Simple Synthesis and Chemicophysical Properties of Polyoxa[*n*]-ferrocenophanes and Its Alkali Metal Complexes

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Polyoxaferrocenophanes were synthesized by a one-pot reaction of 1,1′-diacetoxyferrocene with dichloride. Crystalline 1 : 1 complexes of **3a** with LiSCN, NaSCN, and KSCN were isolated. The ^{1}H-NMR and Mössbauer spectra of these complexes suggest the possibility of a certain interaction between the iron atom of the ferrocene nuclei and complexed cation. The new type of ferrocenophane **3a** extracts a thallium ion most effectively, the extractability of several metal ions being in this order; $Tl^+ > Rb^+ > K^+ > Cs^+ > Na^+$.

Although a number of crown ethers and benzo crown ethers have already been reported,[1] polyoxa[*n*]ferrocenophane and its homologs are rare.[2] Polyoxa[*n*]-ferrocenophane (**3**) is a crown ether-like compound including ferrocene subunit as a ring member; in it, the iron atom may act as a coordinatable heteroatom. Therefore, it is of interest to know what kind of interaction can be expected between the iron atom and the complexed cation. With regard to this expectation, several groups of workers[2] have synthesized this type of compounds. Biernat *et al.*[3] have recently reported the preparation of **3** and concluded, on the basis of their electronic spectral data, that there is no interaction between **3b** and the rubidium cation in methanol. On the other hand, we ourselves previously observed a certain interaction between the iron atom of oxathia-ferrocenophane and the complexed silver ion.[4] We now wish to report on a facile modified Williamson synthesis and some chemicophysical properties of **3** and alkali metal complexes of **3a** and **3b**.

Synthesis of 3a—e. The hydrolysis of **1** was carried out under a nitrogen atmosphere by the usual method. A mixture of the potassium salt of 1,1′-dihydroxyferrocene with the dihalide (**2**) in 60% ethanol was refluxed for 5 h. In every case, cyclization proceeded smoothly to afford the desired product, **3**, in a 25—60% yield. Many other products were also observed, but not confirmed because of their tiny amounts. The yields and physical properties of **3** are summarized in Table 1. The results suggest that the yields of **3** remarkably are dependent on the size of the rings, decreasing in this order: $n=4>3>2>1>0$. It is considered that the potassium cation acts as a template in the cyclization, as has been mentioned by Green.[5] It is noteworthy that this new method for preparing **3** directly starting from **1** avoids the isolation of very unstable 1,1′-dihydroxyferrocene[6] and that the yield of **3** is much higher than that in the Biernat method.[3] The structures of these compounds have been assigned on the basis of the following evidence. The IR spectrum of **3** indicates ether-linkage absorption near 1125 cm^{-1} and ferrocene-ring CH absorption near 1440 cm^{-1}, but no absorption attributable to hydroxyl or carbonyl groups. The UV spectra of **3** (λ_{max} (MeOH) 438 nm) suggest the presence of ferrocene nucleus. The mass spectra show the corresponding molecular ion. The electronic, ^{1}H-NMR, and ^{13}C-NMR spectral data are listed in Table 2. However, our ^{1}H-NMR spectra of **3a—d** are completely different from the data in the literature.[3] For example, Biernat *et al.*[3] reported that the ^{1}H-NMR spectrum of **3a** in $CDCl_3$ showed the ferrocene-ring protons at δ 3.35—3.45 as two doublets (J=6.25 Hz), together with methylene protons at δ 3.50—3.60 as multiplet. In the ^{1}H-NMR spectrum of **3a** (Table 2), the signals at δ 4.14 and 3.86 as triplets (J=2.0 Hz) are attributable to α- and β-protons of cyclopentadienyl rings,[7] while the two singlets at δ 3.70 and 3.78 and the two triplets at δ 3.86 and 4.05 (J=4.6 Hz) are attributable to the methylene protons of macrocycle. Furthermore, the ^{13}C-NMR, electronic and mass spectra and microanalysis data also support the idea that the structures of **3a—c** assigned by us are

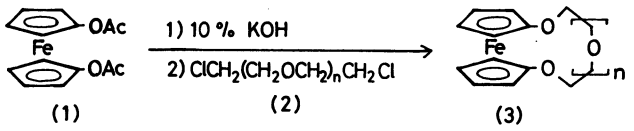
TABLE 1. YIELDS, MASS-SPECTRAL DATA, AND PHYSICOCHEMICAL PROPERTIES OF COMPOUNDS **3a—e**

Compound	Mp θ_m/°C (lit)	Yield %	Molecular formula MW	Mass spectra M^+	Found(%) C	Found(%) H	Calcd(%) C	Calcd(%) H
3a	40—41 (oil)	60	$C_{20}H_{28}O_6Fe$ 420.3	420	57.08	6.81	57.14	6.67
3b	60—61 (59—60.5)	58	$C_{18}H_{24}O_5Fe$ 376.2	376	57.50	6.40	57.45	6.38
3c	58—59 (oil)	50	$C_{16}H_{20}O_4Fe$ 332.2	332	57.75	6.13	57.83	6.02
3d	120—121 (119—120)	32	$C_{14}H_{16}O_3Fe$ 288.1	288	58.38	5.78	58.33	5.56
3e	129—131	26	$C_{12}H_{12}O_2Fe$ 244.1	244	59.08	5.12	59.02	4.92

TABLE 2. ^{1}H-, ^{13}C-NMR, AND ELECTRONIC SPECTRAL DATA OF COMPOUNDS **3a—e**

Compound	^{1}H-NMR (200 MHz, $CDCl_3$)	^{13}C-NMR (22.5 MHz, $CDCl_3$)	λ_{max}/nm(ε)
3a	4.14 (4H, t, J=2.0 Hz, H_α), 3.86 (4H, t, J=2.0 Hz, H_β), 3.70 (4H, s, OCH_2CH_2), 3.78 (8H, s, OCH_2CH_2O), 3.86 (4H, *t*, J=4.6 Hz) and 4.05 (4H, t, J=4.6 Hz, OCH_2CH_2)[b]	127.1 (C_b),[a] 56.2 (C_α), 61.9 (C_β), 71.2, 70.6, 70.1 (methylene)	438 (127)
3b	4.15 (4H, t, J=2.0 Hz, H_α), 3.86 (4H, t, J=2.0 Hz, H_β), 3.71 (8H, s, OCH_2CH_2), 3.83 and 4.06 (4H, t, J=5 Hz, OCH_2CH_2)[b]	126.9 (c_b), 56.4(C_α), 61.9 (C_β), 71.3, 70.7, 70.3, 70.0 (methylene)	438 (126)
3c	4.17 (4H, t, J=2.0 Hz, H_α), 3.85 (4H, t, J=2.0 Hz, H_β), 3.76 and 3.85 (4H, t, J=5.2 Hz, OCH_2CH_2)	127.2 (C_b), 56.5 (C_α), 61.8 (C_β), 71.8 and 70.2 (methylene)	438 (119)
3d	4.22 (4H, t, J=2.0 Hz, H_α), 3.81 (4H, t, J=2.0 Hz, H_β), 3.85—3.94 and 4.06—4.15 (8H, A_2B_2 pattern, OCH_2CH_2)	126.1 (C_b), 56.0 (C_α), 61.5 (C_β), 70.6 and 70.1 (methylene)	438 (132)
3e	4.38 (4H, t, J=2.0Hz, H_α), 3.89 (4H, t, J=2.0 Hz, H_β), 4.32 (4H, s, OCH_2CH_2)	122.5(C_b), 58.9(C_α), 63.6(C_β), 71.8 (methylene)	428 (120)

a) C_b indicates bridge-head carbon. b) Measured at 40 °C.



(1) (2) (3)

2a, 3a : n = 4
2b, 3b : n = 3
2c, 3c : n = 2
2d, 3d : n = 1
2e, 3e : n = 0

correct, although the ^{1}H-NMR spectral data of **3a—d** and the melting points of **3a** and **3c** are different from the results in the literature.

It is noteworthy in Table 2 that **3e** showed a singlet assignable to bridge methylene protons appearing at δ 4.32, in addition to two triplet absorptions of the α- and β-cyclopentadienyl ring protons at δ 4.38 and 3.89 respectively. The downfield shift of about 0.25 ppm of the methylene protons in **3e**, compared with that of the corresponding methylene protons in **3a—d**, may be explained by using the deshielding effect of the ferrocene nucleus proposed by Mulay and Fox,[8] although other possibilities can not be ruled out. The ^{1}H-NMR spectral comparison of **3e** with **3a—d** revealed that the chemical shifts of the β-ring protons of **3a—d** (δ 3.81—3.86) are almost equal to that of **3e** (δ 3.89), whereas in the case of **3e** the α-ring protons appeared considerably downfield (δ 4.38) relative to that of **3a—d** (δ 4.14—4.22) (Table 2). Similar abnormalities are observed in the ^{13}C-NMR and electronic spectra. The ^{13}C-NMR spectra showed that the bridge head carbon of **3e** shifted upfield by about 4.5 ppm compared with that of strain-free **3a—d**, while the α- and β-carbon shifted downfield compared with the corresponding carbon atoms of **3a—d**. The Dreiding ferrocene stereo-model suggests that the ferrocene nucleus can be readily spanned by a four-atom bridge without any distortion of its preferred geometry. Therefore, in the present case, although details are not known at present, the above results may be interpreted in terms of the steric compression[9] or, more probably, in terms of anisotropy effects[10] associated with the OCH_2 bonds. The absorption band of **3e** showed a hypsochromic shift of about 10 nm, although in the case of the ring tilting alkyl bridged [2]- and [3]ferrocenophanes,[9] bridged with two and three methylene groups respectively, the absorption band near 440 nm characteristic of the ferrocene nucleus shifted to 466 nm. The hypsochromic shift may be due to the tilt-deformation of two cyclopentadienyl rings by the bridging, but its real reason is not known at present.

The Additive Effect of Alkali Metal Thiocyanate on the Electronic Spectra of Compounds 3 in Methanol. As is shown in Table 3, all the polyoxaferrocenophanes showed the characteristic peak near 440 nm associated with the d-d transition. On the addition of potassium or sodium thiocyanates to **3a** and **3b** in methanol, a small shift in the absorption peak at 438 nm and a change in the intensity of the absorption band occurred on complexing with cations. Furthermore, the absorption band of the complex of **3c** with KCN and NaCN did not shift, although the absorbance is slightly increased. A similar relationship was observed in the absorption band of **3a—c** when lithium thiocyanate was added. This suggests that the lithium complexes are unstable, probably because lithium ion is too strongly solvated by the solvent. From the above results, it can be concluded that compounds **3a** and **3b** were complexed with sodium and potassium thiocyanate

TABLE 3. ELECTRONIC ABSORPTION SPECTRA DATA AND THEIR METAL COMPLEXES IN METHANOL (λ/nm (ε))[a]

Compound	Additive Salt			
	None	LiSCN	NaSCN	KSCN
3a	438(127)	438(139)	435(129)	434(121)
3b	438(125)	438(127)	434(117)	435(123)
3c	438(117)	438(125)	438(125)	438(125)
3d	438(132)	438(134)	438(132)	438(134)
3e	428(120)	428(122)	428(122)	428(122)

a) Measured in the presence of about a 50-fold molar excess of alkali metal thiocyanate at 20 °C.

Table 4. Extraction of metal picrates from the aqueous to the organic phase (%)

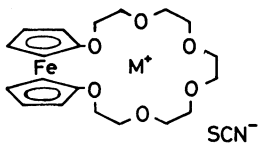
Compound	Li^+ (1.20)	Na^+ (1.90)	K^+ (2.66)	Rb^+ (2.96)	Cs^+ (3.34)	Ag^+ (2.52)	Tl^+ (2.88)	Ba^+ (2.70)
3a	—	1.62	22.7	29.1	18.4	Dec.	79.7	—
3b	—	1.49	4.5	4.6	5.6	Dec.	25.2	—
3c	—	—	—	—	—	Dec.	4.4	—
3d	—	—	—	—	—	Dec.	3.4	—
3e	—	—	—	—	—	Dec.	0.6	—
B18C6		22.3	94.7			84.3	97.3	
B15C5		23.9	50.1			33.6	56.0	

Solvent: water and dichloromethane (1 : 1). Concentration of polyether: 7×10^{-4} M (1 M=1 mol dm^{-3}). Concentration of picric acid: 7×10^{-5} M. Concentration of metal nitrates: 0.1 M.

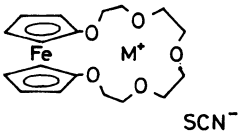
in methanol, although the changes in the absorption band at 438 nm were very complicated.

Extractability. The complexing ability of polyoxaferrocenophanes with alkali, alkaline earth, and transition-metal cations was measured by Pedersen's extraction method.[15] The data are summarized in Table 4, along with that of benzo crown ethers. Unlike from the data obtained by the TLC method,[3] the polyoxaferrocenophanes **3** showed little or no extractability toward alkali and alkaline earth metal cations, the extractability, if any, was much smaller than that of benzo crown ether. This seems reasonable considering that the incorporation of the iron atom of the ferrocene nucleus (a soft atom) or, more likely, the ferrocene nucleus itself into the macrocyclic polyether ring has an influence on the complexing ability with alkali and alkaline earth metal cation (a hard atom). The extractability of these cations is dependent on the size of the crown ether-ring part in polyoxaferrocenophanes. Thus, hexaoxa[16]ferrocenophane (**3a**) and pentaoxa[13]ferrocenophane (**3b**) extract 23 and 4% of the potassium ion respectively, but the ferrocenophanes, with a smaller polyether ring part, showed no extractability toward the potassium ion. Significantly, the selectivity of **3a** and **3b** toward the thallium ion should be noted. Thus, the extractability of **3a** and **3b** toward the thallium ion is remarkably higher than that toward other alkali and alkaline earth metal ions, while benzo crown ether showed a similar extractability toward any of the cations described above. The extractability of several metal ions was in this order: $Tl^+>Rb^+>K^+>Cs^+>Na^+$. No extraction of the silver ion by the polyoxaferrocenophanes was observed because of the oxidative decomposition of the ferrocenophanes.

Isolation of the Complex of Polyoxaferrocenophanes with Alkali Thiocyanates. The uptake of alkali metal cations with **3a** or **3b** containing six or five oxygen atoms was attempted. To an acetonitrile solution of equimolar amounts of **3a** or **3b** and alkali thiocyanate, we added hexane until a yellow or red precipitate appeared. After the precipitate has been completed in a refigerator, the complexes were obtained. These complexes (**4a—c**, **5a**, and **5b**) showed higher melting point than metal-free ligand and were confirmed by microanalysis to be 1 : 1 complexes. Their ^{1}H-NMR spectra gave much information about the character of the complexes **5a** and **5b**. The proton signals of the complexes **5a** and **5b** showed some downfield shift



4a : M = Li
4b : M = Na
4c : M = K



5a : M = Li
5b : M = Na

compared with those of the free ligands **3a** and **3b**. Ferrocene ring protons of the complexes remained in the A_2B_2 pattern, suggesting that the alkali metal cation is strongly incorporated into the center of the cavity of the macrocyclic polyether, because the coordination to one of the sides of the ligand leads to the ABCD pattern of the ring protons. The shifts of the ferrocene ring protons ($\Delta\delta$=0.22(H_α) and 0.05(H_β) in **5b**) were larger than those of the methylene protons of the oxyethylene chain ($\Delta\delta$=0.03 in **5b**). The Mössbauer spectra of **3b**, **5a**, and **5b** were measured at room temperature.[12] It was found in this study that both of the complexes (**5a** and **5b**) give larger values (2.55 mm s^{-1}) of quadrupole splitting (qs) than that (2.50 mm s^{-1}) of metal-free ferrocenophane **3b**, although the chemical isomer shifts have the same value as that (0.44 mm s^{-1}) of **3b**. It has been reported that the electron-attracting substituents[13] decrease the qs of ferrocene and that some ferrocene derivatives with electron-donating substituents[14] give larger values of qs than that of ferrocene. Therefore, if the alkali metal cation exerts an electron-attracting effect through the $Na^+\cdots O\cdots C_b$ on the cyclopentadienyl ring, compounds **4a** and **4b** can be expected to give smaller values of qs than that of metal-free ferrocenophane (**3b**). However, as has been described above, the complexes which incorporated sodium and lithium cations into the macrocyclic ether of ferrocenophane gave larger values of qs than that of **3b**. The results obtained suggest that the larger values of qs estimated for these complexes may be ascribed to some interaction between the alkali metal cation incorporated and the iron atom of ferrocene nucleus, although the possibility of the effect of the counter anion ($^-$SCN) on the e_{2g} (or a_{1g}) d-orbital of the ferrocene nucleus can not be ruled out.[16]

Experimental

The melting point are uncorrected. The IR spectra were

measured on a JASCO IRA-2 Diffraction Grating Infrared Spectrometer. The mass spectra were taken by using a JEOL-JMS-OlSG-2 Spectrometer. The ^{1}H-NMR spectra were measured on Varian XL-200 and a Hitachi R24B Spectrometer, TMS being chosen as the internal standard. The ^{13}C-NMR spectra were obtained on a Hitachi R-900 Spectrometer. The electronic spectra were measured on a Hitachi Model 200-10 spectrometer.

Material. The silica gel used for thin-layer chromatography was Wakogel B-5F. 1,2-Dichloroethane (**2e**), bis(2-chloroethyl) ether (**2d**), and 1,8-dichloro-3,6-dioxaoctane (**2c**) were commercially available and were used without further purification. 1,11-Dichloro-3,6,9-trioxaundecane (**2b**) and 1,14-dichloro-3,6,9,12-tetraoxatetradecane (**2a**) were prepared according to the procedures described in the literature.[17] The solvent were purified by distillation. Lithium thiocyanate, sodium thiocyanate, and potassium thiocyanate of Tokyo Kasei Kogyo (first grade) were used without further purification.

Preparation of 1,1′-Diacetoxyferrocene (1). **1** was prepared by the reaction of 1,1′-dibromoferrocene with copper(I) acetate according to the following modified procedure: 1,1′-Dibromoferrocene (4.5 g, 0.013 mol) and copper(I) acetate (15 g, 0.075 mol) in 50% aqueous ethanol (500 ml) were refluxed for 40 min at the reflux temperature under nitrogen. After the mixture had been cooled to room temperature, the solid was filtered off and the filtrate was added to water (600 ml). The aqueous solution was extracted with ether, washed with water, and dried over anhydrous $MgSO_4$. The residue obtained on the evaporation of the solvent was solidified to give a dark orange solid. Recrystallization from benzene–hexane gave a pure sample (2.2 g, 56% yield) as yellow needles; mp 46—48 °C (lit,[6] 55—56 °C).

Preparation of Polyoxa[n]ferrocenophanes. General Procedure: 1,4,7,10,13,16-Hexaoxa[16]ferrocenophane (3a). **1** (0.670 g, 2.20 mmol) was added to a 10% aqueous potassium hydroxide solution (10 ml) under nitrogen, and the mixture was stirred under reflux. After 30 min, a solution of 1,14-dichloro-3,6,9,12-tetraoxatetradecane (**2a**) (0.920 g, 3.30 mmol) in 60% ethanol (50 ml) was added all at once, the mixture was then stirred for 5 h at reflux temperature. After the solution had been cooled to room temperature, 100 ml of water was added to the reaction mixture. The aqueous solution was extracted with three 25 ml portions of ether. The ether extracts were combined, washed with water, and concentrated *in vacuo*. The residual oil was chromatographed by silica gel TLC (using benzene–ethyl acetate 5 : 1 as the eluent). The main band was eluted with acetone at room temperature, followed by filtration. The evaporation of the solvent gave yellow oil which solidified on standing, The pure product was obtained as yellow needles by recrystallization from hexane.

General Procedure for the Preparation of the Alkali Metal Thiocyanate Complex. Alkali metal thiocyanate (0.14 mmol) and **3a—b** were dissolved in anhydrous acetonitrile. To the mixture, hexane was added until precipitation occurred. The reaction mixture was then cooled in a refrigerator. After the precipitation was complete, the crystalline product was filtered off and washed with small amounts of acetonitrile and hexane. An almost quantitative yield of these complexes was obtained.

Lithium Thiocyanate Complex of 3a (4a). The complex, (yellow needles), exhibited the following physical and spectral properties; mp 123—128 °C. Found: C, 52.19; H, 5.89; N, 2.68%. Calcd for $C_{21}H_{28}O_6NSLiFe$: C, 51.96; H, 5.77; N, 2.89%. ^{1}H-NMR (60 MHz, in $CDCl_3$): δ 4.19 (4H, t, J=2.0 Hz, H_α), 3.93 (4H, t, J=2.0 Hz, H_β), 3.77 (4H, s, OCH_2CH_2O), 3.75 (8H, s, OCH_2CH_2O), 4.00—3.78 (8H, m, OCH_2CH_2O).

Sodium Thiocyanate Complex of 3a (4a). Mp 135—137 °C. Found: C, 50.50; H, 5.87; N, 2.53%. Calcd for $C_{21}H_{28}O_6NSNaFe$: C, 50.30; H, 5.59; N, 2.79%. ^{1}H-NMR ($CDCl_3$): δ 4.14 (4H, t, J=2.0 Hz, H_α), 3.87 (4H, *t*, J=2.0 Hz, H_α), 3.69 (4H, s, OCH_2CH_2O), 3.78 (4H, s, OCH_2CH_2O), and 4.02—3.80 (8H, m, OCH_2CH_2O).

Potassium Thiocyanate Complex of 3a (4c). Mp 164—167 °C. Found: C, 49.05; H, 5.72; N, 2.88%. Calcd for $C_{21}H_{28}O_6SNKFe$: C, 48.74; H, 5.42; N, 2.71%. ^{1}H-NMR ($CDCl_3$): δ 4.16 (4H, t, J=2.0 Hz, H_α), 3.91 (4H, t, J=2.0 Hz, H_β), 3.76 (8H, s, OCH_2CH_2O), 3.75 (4H, s, OCH_2CH_2O), and 4.00—3.78 (8H, m, OCH_2CH_2O).

Lithium Thiocyanate Complex of 3b (5a). Mp 147—149 °C. Found: C, 51.53; H, 5.74; N, 3.12%. Calcd for $C_{19}H_{24}O_5SNLiFe$: C, 51.70; H, 5.44; N, 3.17%. ^{1}H-NMR ($CDCl_3$): δ 4.32 (4H, t, J=2.0 Hz, H_α), 3.98 (4H, t, J=2.0 Hz, H_β), 3.79 (8H, s, OCH_2CH_2O), and 4.12—3.80 (8H, m, OCH_2CH_2O).

Sodium Thiocyanate Complex of 3b (5b). Mp 165.5—167 °C. Found: C, 50.19; H, 5.78; N, 3.01. Calcd for $C_{19}H_{24}O_5SNNaFe$: C, 49.89; H, 5.44; N, 3.17%. ^{1}H-NMR ($CDCl_3$): δ 4.37 (4H, t, J=2.0 Hz, H_α), 3.91 (4H, t, J=2.0 Hz, H_β), 3.74 (8H, s, OCH_2CH_2O), and 4.02—3.80 (8H, m, OCH_2CH_2O).

The Method of Solvent Extraction. Extractability of polyoxaferrocenophanes with the alkali metal cation was examined by the extraction method described by Pedersen.[15] Equal volumes (5 ml) of dichloromethane containing 7×10^{-4} M of polyoxaferrocenophane and an aqueous solution containing 1×10^{-1} M MNO_3 (M; alkali metal cation) and 7×10^{-5} M picric acid were agitated thoroughly at 25 °C. The solution was then equilibrated at 25 °C, the aliquot of the upper aqueous solution was withdrawn, and the electronic spectrum was recorded. A similar extraction was performed with pure dichloromethane. The extractability was determined by reading the difference between the two absorbances of picrate in the aqueous solution. The extractability was calculated by means of the following equation:

$$\text{Extractability} = \frac{A_0 - A}{A_0} \times 100.$$

A_0 is the absorbance in the absence of MNO_3 and A is the absorbance in the presence of MNO_3.

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References

1) R. E. Izatt and J. J. Christensen, "Synthetic Multidentate Macrocyclic Compounds," Academic Press, New York (1978).

2) a) G. Oepen and F. Vögtle, *Justus Liebigs Ann. Chem.*, **1976**, 1094; b) A. P. Bell and C. D. Hall, *J. Chem. Soc., Chem. Commum.*, **1980**, 163; B. Czech and A. Ratajczak, *Polish J. Chem.*, **54**, 767 (1980).

3) J. F. Biernat and T. Wilczewski, *Tetrahedron*, **36**, 2521 (1980).

4) M. Sato. M. Kubo, S. Ebine, and S. Akabori, *Tetrahedron Lett.*, **1982**, 185.

5) R. N. Greene, *Tetrahedron Lett.*, **1972**, 1973.

6) A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Chem. Ber.*, **93**, 2117 (1960).

7) D. W. Slocum and C. R. Ernest, *Tetrahedron Lett.*, **1972**, 5217.

8) L. N. Mulay and M. E. Fox, *J. Chem. Phys.*, **38**, 760 (1963).

9) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Am. Chem. Soc.*, **87**, 5247 (1965).
10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York (1959), p. 176.
11) T. H. Barr and W. E. Watts, *Tetrahedron*, **24**, 6111 (1968).
12) The isomer shift data are reported with respect to metalic iron foil.
13) A. V. Lesikar, *J. Chem. Phys.*, **40**, 2746 (1964).
14) S. Iijima, I. Motoyama, and H. Sano, *Bull. Chem. Soc. Jpn.*, **53**, 3180 (1980).
15) C. J. Pedersen, *Federation Proceedings*, **27**, 1305 (1968).
16) Although no details were reported, an earlier study showed a small difference between the Mössbauer spectra of the ferrocenophanes prepared from ferrocene-1,1′-dicarboxylic acid and those of the corresponding metal complexes.[2a])
17) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).