or ruthenium atoms in ferrocene or ruthenocene nucleus [1]. Since Pederson's studies [2], it is well known that the complexes of crown ethers with various metal salts were generally found to be mostly of 1:1 stoichiometry, however, in some cases where the ion was too large to lie in the "hole" of the polyether ring, 2:1 or 3:2 polyether cation complexes which have "sandwich" structures were obtained. With reference to the characteristics of the metallocene, it is noteworthy that, although the *anti*-form is the more stable conformation, two substituents in 1,1'-disubstituted metallocene derivatives are not fixed in position due to free ring rotation. In general, bis-crown ethers exhibit more selective alkali metal complexation compared with their monocyclic analogs [2b,3], therefore, it is of interest to compare the ca-

tion complexing properties of mono- and 1,1'-bis (crown ether) metallocenes. We report herein the synthesis and complexing properties of metallocene crown ethers which were substituted by 2,3-benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (benzo-15-crown-5) unit at the 1- or the 1,1'-positions of the metallocene. We presume that these compounds can bind the metal cations in the following three ways: (1) 1:1 intramolecular complex in **A**; (2) 2:1 intramolecular sandwich in **B**; (3) 2:1 intermolecular sandwich (half-complex) in **C** (Figure 1).

To confirm these expectations, it is of interest to synthesize three types of crown ethers having benzo-15-crown-5 units at the 1-, the 1,1', or the 1,3-positions of the metallocene ring, and to make a survey of the complexing properties of metal cations. Already, Czech *et al.* [4] and Beer [5] have reported the synthesis of some metallocenes having the benzo-15-crown-5 unit, however, no detailed extractability data for metal cations were published.

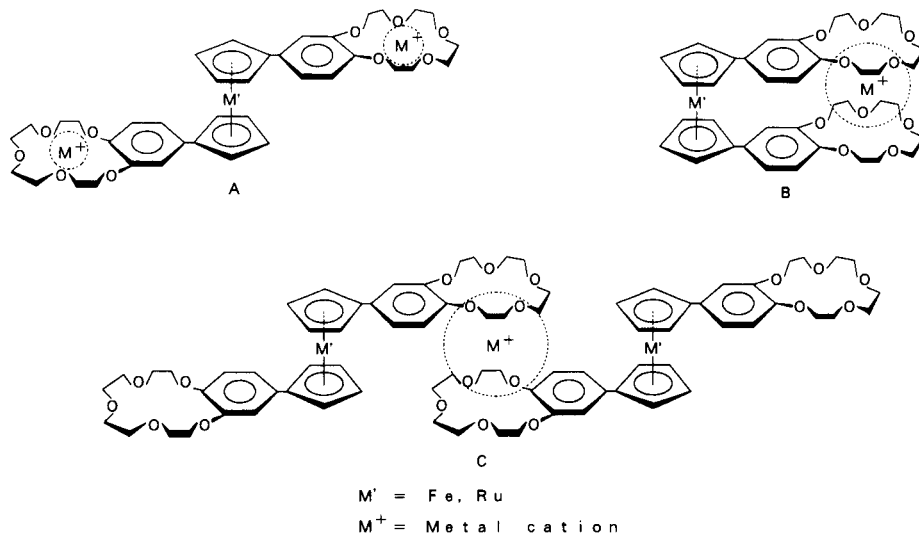


Figure 1

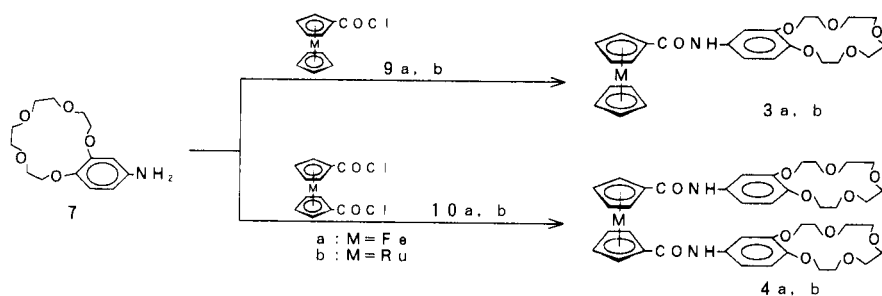
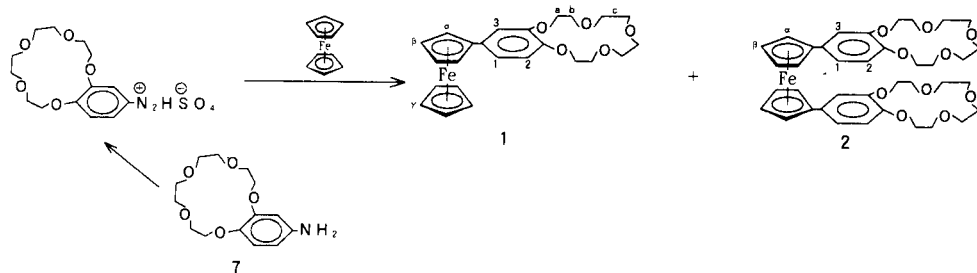


Figure 2-1

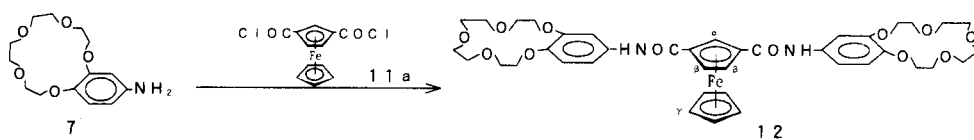
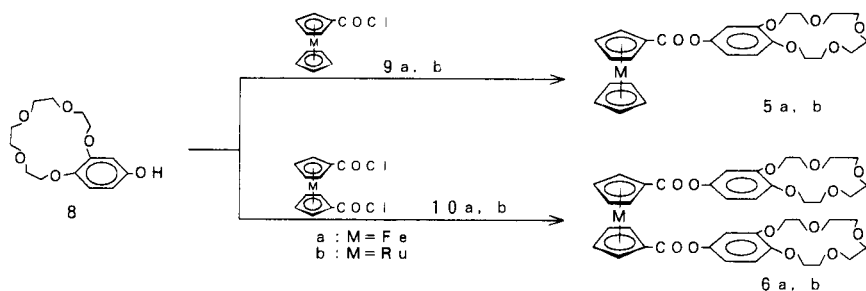


Figure 2-2

Results and Discussion.

Synthesis.

The compounds **1** ~ **12** were synthesized by the routes shown in Figure 2.

Compounds **1** and **2** were synthesized by the Gomberg-Bachmann reaction [6] of ferrocene with 2,3-(4'-aminobenzo)-1,4,7,10,13-pentaoxycyclopentadeca-2-ene (4'-amino-benzo-15-crown-5) (**7**). The condensation reaction of metalocene acid chlorides **9a, 9b, 10a, 10b**, and **11a** with the appropriate aniline (**7**) or phenol derivatives (**8**) resulted in the formation of amido compounds **3a, 3, 4a, 4b**, and **12**

or ester compounds **5a, 5b, 6a**, and **6b**, respectively. The structural assignments for these products were based on spectral evidence and elemental analyses. The ir spectra of the synthesized metallocene crown ethers, except the compounds **1** and **2**, exhibit the characteristic absorption of an amido carbonyl (1650-1640, 1520-1510 cm^{-1} regions) or an ester carbonyl (1720, 1380-1350 cm^{-1} regions). Furthermore, the products showed characteristic absorptions by mono-substituted metallocenes **1, 3a, 3b, 5a**, and **5b** or homoannular disubstituted ferrocene **12** in the 3090-3080, 1100, 1020-990, and 820-800 cm^{-1} regions, and by heteroannular disubstituted metallocenes (**2, 4a, 4b, 6a**, and **6b**)

in the 3100-3070 and 805 cm^{-1} region [7]. The ^1H and ^{13}C nmr spectra were also useful for the structural assignments. For example, the ^1H nmr spectrum of monosubstituted ferrocene **5a** which was substituted with a benzo-15-crown-5 unit by an ester linkage showed the signal of the unsubstituted ferrocene ring protons as a singlet at δ 4.28 and the substituted cyclopentadienyl ring protons as the A_2B_2 pattern at δ 4.93 and 4.47 in addition to the signals of benzo-15-crown-5, which showed three types of methylene signals as a singlet at δ 3.75 and two multiplets at δ 3.88-3.93 and 4.09-4.14, and the 1,3,4-trisubstituted benzene signals at δ 6.68, 6.71, and 6.88. In the completely decoupled ^{13}C nmr spectrum of **5a**, ester carbonyl carbon, bridge head carbon, and α , β , and γ carbons of ferrocene nucleus appeared at δ 170.26, 82.60, 71.16, 70.55, and 69.88, respectively. Furthermore, four methylene carbons in benzo-15-crown-5 unit appeared at δ 70.74, 70.19, 69.55, and 69.21, and the carbons of the 1,3,4-trisubstituted benzene nucleus showed six signals at δ 149.61, 146.72, 145.04, 114.82, 113.64, and 108.42. The mass spectra and

elemental analyses also confirmed the structure. In the ^1H nmr spectrum of 1,1'-disubstituted metallocene crown ethers, ferrocene derivatives **2**, **4a**, and **6a** showed α and β protons of metallocene nucleus appeared as two triplets at δ 4.17-5.03 and 3.92-4.58, respectively. However, ruthenocene derivatives **4b** and **6b** showed two kinds of protons at δ 5.04-5.21 and 5.06-5.35, and β protons at δ 4.74-4.86. These phenomena suggested that the two substituents in **4b** and **6b** are situated in an unsymmetrical position. The structures of the other new compounds were also determined by a similar method as described above.

Extraction Ability.

The complex formation ability of crown ethers with metal cations depends on several factors - cavity size of ligands, cation diameter, special distribution of the ring binding sites, the character of heteroatoms, and other factors [8]. Metallocenes substituted with the benzo-15-crown-5 unit, **2**, **4a**, **4b**, **6a**, and **6b**, are expected to form complexes of the sandwich type and to show enhanced

Table 1
Extraction of Metal Picrates by Metallocene Bis(Crown Ethers) as Compared to Their Mono Analogs
Solvent System: Water-Dichloromethane (50:50, V/V) [a,b]

Compound	Extracted %														
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Al ³⁺	Ce ³⁺	Tl ⁺	Ag ⁺	Hg ²⁺	Pb ²⁺
1	2.7	19.0	37.6	18.3	1.0	2.0	4.0	3.0	1.9	18.8	7.0	47.1	25.3	3.3	6.0
2	2.5	22.4	90.3	68.2	17.0	2.3	0.8	0.0	3.0	11.0	4.1	88.4	44.5	9.9	6.9
3a	7.3	25.0	56.4	38.1	15.0	1.4	2.1	9.3	8.6	17.4	6.7	69.3	27.7	6.1	8.6
4a	66.6	80.0	98.6	90.0	94.9	25.4	31.1	31.4	38.3	24.3	27.9	97.4	92.1	35.7	28.6
3b	2.4	29.8	70.3	36.6	13.1	2.6	1.9	2.0	2.2	12.8	2.5	61.6	40.6	34.7	2.4
4b	54.0	90.9	98.4	100.0	97.2	17.7	12.6	19.3	42.1	22.9	38.9	96.8	93.9	20.5	35.3
5a	5.0	19.1	47.1	28.3	7.1	3.6	1.9	3.6	4.1	14.0	3.6	65.4	36.6	10.1	6.0
6a	77.1	81.1	98.7	99.6	96.4	25.1	24.9	35.7	24.0	37.6	47.0	98.3	94.0	33.6	31.0
5b	10.1	15.2	49.1	23.1	14.2	9.0	12.2	9.6	11.8	25.1	9.5	42.0	32.8	16.4	11.7
6b	68.1	87.8	100.0	100.0	99.2	22.1	18.2	29.1	31.8	26.5	55.8	99.4	99.0	24.8	31.8
12	29.7	44.4	95.7	91.6	54.6	12.9	17.3	16.1	20.0	25.0	14.6	95.3	63.4	27.4	14.3

[a] [Picric acid] = $7.0 \times 10^{-5} M$ ($1M = 1 \text{ mol dm}^{-3}$), [Metallocene crown ether] = $7.0 \times 10^{-4} M$, [Metal nitrate] = $0.1 M$. [b] Rubidium chloride and mercury dichloride were used in place of nitrates.

Table 2
IR Spectral Data of Metallocene Crown Ethers (Potassium Bromide disk)

Compound	ν max/cm ⁻¹
1	3080, 2910, 2850, 1600, 1135, 1100, 1000, 855, 820, 815
2	3090, 2920, 2850, 1600, 1130, 870, 825
3a	3280 (-NH), 3090, 2940-2850, 1650 (-NHCO-), 1600, 1135, 1100, 1000, 850, 820, 805
3b	3240 (-NH), 3080, 2900-2850, 1650 (-NHCO-), 1600, 1510, 1250, 1130, 1100, 990, 850, 810, 800
4a	3370 (-NH), 3080, 2900-2850, 1650 (-NHCO-), 1600, 1510, 1130, 835, 800
4b	3330 (-NH), 3100, 2900-2850, 1655 (-NHCO-), 1600, 1250, 1125, 850, 820
5a	3090, 2900-2850, 1720 (-COO-), 1600, 1510, 1270, 1155, 1125, 1100, 1010, 865, 820, 810
5b	3090, 2950-2850, 1720 (-COO-), 1600, 1500, 1270, 1150, 1120, 1100, 990, 850, 810, 800
6a	3070, 2900, 2850, 1720 (-COO-), 1600, 1505, 1260, 1155, 1120, 880, 825
6b	3080, 2900, 2850, 1720 (-COO-), 1600, 1500, 1270, 1150, 1118, 880, 820
12	3360 (-NH), 3090, 2900, 2850, 1650 (-NHCO-), 1600, 1510, 1130, 1105, 995, 850, 820, 790

complexation capability with metal cations. Therefore, a quantitative comparison of complexation capability of **2**, **4a**, **4b**, **6a**, and **6b** with those of the corresponding mono-substituted crown ethers **1**, **3a**, **3b**, **5a**, and **5b** toward a variety of metal cations was carried out by the method described by Pedersen [2d], and the results are summarized in Table 1. As can be seen from Table 1, all the extractabilities of bis-benzo-15-crown-5 derivatives for metal cations were larger than those of the corresponding mono-benzo-15-crown-5 derivatives, except for the K^+ and Tl^+ cations. The striking differences between mono- and bis-benzo-15-crown-5 derivatives were observed in their extractabilities for the Li^+ , Cs^+ , Mg^{2+} , Sr^{2+} , Ba^{2+} , and Hg^{2+} cations (mainly alkaline earth cations). An appreciable affinity toward K^+ and Tl^+ cations was shown not only for bis-crown ether but also for mono-crown ether derivatives.

The high affinity for the K^+ cation might be ascribed to the intrinsically large selectivity of benzo-15-crown-5 itself for the K^+ cation. High affinity for the Tl^+ cation was already well known for the previously reported metallocene crown ether compounds, and it was explained that

there was some participation of the metal atom of the metallocene ($M = Fe$ and Ru) in the complexation process [11,9].

Increased capability for extraction of cations which have larger ionic radii than the hole size of the crown ring has proved to be a common feature of bis-crown ethers [10]. However, these complexes are often structurally complicated in solution, and, if it is sterically able to form, the two crown ether moieties form an intramolecular sandwich-type complex with metal cations [10,11]. In the case of 1:1 complex **A**, bis-crown ethers are shown to have twofold extractabilities compared with the corresponding mono-crown ethers, because of the twofold concentration of the crown ether rings. We examined the extractability of compound **12** which was substituted with benzo-15-crown-5 units at the 1,3-positions of the cyclopentadienyl ring, because with compound **12** it is possible to form a 1:1 complex **A** and a 2:1 intermolecular sandwich type complex **C**, however, it is impossible to form a 2:1 intramolecular sandwich type complex **B**.

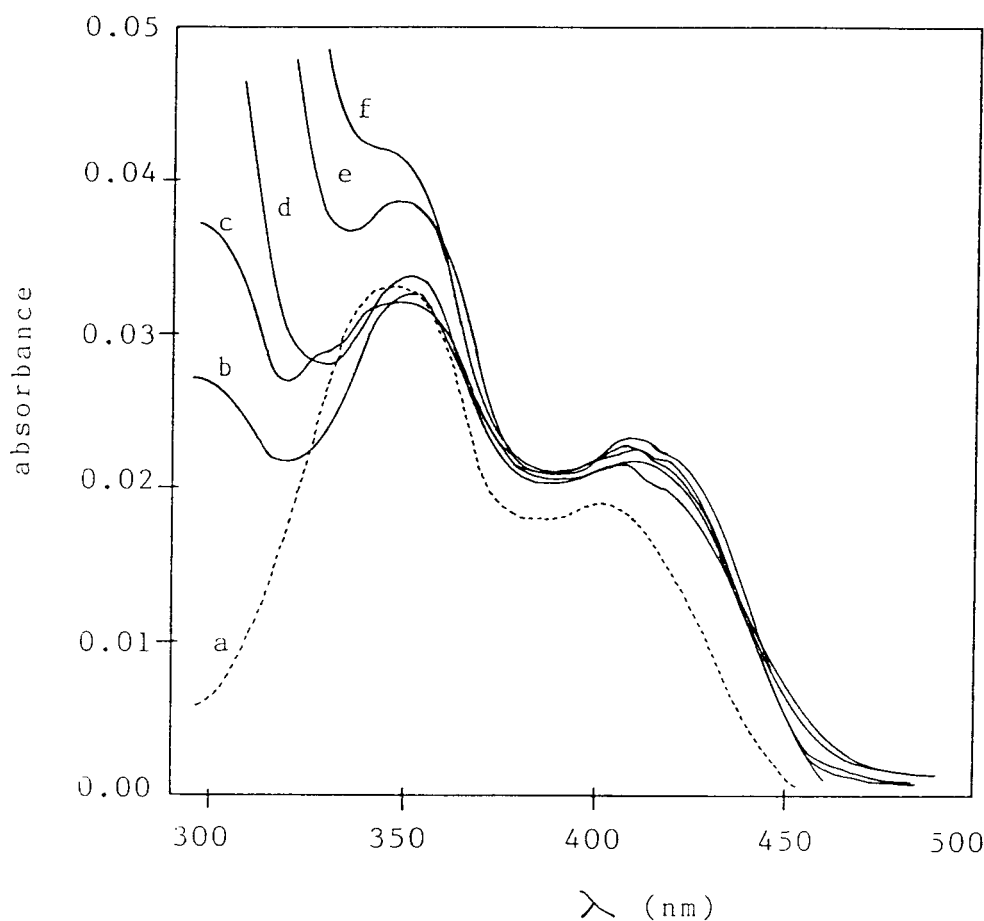


Figure 3. Optical spectra of a $2.0 \times 10^{-6} M$ THF solution of potassium picrate in the presence of varying amounts of crown compound **3a** at 22° . Molar ratio of crown ether to picrate salt: (a) 0, (b) 0.5, (c) 1.0, (d) 2.0, (e) 4.0, (f) 8.0.

Compared with **12**, crown ether **4a** showed a larger extractability toward Li^+ , Na^+ , Cs^+ , Mg^{2+} , Sr^{2+} , Ba^{2+} , Ag^+ , Ce^{2+} , and Pb^{2+} . The irregular increments of extractability of **4a** may be explained by assuming that it exists as a mixture of 1:1 and 2:1 complexes. Two groups of metallocene crown ethers ($M = \text{Fe}$ and Ru) showed a similar tendency with regard to a high affinity toward Na^+ , K^+ , Rb^+ , Tl^+ , and Ag^+ . It should be noted that the high affinity toward alkali metal cations, Li^+ , Na^+ , K^+ , and Rb^+ , observed together with a high affinity toward heavy-metal cations, Ag^+ and Tl^+ , indicates a different phenomenon; from the results of hitherto reported "crowned" ferrocenophanes. This suggests that the benzo-15-crown-5 moiety influenced the cation-selectivity as well as the metallocene moiety. Concerning the effect of chain length and chain structure between the metallocene and the benzo-15-crown-5 units, we examined three types of bonding: $-\text{C}-\text{C}-$, amido, and ester bonds. For example, compound **2** which was directly substituted with two benzo-15-crown-5 moieties showed large extractability toward K^+ , Rb^+ , and Cs^+ , however, there were no apparent noticeable improvement of the extracta-

bility for metal cations, except Cs^+ , compared with the corresponding mono substituted analog **1**. On the other hand, compounds **4a**, **4b**, **6a**, and **6b** (amido and ester bonds) showed a significant increase of extractability for metal cations compared with the mono-substituted analogs **3a**, **3b**, **5a**, and **5b**, respectively. These results indicate that, although a difference in amido and ester bonds has not been elucidated, the flexibility and length of bonding influence the extractabilities. Similar results were already reported in the case of several glycols containing benzo-15-crown-5 moiety as a pendent group [12].

Electronic Spectra.

Wong *et al.* [13] reported that, in the presence of crown ethers, salts of picric acid in low polarity media frequently exhibit pronounced shifts in their optical spectra. Furthermore, they suggested [14] that the shifts occur when a tight ion pair is converted into a loose pair by a cation chelating crown compound, or, to put it more generally, when complexation leads to a significant increase in the interionic distance of the tight ion pair. In our compounds, it is not

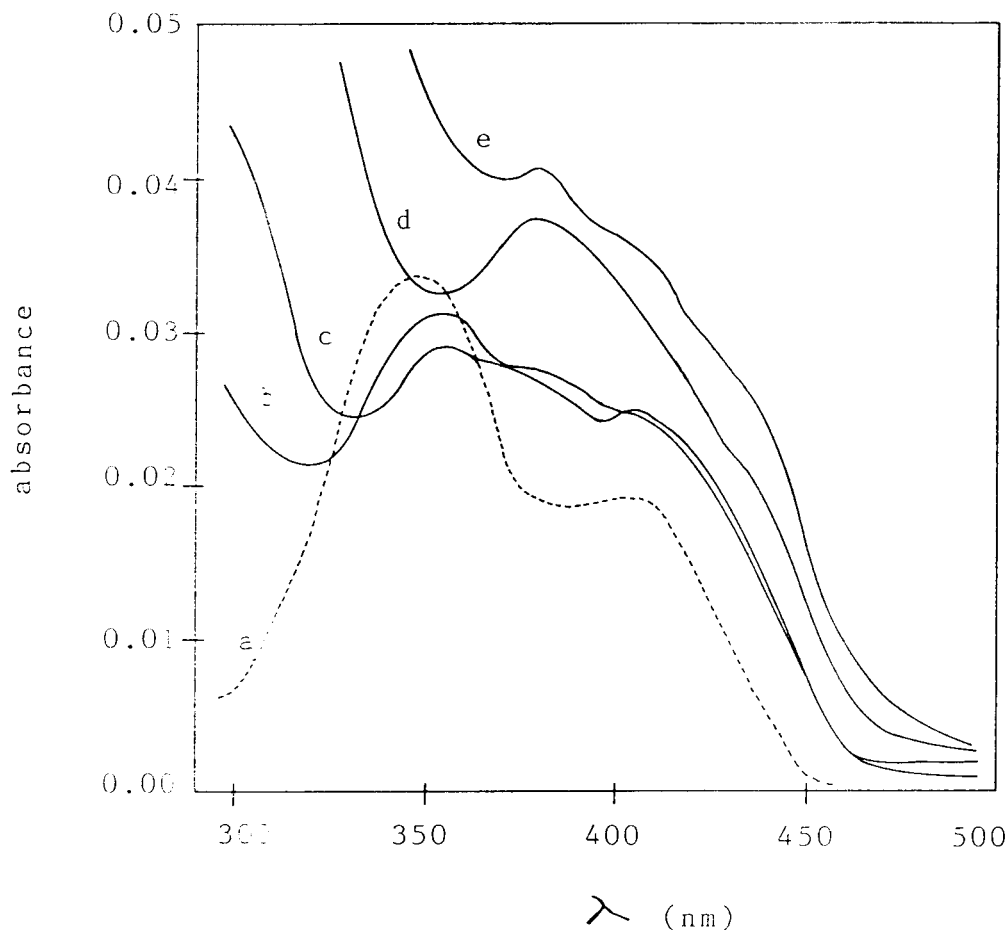


Figure 4. Optical spectra of a $2.0 \times 10^{-6} M$ THF solution of potassium picrate in the presence of varying amounts of crown compound **4a** at 22° . Molar ratio of crown ether to picrate salt: (a) 0, (b) 0.5, (c) 1.0, (d) 4.0, (e) 10.0.

Table 3
¹H NMR Spectral Data of Metallocene Crown Ethers in Deuteriochloroform (Chemical Shift/ppm) [a]

Compound	Cp-ring-H	-CH ₂ -O-	Ar-ring-H	N-H proton
1	4.02 (s, 5H)	3.79 (s, 8H)	6.79 (d, 1H, J = 9 Hz)	
	4.25 (t, 2H, J = 4 Hz)	3.88-4.00 (m, 4H)	6.99 (d, 1 H, J = 3 Hz)	
	4.54 (t, 2H, J = 4 Hz)	4.16-4.28 (m, 5H)	7.04 (d-d, 1H, J = 3 and 9 Hz)	
2	4.03 (m, 4H)	3.75 (s, 16H)	6.87 (d, 2H, J = 9 Hz)	
	4.31 (m, 4H)	3.83-3.98 (m, 8H)	7.80 (d, 2H, J = 2 Hz)	
		4.08-4.27 (m, 8H)	7.93 (d-d, 2H, J = 2 and 9 Hz)	
3a	4.25 (s, 5H)	3.76 (s, 8H)	6.87 (s, 1H)	7.60 (br-s, 1H)
	4.41 (t, 2H, J = 4 Hz)	3.87 (m, 4H)	7.31 (d, 1H, J = 9 Hz)	
	4.78 (t, 2H, J = 4 Hz)	4.13-4.20 (m, 4H)	7.40 (d, 1H, J = 9 Hz)	
4a	4.34 (t, 4H, J = 4 Hz)	3.68 (s, 16H)	6.77 (d, 2H, J = 9 Hz)	8.82 (br-s, 2H)
	4.57 (t, 4H, J = 4 Hz)	3.80-3.88 (m, 8H)	7.17 (d, 2H, J = 9 Hz)	
		4.03-4.12 (m, 8H)	7.50 (s, 2H)	
3b	4.60 (s, 5H)	3.74 (s, 8H)	6.80 (s, 1H)	7.45 (br-s, 1H)
	4.69 (t, 2H, J = 4 Hz)	3.85-3.95 (m, 4H)	7.33-7.40 (m, 2H)	
	5.11 (t, 2H, J = 4 Hz)	4.07-4.18 (m, 4H)		
4b	4.74 (t, 4H, J = 4 Hz)	3.73 (s, 16H)	6.74 (d, 2H, J = 8 Hz)	8.27 (br-s, 2H)
	5.04 (t, 2H, J = 4 Hz)	3.82-3.91 (m, 8H)	7.05 (d, 2H, J = 8 Hz)	
	5.06 (t, 2H, J = 4 Hz)	4.02-4.14 (m, 8H)	7.38 (s, 2H)	
5a	4.28 (s, 5H)	3.75 (s, 8H)	6.68 (d, 1H, J = 9 Hz)	
	4.47 (t, 2H, J = 4 Hz)	3.88-3.93 (m, 4H)	6.71 (s, 1H)	
	4.93 (t, 2H, J = 4 Hz)	4.09-4.14 (m, 4H)	6.88 (d, 1H, J = 9 Hz)	
6a	4.58 (t, 4H, J = 4 Hz)	3.75 (s, 16H)	6.60-6.93 (m, 6H)	
	5.03 (t, 4H, J = 4 Hz)	3.86-3.95 (m, 8H)		
		4.05-4.16 (m, 8H)		
5b	4.64 (s, 5H)	3.74 (s, 8H)	6.61 (d, 1H, J = 9 Hz)	
	4.77 (t, 2H, J = 4 Hz)	3.84-3.95 (m, 4H)	6.64 (s, 1H)	
	5.25 (t, 2H, J = 4 Hz)	4.01-4.18 (m, 4H)	6.86 (d, 1H, J = 9 Hz)	
6b	4.86 (m, 4H)	3.73 (s, 16H)	6.63 (d, 2H, J = 9 Hz)	
	5.21 (t, 2H, J = 4 Hz)	3.81-3.91 (m, 8H)	6.67 (s, 2H)	
	5.35 (t, 2H, J = 4 Hz)	4.05-4.14 (m, 8H)	6.81 (d, 2H, J = 9 Hz)	
12	4.89 (s, 5H)	3.72 (s, 8H)	6.97 (d, 2H, J = 9 Hz)	
	5.44 (s, 2H)	3.74 (s, 8H)	7.52 (d-d, 2H, J = 2 and 9 Hz)	
	6.35 (s, 1H)	3.75-3.92 (m, 8H)	7.81 (d, 2H, J = 2 Hz)	
	4.05-4.19 (m, 8H)			

[a] The spectra of compound **12** were measured in pyridine-d₅.

Table 4
¹³C NMR Spectra Data of Metallocene Crown Ethers in Deuteriochloroform (22.5 MHz, ppm) [a]

Compound	C _b [b]	Cp-ring C _α	C _β	C _γ	-CH ₂ -O-	Aromatic-ring	Carbonyl
1	85.58	68.30	65.98	69.27	69.52, 69.70, 70.40, 70.86	112.63, 114.12, 118.88 132.14, 147.48, 148.76	
2	84.30	68.72	68.26		69.24, 69.33, 70.34, 71.07	111.47, 112.02, 115.37 138.06, 141.72, 148.06	
3a	76.35	70.74	68.14	69.76	68.94, 69.49, 70.49, 71.01	107.17, 112.08, 115.16 132.51, 145.56, 149.49	168.30
3b	80.98	72.26	69.97	71.80	68.91, 69.46, 69.70, 69.88 70.46, 70.64, 70.95	109.99, 111.84, 115.10 132.39, 145.50, 149.46	167.05
4a	79.27	71.16	(C _α + C _β)		68.94, 69.49, 69.70, 69.79 70.46, 70.61, 71.01	107.26, 112.54, 115.01 132.81, 145.59, 149.25	168.70
4b	83.39	73.33	72.69		68.85, 69.46, 69.70, 70.43 70.58, 70.95, 71.01	107.17, 112.51, 114.86 132.51, 145.56, 149.19	166.96
5a	82.60	71.16	70.55	69.88	69.21, 69.55, 70.19, 70.74	108.42, 113.64, 114.82 145.04, 146.72, 149.61	170.26
5b	74.73	73.21	71.96	71.86	69.12, 69.46, 69.64, 69.82 70.52, 70.61, 71.04	108.21, 113.39, 114.73 144.95, 146.66, 149.58	168.73
6a	74.35	72.81	72.11		68.69, 69.27, 69.61, 69.73 70.40, 70.55, 70.92, 71.04	108.48, 113.48, 114.49 144.74, 146.66, 149.52	168.88
6b	75.16 75.40	74.00	73.75		68.97, 69.39, 69.64, 69.82 70.46, 70.61, 71.01	108.21, 113.33, 114.67 144.70, 146.69, 149.58	164.43 167.36
12	80.19	71.74	70.86		69.30, 69.91, 70.04, 70.31 70.98, 71.35, 71.55	108.54, 113.67, 115.25 134.03, 146.05, 149.64	167.51

[a] The spectra of compound **12** were measured in pyridine-d₅. [b] C_b means a bridge-head carbon.

obvious that two crown ether units in 1,1'-bis(crown ethers) act either independently or in concert to form sandwich complexes. However, electronic spectra offered some information about the stoichiometry of the bis(crown ether)-cation complexes. Therefore, we tried to measure the electronic spectra with metallocene crown compounds **3a** and **4a** and alkali metal picrates of Li⁺, Na⁺, and K⁺. Addition of a small quantity of bis(crown ether) **4a** to a lithium or sodium picrate-THF solution caused a slight red shift of the picrate anion, but large red shifts were not recognized upon further additions of **4a**, because of overlapping absorption of ferrocene (326 and 440 nm). On the other hand, stepwise addition of **3a** or **4a** to a potassium picrate-THF solution barely produced a spectral change, as shown in Figure 3 and 4. Benzo-15-crown-5 is known to be one of the most effective crown compounds for binding the K⁺ cation [15], therefore, K⁺ ion is not suitable for the sandwich complex model metal, and the behavior of the complexes in the solvent are expected to be complicated. However, the results can be rationalized in terms of tight and loose ion pair crown ether complexes. For example, on addition of ferrocene mono crown ether **3a** to a 2.0 x 10⁻⁶ M THF solution of potassium picrate, an absorption maximum (352 nm) appeared in the initial stage and was not altered by further addition of **3a** (Figure 3). It can be explained that a 1:1 tight ion pair complex is formed. However, when **4a** was added to potassium picrate, the initially formed 1:1 tight ion pair complex (λ max 354 nm) was converted gradually into a 2:1 loose ion pair with a λ max of 380 nm depending upon the concentration of the crown ether. It seems that the conversion is completed on addition of about a fourfold molar excess of **4a** (eightfold per crown ring), but it is not clear because of the overlapping of the ferrocene absorption (Figure 4). The results indicated that, in solution, bis(crown ether) complexing models are variable depending upon the concentration of crown ether, therefore, they possibly exist as a mixture of a 1:1 complex **A**, a 2:1 complex **B**, and a half-complex **C**. This assumption is consistent with the solvent extraction results.

EXPERIMENTAL

Infrared and electronic spectral data were measured with a Hitachi 260-10 and a Hitachi 200-10 spectrometers, respectively. The ¹H and ¹³C nmr spectra were obtained in deuteriochloroform with TMS as the internal standard and recorded on Hitachi R-22 and R-90H NMR spectrometers. Mass spectra were obtained at 70 eV with a Hitachi RMU-6M spectrometer. Elemental analyses were determined on a Yanagimoto CHN-Corder, Type II. All melting points are uncorrected. The ir, ¹H, and ¹³C nmr spectra of the products are summarized in Tables 2, 3, and 4, respectively.

4'-Aminobenzo-15-crown-5 [16], 4'-hydroxybenzo-15-crown-5 [17], 1,1'-ferrocenedicarboxylic acid [18], 1,1'-ruthenocenedicar-

boxylic acid [19], and 1,3-ferrocenedicarboxylic acid [20] were prepared by methods described in the literature. Alkali metal picrates of Li⁺, Na⁺, and K⁺ were prepared in ethanol by neutralizing picric acid with the corresponding metal hydroxide as outlined by Coplan and Fuoss [21]. The other reagents employed were commercial materials or were prepared by the usual methods. All inorganic compounds were reagents grade.

[3,4-(1',4',7',10',13'-Pentaoxacyclopentadec-2'-ene)phenyl]ferrocene (**1**) [4'-(Ferrocenyl)benzo-15-crown-5 (**1**)] and 1,1'-Bis[3'',4''-(1''',4''',7''',10''',13'''-pentaoxacyclopentadec-2'''-ene)phenyl]ferrocene (**2**).

The amine **7** (31 g, 110 mmoles) was diazotized in 10% sulfuric acid (200 ml) at 0-3° using sodium nitrite (9.1 g, 132 mmoles) in water (50 ml). After the diazotization, the solution was added dropwise to a solution of ferrocene (10.2 g, 55 mmoles) in acetic acid (900 ml) under a nitrogen atmosphere. The resulting dark brown solution was stirred overnight at room temperature and then poured into water (2000 ml). The reaction mixture was extracted with chloroform and the chloroform extracts were washed with 5% aqueous sodium hydrogen carbonate solution and with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography with silica gel. The first elution with hexane gave the starting material ferrocene (2.4 g, 24%), mp 173°. The second elution with benzene gave 4.7 g (16% yield based on amine **7**) of benzo-15-crown-5, mp 79-80°. The third elution with benzene gave 2.7 g (11% yield based on ferrocene) of orange crystals, mp 117-118°, which were determined to be **1**; ms: m/z 452 [M⁺].

Anal. Calcd. for C₂₄H₂₈FeO₅: C, 63.73; H, 6.24; M, 452.33. Found: C, 63.85; H, 6.30.

The fourth elution with chloroform gave 3.6 g (9% yield based on ferrocene) of yellow crystals, mp 167°, which were determined to be **2**; ms m/z 718 [M⁺].

Anal. Calcd. for C₃₈H₄₆FeO₁₀: C, 63.51; H, 6.45; M, 718.62. Found: C, 63.20; H, 6.53.

[3,4-(1',4',7',10',13'-Pentaoxacyclopentadec-2'-ene)phenylimino-carbonyl]ferrocene (**3a**).

The acid chloride **9a** was prepared from ferrocenecarboxylic acid and oxalyl dichloride by a method described in the literature [22]. Under an atmosphere of nitrogen, to a solution of **7** (1.1 g, 4 mmoles) and triethylamine (0.8 g, 8 mmoles) in dry benzene (200 ml), **9a** (1.1 g, 4 mmoles) in dry benzene (100 ml) was added dropwise over 1 hour with stirring. After gentle refluxing for 12 hours, the solvents were evaporated *in vacuo*, and the residue was extracted with chloroform. The chloroform extracts were washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated. To the reddish residue, methanol was added, then orange crystals were obtained, which were recrystallized from benzene, 1.2 g of **3a** (62%), mp 204-205°; ms: m/z 495 [M⁺].

Anal. Calcd. for C₂₅H₂₉FeNO₆: C, 60.68; H, 5.91; N, 2.83; M, 494.84. Found: C, 60.81; H, 5.80; N, 2.76.

[3,4-(1',4',7',10',13'-Pentaoxacyclopentadec-2'-ene)phenylimino-carbonyl]ruthenocene (**3b**).

The reaction of **9b** (0.6 g, 2.1 mmoles) with **7** (0.6 g, 2.1 mmoles) was carried out by the same procedure described for the preparation of **3a**. The product was chromatographed on silica gel and the fraction eluted with chloroform-methanol (50:1) gave

0.9 g of **3b** (79%) as yellow crystals, which were recrystallized from methanol, mp 223-224°; ms: m/z 540 [M*].

Anal. Calcd. for C₂₅H₂₉NO₂Ru: C, 55.55; H, 5.41; N, 2.59; M, 540.58. Found: C, 55.71; H, 5.46; N, 2.64.

1,1'-Bis[3'',4''-(1''',4''',7''',10''',13'''-pentaoxacyclopentadec-2''-ene)phenyliminocarbonyl]ferrocene (**4a**).

Under a nitrogen atmosphere, the acid chloride **10a** (0.5 g, 1.6 mmoles) in dry benzene (100 ml) was dropped to a mixture of **7** (1.0 g, 3.5 mmoles) and triethylamine (0.7 g, 7 mmoles) in dry benzene (200 ml) for 8 hours at room temperature. After the mixture was stirred for an additional 12 hours and yellow crystals were filtered and the solvents were evaporated *in vacuo*. The crystals and residue were dissolved in chloroform, and the organic layers were washed with water, dried over anhydrous magnesium sulfate and concentrated. The residue was recrystallized from methanol to afford 0.8 g of **4a** (62%) as orange crystals, mp 198-199° (lit [5] mp 198-199°); ms: m/z 805 [M*].

Anal. Calcd. for C₄₀H₄₈FeN₂O₁₂: C, 59.71; H, 6.01; N, 3.48; M, 804.67. Found: C, 59.84; H, 5.96; N, 3.39.

1,1'-Bis[3'',4''-(1''',4''',7''',10''',13'''-pentaoxacyclopentadec-2''-ene)phenyliminocarbonyl]ruthenocene (**4b**).

Compound **4b** was also prepared by a reaction of **10b** (1.2 g, 3.4 mmoles) and **7** (1.9 g, 6.8 mmoles) by the same procedure described for the preparation of **4a**. Recrystallization of the crude product from methanol gave **4b** (2.2 g, 75%) as pale yellow crystals, mp 205-206° (lit [5] mp 206-207°); ms: m/z 850 [M*].

Anal. Calcd. for C₄₀H₄₈N₂O₁₂Ru: C, 56.53; H, 5.69; N, 3.30; M, 849.90. Found: C, 56.33; H, 5.74; N, 3.24.

[3,4-(1',4',7',10',13'-Pentaoxacyclopentadec-2'-ene)phenyloxycarbonyl]ferrocene (**5a**).

Under a nitrogen atmosphere, to a solution of **8** (0.9 g, 3.2 mmoles) and triethylamine (1.4 g, 6.4 mmoles) in dry acetonitrile (150 ml), compound **9a** (0.8 g, 3.2 mmoles) in dry benzene (150 ml) was added dropwise over 10 hours with stirring at 80-82°. After gentle refluxing for an additional 12 hours the solvents were evaporated *in vacuo* and the residue was dissolved in chloroform (200 ml). The organic layers were washed successively with 5% aqueous hydrochloric acid and water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was chromatographed on silica gel, and the fractions eluted with chloroform gave 0.98 g of **5a** (62%) as orange yellow crystals, which were recrystallized from hexane-benzene (5:1), mp 140-142°; ms: m/z 496 [M*].

Anal. Calcd. for C₂₅H₂₈FeO₇: C, 60.50; H, 5.69; M, 496.34. Found: C, 60.74; H, 5.72.

[3,4-(1',4',7',10',13'-Pentaoxacyclopentadec-2'-ene)phenyloxycarbonyl]ruthenocene (**5b**).

The reaction of **9b** (0.5 g, 1.7 mmoles) with **8** (0.5 g, 1.7 mmoles) was carried out by a procedure similar to that described for **5a**. The product **5b** was obtained in 68% yield (0.63 g) as white crystals, which were recrystallized from acetone, mp 125-126°; ms: m/z 542 [M*].

Anal. Calcd. for C₂₅H₂₈O₇Ru: C, 55.45; H, 5.21; M, 541.56. Found: C, 55.75; H, 5.17.

1,1'-Bis[3'',4''-(1''',4''',7''',10''',13'''-pentaoxacyclopentadec-2''-ene)phenyloxycarbonyl]ferrocene (**6a**).

The reaction of **10a** (0.5 g, 1.6 mmoles) with **8** (0.9 g, 3.2

mmoles) was carried out by a procedure similar to that described for **5a**. The product **6a** was obtained in 72% yield (0.93 g) as orange crystals, which were recrystallized from acetone-hexane (1:10), mp 165-166°; ms: m/z 807 [M*].

Anal. Calcd. for C₄₀H₄₆FeO₁₄: C, 59.56; H, 5.75; M, 806.64. Found: C, 59.67; H, 5.59.

1,1'-Bis[3'',4''-(1''',4''',7''',10''',13'''-pentaoxacyclopentadec-2''-ene)phenyloxycarbonyl]ruthenocene (**6b**).

The reaction of **10b** (1 g, 2.8 mmoles) with **8** (1.6 g, 5.6 mmoles) was carried out by a procedure similar to that described for **5a**. The product **6b** was obtained in 76% yield (1.8 g) as white crystals, which were recrystallized from acetone, mp 166-167°; ms: m/z 852 [M*].

Anal. Calcd. for C₄₀H₄₆O₁₄Ru: C, 56.40; H, 5.44; M, 851.87. Found: C, 56.18; H, 5.51.

1,3-Bis[3',4'-(1'',4'',7'',10'',13''-pentaoxacyclopentadec-2''-ene)phenyliminocarbonyl]ferrocene (**12**).

The acid chloride **11a** was prepared from 1,3-ferrocenedicarboxylic acid and oxalyl dichloride. The reaction of **11a** (2.2 g, 7.1 mmoles) with **7** (2 g, 7.1 mmoles) was carried out by a procedure similar to that described for **5a** and gave 41% of **12** (2.3 g) as pale yellow crystals, mp 243-244°; ms: m/z 805 [M*].

Anal. Calcd. for C₄₀H₄₈FeN₂O₁₂: C, 59.71; H, 6.01; N, 3.48; M, 804.67. Found: C, 59.80; H, 5.95; N, 3.52.

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