

ORGANOMETALLIC COMPOUNDS

XXXIX *. SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF [4][3][4][3](1,2,3,4)FERROCENOPHANE

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Summary

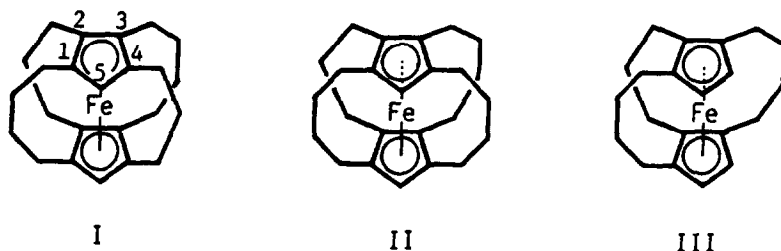
[4][3][4][3](1,2,3,4)Ferrocenophane (I) and some related tetrabridged ferrocenophanes have been synthesized via cyclization of 2-[4][4][3](1,3,4)ferrocenophanepropanoic acid with polyphosphate ester (PPE). Treatment of 5-[4][4][3](1,3,4)ferrocenophanepropanoic acid with PPE or polyphosphoric acid does not give an additionally bridged compound but a bridge-rearrangement product containing two homoannular rings. The crystal structure of I has been determined by X-ray diffraction. Compound I crystallizes in the monoclinic system, space group $P2_1/a$ with unit cell parameters a 17.490(4), b 8.489(1), c 12.157(2) Å, β 101.51(1)°, and $Z = 4$. The two cyclopentadienyl (Cp) rings are in an eclipsed conformation and almost parallel to each other (dihedral angle, 1.1°). The bond lengths and angles in the Cp rings and methylene chains are normal but the distances between the Cp ring and the iron atom are unusually short (1.589 and 1.591 Å) in comparison with multibridged ferrocenophanes containing tetramethylene chains.

Introduction

We already reported syntheses of several tri-, tetra- and penta-bridged ferrocenophanes containing tetramethylene bridges [2–6] and some of their crystal structures were determined by X-ray diffraction [3,5–8]. These investigations demonstrate that reactions and structures of multibridged ferrocenophanes are significantly

* For part XXXVIII, see ref. 1.

influenced by the lengths and number of bridging chains. These results primarily arise from the circumstances that the trimethylene chain is too short to connect the two cyclopentadienyl (Cp) rings of ferrocene [5,8] fitly. Actually, the effect of this short trimethylene bridge on the molecular structure is clear from the unusual bond lengths and angles in [4][3][4][4]ferrocenophane (II) *, bridged with one trimethylene and three tetramethylene chains [3]. The crystal structure of [4][3][4]ferrocenophane (III) indicates that the side of 4,4'-positions of the ferrocene moiety is opened and the tilting of the two Cp rings is 10.4° (dihedral angle) [8]. Therefore, the unusual elongation of the C–C bonds of the 2,2'-trimethylene bridge in II was explained to be due to bridging with an additional tetramethylene chain at the opened 4,4'-posi-



tions of III [8]. If the 4,4'-positions of III can be connected with a short trimethylene chain, the phenomenon of a more unusual molecular structure than that of II may be expected. In addition to the above reasons [4][3][4][3]ferrocenophane (I) is interesting as it is the first ferrocenophane bridged alternately with two short and two long methylene chains.

We now report the synthesis of I and some related ferrocenophanes and the X-ray crystallographic analysis of I.

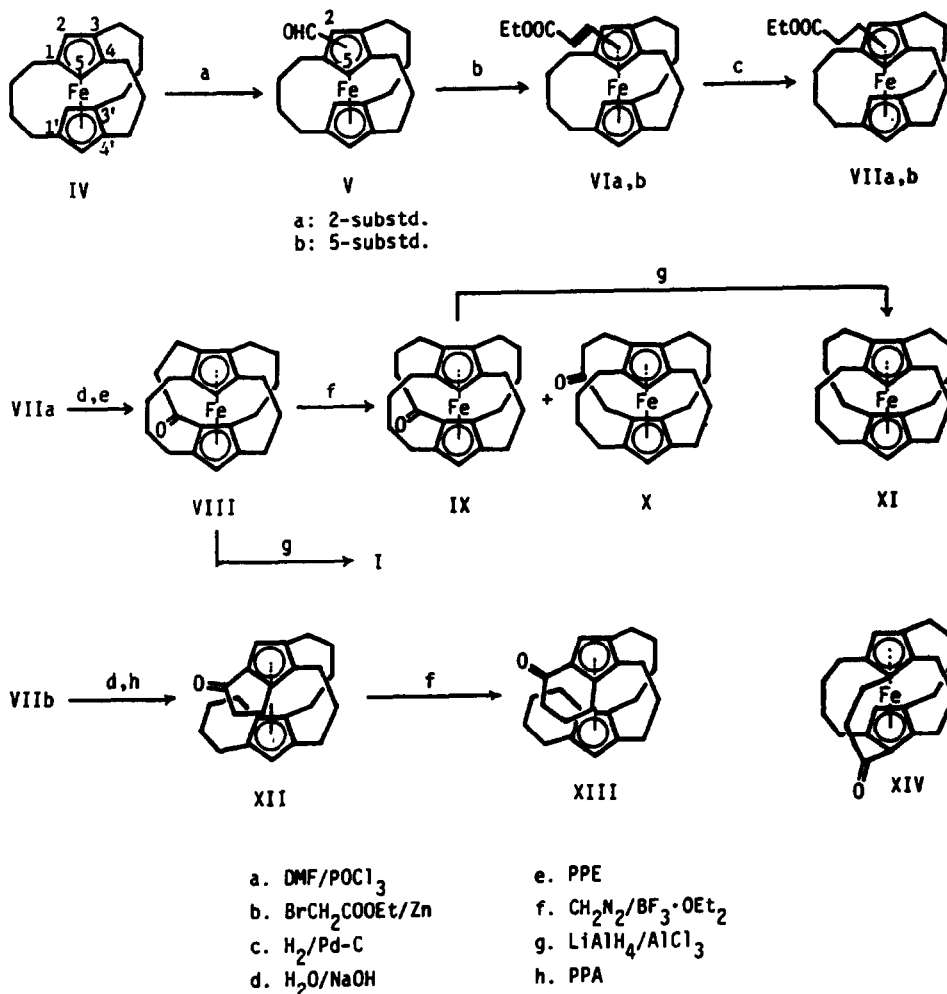
Results and discussion

Synthesis of [4][3][4][3]ferrocenophane (I) and related ferrocenophanes

According to similar procedures as those for the synthesis of tetra- and penta-bridged ferrocenophanes [3,6], tribridged [4][4][3](1,3,4)ferrocenophane (IV) [2] was formylated followed by Reformatsky treatment and catalytic hydrogenation to give 2- and 5-[4][4][3]ferrocenophanepropanoate (VIIa and VIIb). Cyclization of the carboxylic acid, prepared by hydrolysis of the 2-isomer (VIIa), with ethyl polyphosphate (PPE) afforded tetrabridged ferrocenophane (VIII) in good yield (69%), in spite of its extremely strained structure considering a molecular model. [4][3][4][3]ferrocenophane (I) was derived from the ketone (VIII) by reduction with $\text{LiAlH}_4/\text{AlCl}_3$ (Scheme 1). The singlet signal of the two Cp ring protons of I appeared at δ 3.78 ppm in the ^1H NMR spectrum. The molecular structure of I was determined by X-ray crystallographic analysis, and is discussed later.

Treatment of the ketone VIII with diazomethane/ BF_3 etherate in benzene gave bridge-enlarged α - and β -ketones (IX and X) in a ratio of 1/2. Reduction of α -ketone IX yielded [4][4][4][3](1,2,3,4)ferrocenophane (XI), which is a regioisomer of [4][3][4][4](1,2,3,4)ferrocenophane (II) regarding the position of the trimethylene

* The nomenclature of ferrocenophanes and the numbering of Cp rings in the present work are modifications [1] of those by Vögtle and Neumann [9].



Scheme 1. Synthesis of [4][3][4][3](1,2,3,4)ferrocenophane (I) and related ferrocenophanes.

bridge. The ring proton signal of XI appeared at a higher field (δ 3.74 ppm) than that of II (δ 3.91 ppm). This shift difference presumably reflects the difference of their molecular structures. The two Cp rings of XI lean toward 5,5'-positions because of the presence of a short trimethylene bridge at 4,4'-positions, while the side of 5,5'-positions in II opens more than the other side (dihedral angle, 5.7° [3]) due to tension by the trimethylene bridge at the diagonal 2,2'-positions. It is known that in the ^1H NMR spectra of tilted ferrocenophanes signals of ring protons at the nearer side of two Cp rings are shifted to higher fields than those of the farther side [10].

Cyclization of the 5-isomer was attempted with the aim to compare the molecular structure of the expected tetrabridged [4][4][3][3](1,3,4,5)ferrocenophane (XIV) with that of compound I. However, no tetrabridged product was formed in the hydrolysis of VIIb followed by the cyclization reaction under the same conditions as those for

the 2-isomer, but the formation of a dibridged compound (XII) containing two condensed-rings was found in 8% yield besides many unknown products. Treatment of the 5-isomeric acid with polyphosphoric acid (PPA) gave only the rearrangement product XII (10%), together with recovered starting material. The chemical structure of XII was determined by identification of compound XIII, which was derived from XII by ring-enlargement with diazomethane/ BF_3 etherate, and the data agreed those of the authentic sample already described [1,11]. Two examples of such an unusual homoannular cyclization accompanied by rearrangement of the existing bridge were known in the reactions of tribridged ferrocenophanecarboxylic acids [1,12].

The molecule XIV can be constructed with a Dreiding molecular model with a little strain, while the molecule of the synthesized compound VIII cannot. It is very interesting that the strained compound VIII could be readily produced but the less strained XIV could not. The fact supports our suggestion [11] that selectivity of bridging and rearrangement in the cyclization reaction of tribridged ferrocenophanecarboxylic acids is not governed only by thermodynamical control.

In [4][4][3](1,3,4)ferrocenophane the distance between 5- and 5'-carbons is less than that between 2- and 2'-positions because of the presence of a short trimethylene bridge at the 4,4'-positions. The acylium ion of the reaction intermediate should attack the corresponding position of the other ring from the side of the iron atom to form a bridge in cyclization. Accordingly, bridging between 5- and 5'-positions with carboxyethyl group in VIIb is sterically disadvantageous, because the acylium ion should inevitably approach the other ring from the same direction as the 5'-hydrogen. In contrast ready formation of a bridge between 2- and 2'-positions in VIIa is explained by taking into consideration the conformation opening between the 2- and 2'-positions, as the acylium ion can readily attack the 2'-carbon from the inside of the 2'-hydrogen. The occurrence of selective homoannular cyclization in ferrocene- and ferrocenophane-butanoic acids [1,13] may be explained also by taking into account the same situation as that of VIIb in the attack of acylium ion to the carbon atom of the other ring.

Crystal structure of [4][3][4][3]ferrocenophane (I)

An ORTEP drawing [14] of the molecular structure of I and the atomic numbering scheme are shown in Fig. 1. Figure 2 is a projection on the plane defined by the iron atom and an intersection of the two Cp least-squares planes. Selected bond lengths and angles are given in Tables 1 and 2, respectively.

The two Cp rings are in eclipsed conformation around the Cp-Fe-Cp axis. The tetramethylene bridge at 1,1'-positions is in a boat form and the other has a zig-zag conformation. Figure 2 shows that the bridging methylene chains are folded to minimize steric interactions between the four bridges.

The two Cp rings are almost parallel to each other (dihedral angle, 1.1°). The planarity of each Cp ring is maintained but the α -carbon atoms of the bridges fairly deviate from the least-squares planes of the rings except for the 6- and 9-carbons of the 1,1'-bridge (Table 3). The directions of the deviations reflect the lengths and the conformations of the bridges. The α -carbon atoms on the short trimethylene bridges deviate "inside" from the ring plane to the iron atom. In the case of the long tetramethylene bridges, the carbon atoms of the zig-zag 3,3'-bridge deviate "outside", while the deviation of those on the 1,1'-bridge which is in a boat conformation is negligible. Inspection of a Dreiding molecular model shows that the distance

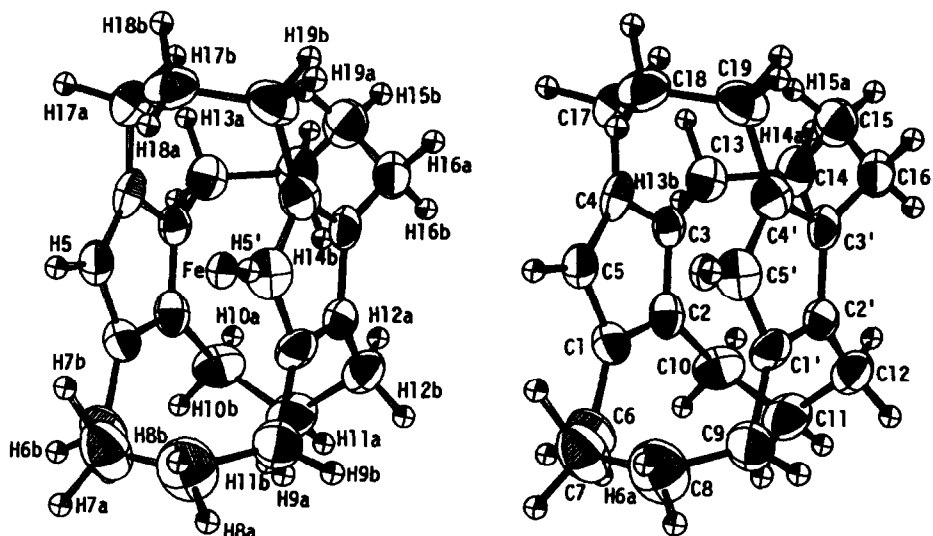


Fig. 1. ORTEP stereoview and atomic numbering of [4][3][4][3](1,2,3,4)ferrocenophane (1).

between the two α -carbon atoms of the bridge which is in a zig-zag conformation is larger than that in a boat form, when the two Cp rings are eclipsed. Such a dependence of the deviation on the conformation of the bridges has been generally found in multibridged ferrocenophanes [3,5–8].

Two characteristics correlating with deviations of the α -carbon atoms are revealed in the bond lengths: (i) The mean $C(sp^3)-C(sp^3)$ bond distances of the trimethylene bridges (2,2'-bridge, 1.565 Å; 4,4'-bridge, 1.567 Å) are longer than those of the tetramethylene bridges at the 3,3'-bridge (1.522 Å). The unusually short mean-distance of the 1,1'-bridge (1.483 Å) which is in a flexible boat conformation, is

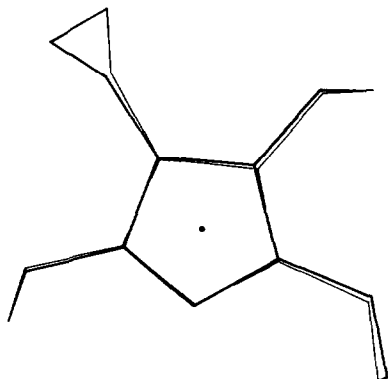


Fig. 2. Projection of the whole molecule of the plane defined by the iron atom and the intersection of the two cyclopentadienyl least-squares planes.

TABLE 1
BOND LENGTHS (in Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond	Length	Bond	Length
Fe–C(1)	2.007(5)	C(5')–C(1')	1.437(7)
Fe–C(2)	1.992(5)	C(1)–C(6)	1.497(8)
Fe–C(3)	2.017(5)	C(6)–C(7)	1.490(9)
Fe–C(4)	1.990(5)	C(7)–C(8)	1.467(10)
Fe–C(5)	2.010(5)	C(8)–C(9)	1.493(10)
Fe–C(1')	2.009(5)	C(9)–C(1')	1.501(8)
Fe–C(2')	1.998(5)	C(2)–C(10)	1.523(8)
Fe–C(3')	2.025(5)	C(10)–C(11)	1.574(9)
Fe–C(4')	1.999(5)	C(11)–C(12)	1.555(8)
Fe–C(5')	2.009(5)	C(12)–C(2')	1.501(7)
C(1)–C(2)	1.437(7)	C(3)–C(13)	1.505(7)
C(2)–C(3)	1.453(7)	C(13)–C(14)	1.523(8)
C(3)–C(4)	1.438(7)	C(14)–C(15)	1.517(8)
C(4)–C(5)	1.416(7)	C(15)–C(16)	1.525(8)
C(5)–C(1)	1.434(7)	C(16)–C(3')	1.502(7)
C(1')–C(2')	1.444(7)	C(4)–C(17)	1.512(8)
C(2')–C(3')	1.455(7)	C(17)–C(18)	1.567(8)
C(3')–C(4')	1.439(7)	C(18)–C(19)	1.567(9)
C(4')–C(5')	1.424(7)	C(19)–C(4')	1.508(8)

TABLE 2
BOND ANGLES IN DEGREE WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond	Angle	Bond	Angle
C(5)–C(1)–C(2)	107.2(4)	C(1')–C(2')–C(12)	127.2(4)
C(1)–C(2)–C(3)	107.8(4)	C(3')–C(2')–C(12)	125.0(4)
C(2)–C(3)–C(4)	107.6(4)	C(2')–C(3')–C(16)	125.9(4)
C(3)–C(4)–C(5)	107.7(4)	C(4')–C(3')–C(16)	125.8(4)
C(4)–C(5)–C(1)	109.6(4)	C(3')–C(4')–C(19)	126.4(4)
C(5')–C(1')–C(2')	107.6(4)	C(5')–C(4')–C(19)	125.2(5)
C(1')–C(2')–C(3')	107.3(4)	C(1)–C(6)–C(7)	116.4(5)
C(2')–C(3')–C(4')	108.0(4)	C(6)–C(7)–C(8)	123.5(6)
C(3')–C(4')–C(5')	107.8(4)	C(7)–C(8)–C(9)	124.7(6)
C(4')–C(5')–C(1')	109.1(4)	C(8)–C(9)–C(1')	117.9(6)
C(5)–C(1)–C(6)	126.2(5)	C(2)–C(10)–C(11)	115.7(5)
C(2)–C(1)–C(6)	126.6(5)	C(10)–C(11)–C(12)	120.4(5)
C(1)–C(2)–C(10)	127.3(5)	C(11)–C(12)–C(2')	116.7(5)
C(3)–C(2)–C(10)	124.6(4)	C(3)–C(13)–C(14)	119.0(5)
C(2)–C(3)–C(13)	125.4(4)	C(13)–C(14)–C(15)	114.9(5)
C(4)–C(3)–C(13)	126.9(4)	C(14)–C(15)–C(16)	114.6(5)
C(3)–C(4)–C(17)	127.0(4)	C(15)–C(16)–C(3')	118.7(5)
C(5)–C(4)–C(17)	124.6(5)	C(4)–C(17)–C(18)	144.3(5)
C(5')–C(1')–C(9)	126.0(5)	C(17)–C(18)–C(19)	116.7(5)
C(2')–C(1')–C(9)	126.4(5)	C(18)–C(19)–C(4')	113.8(5)

TABLE 3

LEAST-SQUARES PLANES THROUGH THE CYCLOPENTADIENYL RINGS AND DEVIATIONS OF ATOMS (Å) FROM THE PLANES (X , Y and Z are coordinates referred to the a , b and c^* axes in Å)

Atom	Deviation	Atom	Deviation
$-0.1220X - 0.5825Y + 0.8037Z + 0.4416 = 0$			
C(1)	-0.001	C(6) ^a	0.047
C(2)	0.009	C(10) ^a	0.190
C(3)	-0.019	C(13) ^a	-0.183
C(4)	0.026	C(17) ^a	0.291
C(5)	-0.012	H(5) ^a	0.005
		Fe ^a	1.589
$0.1177X + 0.5668Y - 0.8154Z + 2.8043 = 0$			
C(1')	-0.004	C(9) ^a	-0.015
C(2')	0.014	C(12) ^a	0.225
C(3')	-0.019	C(16) ^a	-0.204
C(4')	0.018	C(19) ^a	0.254
C(5')	-0.009	H(5') ^a	0.000
		Fe ^a	1.591

^a Atoms not included in the calculation of the planes.

possibly due to the high thermal motion of the 7- and 8-carbon atoms. (ii) The mean distance between the iron atom and the Cp ring carbon atoms at the trimethylene bridge (both 2,2'- and 4,4'-bridges, 1.995 Å) is slightly shorter than those at the tetramethylene bridges (1,1'-bridge, 2.008 Å; 3,3'-bridge, 2.021 Å).

The distances between the iron atom and the Cp ring planes are 1.589 and 1.591 Å. These values are considerably smaller than those for ferrocene (1.66 Å [15]) and [4][4][4](1,2,4)ferrocenophane (1.630 Å [16]), and the values for I are intermediate between those for II (1.618 Å [3]) and [3][3][3](1,2,4)ferrocenophane (1.573 Å [17]). The results indicate that iron-ring distances in multibridged ferrocenophanes depend on the number of trimethylene bridges, and that two or three short bridges squeeze the iron atom into the two Cp rings [18]. X-ray crystal analyses of II and III proved the elongation of the C-C bonds in the trimethylene 2,2'-bridge (mean C(sp³)-C(sp³) bond distance, 1.625 Å [3]) and the tilting of the two Cp rings (10.4° [8]), respectively. Unusual deformation of I was expected from considerations of the features of II and III, but the bond lengths and angles of I are normal in comparison with the other multibridged ferrocenophanes [3,5-8,16,17]. The shortening of the Cp-Cp distance may result in the usual bond lengths and angles of the trimethylene chain of I.

Experimental

Synthesis of multibridged ferrocenophanes

All melting points are uncorrected. IR spectra were measured using a Hitachi model 215 spectrometer. All IR spectral data are given in cm⁻¹. ¹H and ¹³C NMR spectra were measured on a JEOL JNM FX-100 spectrometer at 100 MHz and 25.1 MHz, respectively, relative to tetramethylsilane as an internal standard. All chemical shifts and coupling constants are shown in ppm on the δ scale and Hz, respectively.

Mass spectra were obtained with a Hitachi RMU-7M or a Hitachi M-80 double focusing mass spectrometer at 70 eV ionizing energy by direct insertion method. Mass spectral data are given as m/z , with relative intensities in parentheses. High-resolution mass spectra were analyzed on a Hitachi M-002 or a Hitachi M-003 data processing system. Empirical formulae of oily or unstable compounds and of small amounts of products were determined by means of high-resolution mass spectra.

Formylation of [4][4][3](1,3,4)ferrocenophane (IV)

A solution of IV (500 mg, 1.50 mmol), which was prepared according to the procedure reported by the authors [2], and dimethylformamide (400 mg, 5.48 mmol) in chloroform (50 ml) was stirred at room temperature for 15 min under an N_2 atmosphere. Phosphorus oxychloride (850 mg, 5.59 mmol) was slowly added dropwise to the mixture, then the reaction mixture was stirred at 50°C for 6 h, and evaporated to dryness. Ice-water was added to the residue, then 20% aq. NaOH and benzene. The mixture was stirred for 1 h, and the organic layer was separated. The extracts were washed with saturated aq. NaCl, dried over Na_2SO_4 and evaporated. The residue was column-chromatographed over silica gel with benzene as an eluent to give three bands. The first band contained the starting material (54 mg, 11%). The second band yielded 5-formyl[4][4][3](1,3,4)ferrocenophane (Vb) (192 mg, 35%), which could not be purified satisfactorily by recrystallization because of its instability on heating. Orange crystals, m.p. 118–122°C (crude product). (Found: M^+ 362.1310. $C_{22}H_{26}OFe$ calcd.: mol. wt. 362.1330.) IR(KBr): 1665 ($\nu(C=O)$). 1H NMR ($CDCl_3$): 3.92 (2H, s, 2',5'-H), 4.34 (1H, s, 2-H), 10.38 (1H, s, -CHO). MS: 362 (M^+ , 100), 333 ($[M - CHO]^+$, 6).

The third eluted component was 2-formyl[4][4][3](1,3,4)ferrocenophane (Va) (311 mg, 57%), which was recrystallized from hexane to give deep red needles, m.p. 146–147°C. (Found: C, 73.36; H, 7.39. $C_{22}H_{26}OFe$ calcd.: C, 72.94; H, 7.23%.) IR(KBr): 1660 ($\nu(C=O)$). 1H NMR ($CDCl_3$): 3.80 and 4.15 (each 1H, AX system, J 1.5 Hz, 5',2'-H), 4.23 (1H, s, 5-H), 10.42 (1H, s, -CHO). MS: 362 (M^+ , 100), 333 ($[M - CHO]^+$, 12).

Ethyl 2- and 5-[4][4][3](1,3,4)ferrocenophanepropenoate (VIIa and VIIb)

A mixture of 2-formylferrocenophane (Va) (182 mg, 0.50 mmol), purified zinc powder (1.0 g), ethyl bromoacetate (300 mg, 1.80 mmol) and iodine (10 mg) in dry benzene/ether (5/1, 25 ml) was heated on an oil bath at 100°C. After the reaction was initiated with violent boiling, the mixture was heated for an additional 10 min, and then cooled to room temperature followed by addition of conc. HCl. The extracts with benzene were washed with saturated aq. Na_2CO_3 and then with saturated aq. NaCl, dried over Na_2SO_4 and evaporated. The residue was column-chromatographed over alumina with benzene to yield ethyl 2-[4][4][3](1,3,4)ferrocenophanepropenoate (VIa) (184 mg, 85%). The crude product was recrystallized from hexane to give deep red rodlike crystals, m.p. 142–143°C. (Found: C, 71.97; H, 7.39. $C_{26}H_{32}O_2Fe$ calcd.: C, 72.22; H, 7.46%.) IR (KBr): 1710 ($\nu(C=O)$), 1620 ($\nu(C=C)$). 1H NMR ($CDCl_3$): 1.32 and 4.21 (3H and 2H, t and q, J 7.0 Hz, OCH_2CH_3), 3.76 and 3.84 (each 1H, AB system, J 1.4 Hz, 5',2'-H), 4.07 (1H, s, 5-H), 6.06 and 7.85 (each 1H, AX system, J 16 Hz, olefin-H). MS: 432 (M^+ , 100).

The propenoate VIa (259 mg, 0.60 mmol) in acetone (50 ml) was reduced with

10% Pd-C (50 mg) under H_2 at 3 kg/cm² pressure for 12 h. The filtrate of the mixture was evaporated to dryness. The residue was column-chromatographed over alumina to yield ethyl 2-[4][4][3]ferrocenophanepropanoate (VIIa) (251 mg, 97%) as a yellow oil. (Found: M^+ 434.1905. $C_{26}H_{34}O_2Fe$ calcd.: mol. wt. 434.1905.) IR (neat): 1730 ($\nu(C=O)$). 1H NMR ($CDCl_3$): 1.25 and 4.12 (3H and 2H, t and q, J 7.0 Hz, OCH_2CH_3), 3.72 and 3.78 (each 1H, AB system; J 1.4 Hz, 5',2'-H), 3.80 (1H, s, 5-H). MS: 432 (M^+ , 100), 404 ($[M - CO]^+$, 6).

A solution of 5-formylferrocenophane (Vb) (192 mg, 0.53 mmol) in dry benzene (10 ml) was slowly added dropwise to a mixture of purified zinc powder (1.0 g), ethyl bromoacetate (300 mg, 1.80 mmol) and a crystal of iodine in dry benzene/ether (5/2, 14 ml) on an oil bath at 100°C. After heating at 100°C for an additional 10 min, the reaction mixture was worked up according to the procedure for VIa. Ethyl 5-[4][4][3]ferrocenophanepropanoate (VIb) (186 mg, 81%) purified by column chromatography over alumina with benzene/ethyl acetate (5/1) was recrystallized from hexane to give deep red rodlike crystals, m.p. 98–99°C. (Found: C, 71.86; H, 7.36. $C_{26}H_{32}O_2Fe$ calcd.: C, 72.22; H, 7.46%.) IR(KBr): 1705 ($\nu(C=O)$), 1620 ($\nu(C=C)$). 1H NMR($CDCl_3$): 1.32 and 4.20 (3H and 2H, t and q, J 7.0 Hz, OCH_2CH_3), 3.66 and 3.87 (each 1H, AX system, J 1.4 Hz, 5',2'-H), 4.20 (1H, s, 2-H), 5.98 and 7.78 (each 1H, AX system, J 16 Hz, olefin-H). MS: 434 (M^+ , 100).

The propanoate VIb (186 mg, 0.43 mmol) in acetone (20 ml) was reduced with gaseous H_2 and 10% Pd-C (20 mg) under the similar conditions as in hydrogenation of VIa. The crude product was column-chromatographed over alumina to yield ethyl 5-[4][4][3]ferrocenophanepropanoate (VIIb) (187 mg, a quantitative yield) as a yellow oil. (Found: M^+ 434.1888. $C_{26}H_{34}O_2Fe$ calcd.: mol. wt. 434.1905.) IR(neat): 1735 ($\nu(C=O)$). 1H NMR ($CDCl_3$): 1.23 and 4.09 (3H and 2H, t and q, J 7.0 Hz, OCH_2CH_3), 3.44 and 3.88 (each 1H, AX system, J 1.4 Hz, 5',2'-H), 3.90 (1H, s, 2-H). MS: 434 (M^+ , 100).

[4][3][4][3](1,2,3,4)Ferrocenophane (I)

2-Ferrocenophanepropanoate (VIIa) (175 mg, 0.40 mmol) was dissolved into ethanol by warming, and 10% aq. NaOH was added to the solution. The mixture was refluxed for 10 min, and 6*N* HCl was added to neutralize. The extracts with benzene were washed with saturated aq. NaCl, dried over Na_2SO_4 and evaporated. The residual crude of the resulting propanoic acid derivative was dissolved into dichloromethane. To the solution ethyl polyphosphate (PPE) (2 ml) was added and the mixture was heated to 80°C with stirring. Upon heating at 80°C for an additional 10 min after vaporization of dichloromethane, the reaction went to completion. Ice/water and then saturated aq. Na_2CO_3 were added to the mixture, and extracts with benzene were washed with saturated aq. NaCl, dried over Na_2SO_4 and evaporated. The residue was column-chromatographed over silica gel with benzene to yield [4]- α -oxo[3][4][3](1,2,3,4)ferrocenophane (VIII) (108 mg, 69%). The crude product was recrystallized from ethyl acetate to give yellow flakes, m.p. 214–216°C. (Found: C, 73.98; H, 7.16. $C_{24}H_{28}OFe$ calcd.: C, 74.23; H, 7.27%.) IR (KBr): 1665 ($\nu(C=O)$). 1H NMR ($CDCl_3$): 3.79 (1H, s, 5-H), 3.99 (1H, s, 5'-H). MS: 388 (M^+ , 100).

A solution of VIII (54 mg) in dry benzene (3 ml) was added dropwise to a suspension of excess $LiAlH_4/AlCl_3$ in dry ether (10 ml), and the mixture was stirred at room temperature for 3 h. Wet ether was added and the product was extracted

TABLE 4

ATOMIC POSITIONAL PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS AND ISOTROPIC EQUIVALENT THERMAL PARAMETERS, B_{eq} (B_{eq} is defined as $B_{\text{eq}} = \frac{1}{3} \sum_i \Sigma_j \beta_j \cdot a_j \cdot a_j$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)^a$
Fe	0.27239(3)	0.11351(7)	0.23207(5)	2.46
C(1)	0.3352(3)	0.1834(6)	0.1195(4)	3.51
C(2)	0.3131(3)	0.3143(6)	0.1813(4)	3.44
C(3)	0.2284(3)	0.3181(6)	0.1621(4)	3.15
C(4)	0.1997(3)	0.1845(6)	0.0935(4)	3.32
C(5)	0.2647(3)	0.1070(6)	0.0649(4)	3.86
C(1')	0.3440(3)	-0.0284(6)	0.3380(4)	3.55
C(2')	0.3197(3)	0.1056(6)	0.3957(4)	3.28
C(3')	0.2350(3)	0.1002(6)	0.3790(4)	3.35
C(4')	0.2081(3)	-0.0309(5)	0.3066(4)	3.36
C(5')	0.2749(3)	-0.1112(6)	0.2844(4)	3.78
C(6)	0.4166(3)	0.1319(7)	0.1162(5)	5.38
C(7)	0.4314(4)	-0.0411(8)	0.1214(6)	6.34
C(8)	0.4429(4)	-0.1327(8)	0.2257(6)	7.36
C(9)	0.4264(3)	-0.0736(8)	0.3343(5)	5.71
C(10)	0.3668(3)	0.4198(7)	0.2641(5)	5.04
C(11)	0.4135(3)	0.3356(7)	0.3722(5)	5.56
C(12)	0.3697(3)	0.2395(7)	0.4493(4)	4.54
C(13)	0.1805(3)	0.4472(6)	0.1998(4)	4.37
C(14)	0.1769(3)	0.4592(7)	0.3237(5)	4.96
C(15)	0.1331(3)	0.3265(7)	0.3675(4)	4.76
C(16)	0.1851(3)	0.2030(7)	0.4366(4)	4.27
C(17)	0.1174(3)	0.1203(7)	0.0704(4)	4.66
C(18)	0.1096(3)	-0.0487(7)	0.1188(5)	5.21
C(19)	0.1249(3)	-0.0643(7)	0.2498(5)	4.76
H(5)	0.260(3)	0.014(7)	0.019(5)	
H(5')	0.270(3)	-0.208(7)	0.236(4)	
H(6a)	0.461(3)	0.205(7)	0.156(5)	
H(6b)	0.433(3)	0.173(7)	0.056(5)	
H(7a)	0.479(3)	-0.073(7)	0.082(5)	
H(7b)	0.371(3)	-0.081(7)	0.071(5)	
H(8a)	0.500(3)	-0.164(7)	0.240(5)	
H(8b)	0.418(3)	-0.242(7)	0.208(4)	
H(9a)	0.467(3)	0.004(7)	0.370(5)	
H(9b)	0.446(3)	-0.166(7)	0.392(5)	
H(10a)	0.340(3)	0.491(7)	0.289(5)	
H(10b)	0.398(3)	0.468(7)	0.211(5)	
H(11a)	0.444(3)	0.415(6)	0.419(5)	
H(11b)	0.454(3)	0.259(7)	0.350(5)	

with benzene. The extracts were washed with saturated aq. NaHCO_3 and then saturated aq. NaCl , dried over Na_2SO_4 and evaporated. The residue was purified by column-chromatography over alumina with benzene to yield [4][3][4][3]ferrocenophane (I) (58 mg, quantitative yield), which was recrystallized from hexane/benzene to give yellow prisms, m.p. 236–237°C. (Found: M^+ 374.1672. $\text{C}_{24}\text{H}_{30}\text{Fe}$ calcd.: mol. wt. 374.1694.) ^1H NMR (CDCl_3): 3.78 (2H, s, 5,5'-H). ^{13}C NMR (CDCl_3): 19.30, 21.69, 25.39, 26.22, 26.85, 27.92, 38.74 and 39.13 (bridge methylene-C), 69.68 (unsubstituted Cp-C), 81.19, 81.38, 86.55 and 91.27 (substituted Cp-C). MS: 374 (M^+ , 100).

TABLE 4 (continued)

Atom	x	y	z	$B_{eq}(\text{Å}^2)^a$
H(12a)	0.340(3)	0.328(7)	0.482(5)	
H(12b)	0.413(3)	0.190(7)	0.507(5)	
H(13a)	0.124(3)	0.440(7)	0.155(5)	
H(13b)	0.198(3)	0.543(7)	0.171(4)	
H(14a)	0.143(3)	0.555(7)	0.328(5)	
H(14b)	0.238(3)	0.458(7)	0.371(5)	
H(15a)	0.093(3)	0.278(7)	0.297(4)	
H(15b)	0.092(3)	0.374(3)	0.411(5)	
H(16a)	0.148(3)	0.124(6)	0.464(5)	
H(16b)	0.220(3)	0.260(7)	0.504(5)	
H(17a)	0.100(3)	0.107(7)	-0.008(5)	
H(17b)	0.083(3)	0.191(7)	0.099(5)	
H(18a)	0.144(3)	-0.121(7)	0.091(5)	
H(18b)	0.055(3)	-0.076(6)	0.089(5)	
H(19a)	0.110(3)	-0.177(7)	0.268(5)	
H(19b)	0.087(3)	0.005(7)	0.276(5)	

^a Isotropic B for hydrogen atoms is fixed, $B = 4.5 \text{ Å}^2$.

[4][4][4][3](1,2,3,4)Ferrocenophane (XI)

To a solution of α -oxoferrocenophane (VIII) (140 mg, 0.35 mmol) in dry benzene was added BF_3 etherate (0.88 mmol), and the mixture was stirred for 1 h. A dry ether solution of alcohol-free diazomethane (30 ml) was rapidly added to the solution of the complex and stirred for 5 min. Saturated aq. Na_2CO_3 and ascorbic acid were added to the reaction mixture. The extracts with benzene were washed with saturated aq. NaCl , dried over Na_2SO_4 and evaporated. The residue was chromatographed over thin layer silica gel on a preparative scale with benzene as a developing solvent to give three bands. The first band yielded [4]- β -oxo[4][4][3](1,2,3,4)ferrocenophane (X) (36 mg, 26%), which was recrystallized from ethyl acetate to give yellow crystals, m.p. 254–257°C. (Found: M^+ 402.1634. $\text{C}_{25}\text{H}_{30}\text{OFe}$ calcd.: mol. wt. 402.1644.) IR(KBr): 1685 ($\nu(\text{C}=\text{O})$). ^1H NMR (CDCl_3): 3.31 (2H, s, isolated methylene-H), 3.78 and 3.82 (each 1H, each s, 5,5'-H). MS: 402 (M^+ , 100), 374 ($[\text{M} - \text{CO}]^+$, 15).

The starting material was recovered from the second band (47 mg, 34%). The third band yielded [4]- α -oxo[4][4][3](1,2,3,4)ferrocenophane (IX) (20 mg, 14%), which was recrystallized from ethyl acetate, m.p. 210°C (dec.). (Found: M^+ 402.1660. $\text{C}_{25}\text{H}_{30}\text{OFe}$ calcd.: mol. wt. 402.1644.) IR(KBr): 1645 ($\nu(\text{C}=\text{O})$). ^1H NMR (CDCl_3): 3.82 (1H, s, 5-H), 4.04 (1H, s, 5'-H). MS: 402 (M^+ , 100).

According to the same procedure as for the preparation of I, α -oxoferrocenophane (IX) (17 mg) was reduced with excess $\text{LiAlH}_4/\text{AlCl}_3$ to yield [4][4][4][3](1,2,3,4)ferrocenophane (XI) (14 mg, 86%). Recrystallization of the crude phane (XI) gave yellow prisms, m.p. 245–247°C. (Found: M^+ 388.1842. $\text{C}_{25}\text{H}_{32}\text{Fe}$ calcd.: mol. wt. 388.1851.) ^1H NMR (CDCl_3): 3.73 (2H, s, 5,5'-H). ^{13}C NMR (CDCl_3): 21.30, 26.95, 27.48, 27.73 (3C), 29.09 and 36.65 (bridge methylene-C), 68.42 (unsubstituted Cp-C), 81.38, 83.13, 85.67 and 86.25 (substituted Cp-C). MS: 388 (M^+ , 100), 360 ($[\text{M} - \text{C}_2\text{H}_4]^+$, 6).

Cyclization of 5-[4][4][3](1,3,4)ferrocenophanepropanoate (VIIb)

Ethyl propanoate (VIIb) (504 mg, 1.16 mmol) was hydrolyzed with aq. NaOH/EtOH and then treated with PPE/dichloromethane according to the same procedure as for the preparation of VIII. The crude product was chromatographed over thin layer alumina on a preparative scale to be separated into a number of bands. The main band in them yielded homoannular cyclization product (XII) (36 mg, 8%), which was recrystallized from ethyl acetate to give orange prisms, m.p. 195–196°C. (Found: M^+ 388.1476. $C_{24}H_{28}OFe$ calcd.: mol. wt. 388.1487.) IR (KBr): 1685 ($\nu(C=O)$). 1H NMR ($CDCl_3$): 2.98 (1H, s, 5'-H), 3.94 (1H, s, 2-H). MS: 388 (M^+ , 100).

Treatment of the carboxylic acid, derived from the ester (VIIb) (377 mg, 0.87 mmol) by hydrolysis, with polyphosphoric acid (PPA) (2 ml) instead of PPE gave only XII (35 mg, 10%) and the starting material and no by-product.

Ring enlargement reaction of XII (39 mg, 0.10 mmol) in dry benzene (2 ml) with BF_3 etherate (0.02 ml, 0.16 mmol) and an ether solution of diazomethane (10 ml) was carried out by the same procedure as the preparation of IX and X. Thin layer chromatography of the crude product over silica gel on a preparative scale separated it into three bands which yielded an unknown yellow oil, the starting material (XII) (16 mg, 41%) and an orange solid (13 mg, 32%). Recrystallization of the solid from hexane/ethyl acetate gave orange-red prisms, m.p. 190–191°C, which was in agreement with XIII described already by the authors [1].

X-Ray diffraction and crystallographic analysis

Material. Pale yellow crystals used for the X-ray diffraction were grown from a benzene solution of I by vapor-diffusion of hexane.

Data collection. Systematic extinctions on Weissenberg photographs, using Ni-filtered $Cu-K_\alpha$ radiation, uniquely identified space group $P2_1/a$. A crystal with dimensions $0.40 \times 0.30 \times 0.15$ mm was mounted with the b axis parallel to the ϕ axis of a Hilger & Watts Y290 four-circle diffractometer. The cell parameters and intensity data were obtained with Zr-filtered $Mo-K_\alpha$ radiation (λ 0.7107 Å) at 21°C. The intensities of the 4342 unique reflections with $2\theta \leq 55^\circ$ were collected by a $2\theta-\omega$ step scan (1 s count at each of 80 steps of 0.02° in 2θ , background count of 10 s at each end of the scan range), and 2759 reflections [$F_o \geq 3\sigma(F)$] were used in the calculations. Three standard reflections, monitored every 50 measurements, showed no significant intensity variations throughout the data collection. Lorentz and polarization corrections were made but no absorption correction was applied. The density was measured by the flotation method in an aqueous solution of K_2HgI_4 .

Crystal data: $C_{24}H_{30}Fe$, $M_r = 374.35$; monoclinic, space group $P2_1/a$, a 17.490(4), b 8.489(1), c 12.157(2) Å, β 101.51(1)°, V 1768.7 Å³; D_m 1.41, D_x 1.406 Mg m⁻³, $Z = 4$, $\mu(Mo-K_\alpha)$ 8.82 cm⁻¹, $F(000) = 800$.

Structure determination and refinement. The structure was solved by the heavy atom method. The position of the Fe atom was located from a Patterson map and the C atoms by Fourier methods. After five cycles of block-diagonal least-squares refinement with anisotropic thermal parameters, the difference Fourier map revealed all the remaining H atoms. The refinements converged to a final residual, R to 0.069 with the fixed isotropic thermal parameters B of 4.5 Å² for the H atoms. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F) + 0.0006|F_o|^2]^{-1}$. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.066$. The atomic scattering factors were taken

from the International Tables for X-ray Crystallography [19]. All the computations were carried out on HITAC M-200H computer system at the Computer Center of the University of Tokyo with the UNICS program system [20].

The final difference Fourier map showed no additional peaks. The positional parameters with associated esd's are listed in Table 4.

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