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Synthesis and X-Ray Crystal Structure of $[5_4]$(1,2,3,4)Ferrocenophane[1]

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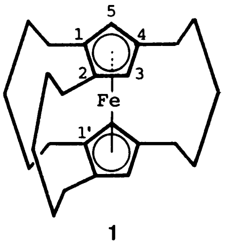
The title compound bridged with four pentamethylene chains has been synthesized by stepwise construction of a pentamethylene bridge via formation of a three-carbon bridge followed by insertion of two carbon units. Crystal structure of the phane has been determined by X-ray diffraction. The compound crystallizes in the monoclinic system, space group $P2_1/n$ with unit cell parameters a=16.691(10), b=9.858(5), c=15.237(8) Å, β=112.43(6)°, and z=4. The structure parameters of the ferrocene moiety fall in normal ranges. Characteristic features are noted in the methylene bridges. The γ-methylene carbons undergo large thermal vibration, and apparent shortening of the bond lengths by oscillatory motions of atoms is seen.

A number of intramolecularly multibridged $[3_n]$- and $[4_n]$ferrocenophanes[2,3] with tri- and tetramethylene chains have been synthesized[4,5] since the discovery of ferrocene. Especially, recent years have seen developments in the preparation of tetra- and pentabridged ferrocenophanes,[6–10] and symmetrically perbridged $[4_5]$(1,2,3,4,5)ferrocenophane, which was named superferrocenophane, was reported by the authors[11] in 1986. On the other hand, there have been only two reports[12,13] on multibridged $[5_n]$ferrocenophanes (n>1) with pentamethylene chains; the one reported by Nesmeyanov et al.[12] is $[5_2]$ferrocenophane with substituents on the bridge and the others by one of the authors[13] are $[5_2]$- and $[5_3]$ferrocenophanes. One of the reason why $[5_n]$ferrocenophane could not be easily prepared is the difficulty of construction of additional pentamethylene bridges. Condensations between the two substituents in the two cyclopentadienyl (Cp) rings, described by several groups[12,14–17] for the preparation of monobridged [5]ferrocenophanes, are unfavorable for synthesis of multibridged phanes, because selective substitution at the desired positions of the Cp rings is impossible. One of the authors[13] succeeded in the formation of the pentamethylene chain by extension of α-oxotrimethylene bridge, and reported the synthesis of $[5_3]$(1,2,4)ferrocenophane (**1**) via stepwise formation of pentamethylene bridges. In this paper, the synthesis of tetrabridged $[5_4]$(1,2,3,4)-ferrocenophane (**2**) from **1** by application of the bridge enlargement is reported, and its molecular structure determined by X-ray diffraction is described.



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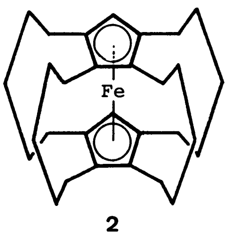

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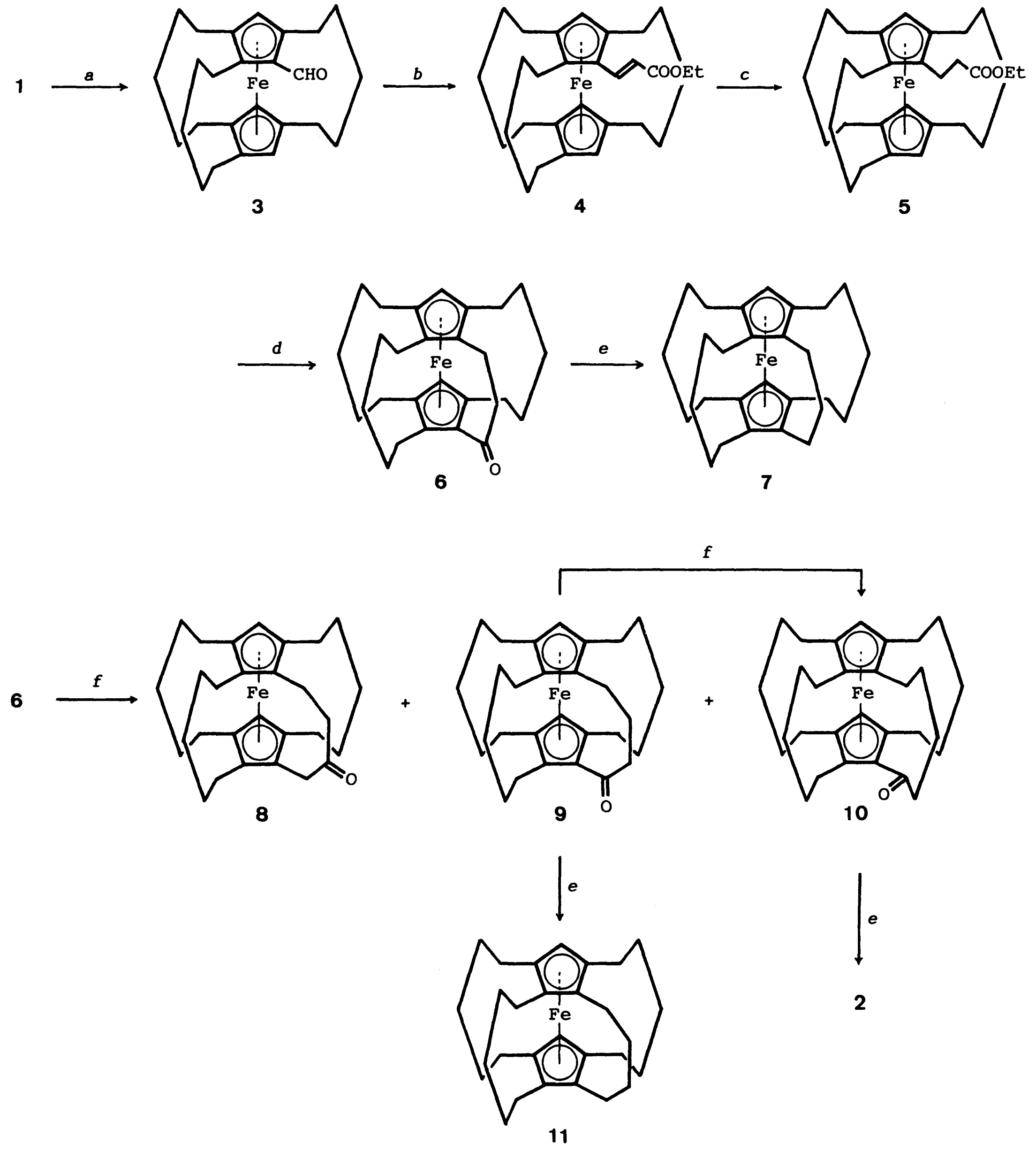
Results and Discussion

Synthesis. The synthetic method of $[5_4]$ferrocenophane (**2**) and the related compounds from $[5_3]$ferrocenophane (**1**) is summarized in Scheme 1. In the preparation of tribridged ferrocenophane **1**,[13] malonic acid/piperidine and trifluoroacetic anhydride were used for condensation of formylferrocene and bridging reaction of propionic acid, respectively. However, these conventional methods were inapplicable to the construction of fourth bridge because of much more steric hindrance of the existing bridges. Accordingly, Reformatsky reaction and cyclization with polyphosphoric acid ethyl ester (PPE) were applied to these steps.

The starting material **1** was formylated according to Vilsmeyer reaction followed by Reformatsky reaction and catalytic hydrogenation to give $[5_3]$ferrocenophanepropionate (**5**) in a good yield (86% from **1**). Cyclization of propionic acid, prepared by hydrolysis of **5**, with PPE (concn 50%) in 1,2-dichloroethane under the conditions free from oxygen and moisture afforded tetrabridged compound **6** in quantitative yield. Running the reaction in the presence of a trace amount of oxygen and moisture resulted in considerable decrease in the yield of **6** (44%). Therefore, the cyclization must be carried out under strict control of reaction conditions. The signals of the Cp rings in the ^{1}H NMR spectrum of **6** appeared at δ 3.68 and 3.63 as two singlets. The NMR spectrum of phane **7** derived by reduction of **6** showed only one singlet of the Cp ring protons and eleven carbon signals of the methylene groups. The spectral pattern indicates that **7** has a C_s symmetric structure.

Treatment of ketone **6** with a large excess of diazomethane (over 10 equiv to the substrate) in the presence of BF_3 etherate (3.5 equiv) afforded three bridge-enlarged products **8**, **9**, and **10** in 35, 33, and 30% yields, respectively. β-Ketone **8** was contaminated with minor compounds, which were presumably further enlarged compounds, and attempted purification was unsuccessful. When 1.2 equivalent of BF_3 etherate to the substrate was used, the yield of α-oxo[5]ferrocenophane **10** was only 3.3%. Bridge enlargement of α-oxo[4]ferrocenophane **9** in a similar manner to the reaction of **6** also gave the desired compound **10** (42%).



Scheme 1. Synthesis of [5_4](1,2,3,4)ferrocenophane (**2**) and related compounds. *a*. DMF/$POCl_3$. *b*. $BrCH_2COOEt$/Zn. *c*. H_2/Pd-C. *d*. 1) aq. NaOH, 2) PPE. *e*. $LiAlH_4/AlCl_3$. *f*. $CH_2N_2/BF_3 \cdot OEt_2$ in benzene.

Reduction of **9** and **10** with $LiAlH_4/AlCl_3$ afforded the corresponding tetrabridged ferrocenophanes **11** and **2**. In the ^1H NMR spectrum of **2**, the two protons of the Cp rings appeared as a singlet at δ 3.70. The C_{2v} symmetric structure of **2** was confirmed by observation of a simple ^{13}C NMR spectral pattern consisting of six and three signals of the methylene and Cp ring carbons, respectively.

Molecular Structure. The crystal structure of [5_4]ferrocenophane (**2**) was determined by X-ray diffraction. The structural parameters are given in Tables 1—6. The molecular structure and the numbering of the atoms used in this section are shown in Fig. 1.[18]

As is clear from Fig. 1, the bridging methylene chains C1⋯C6 and C4⋯C9 are in a "boat" conformation, whereas the chains C2⋯C7 and C3⋯C8 are in a "zigzag-like" conformation. In the crystal structure of tribridged phane **1** reported by Hillman et al.,[19] the conformations of the methylene chains are all boat forms. From the results it is noted that boat conformation is favorable for bridging between two Cp rings with pentamethylene chains when one of the neighboring positions of the bridge, at least, is unoccupied with other bridge. The pentamethylene chains in a boat form bend in a

Table 1. Fractional Coordinates ($\times 10^5$ for Fe; $\times 10^4$ for C; $\times 10^3$ for H) and the Equivalent Isotropic Temperature Factor (in $Å^2$ unit) of **2** with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Fe	16594(11)	15459(17)	41569(11)	3.03	H5	116(5)	301(8)	254(5)	
C1	2288(8)	1828(12)	3247(8)	3.8	H10	−5(8)	88(14)	302(9)	
C2	2882(8)	1940(12)	4200(8)	4.0	H11	254(9)	−9(15)	279(9)	
C3	2614(8)	3032(12)	4647(8)	3.6	H11′	281(7)	127(12)	225(7)	
C4	1832(8)	3575(13)	3972(8)	4.0	H12	153(13)	160(23)	125(15)	
C5	1666(8)	2843(13)	3123(8)	4.1	H12′	171(10)	4(17)	118(11)	
C6	1075(9)	−311(13)	3784(10)	4.8	H13	31(10)	51(17)	100(11)	
C7	1636(8)	−314(13)	4772(9)	4.3	H13′	59(8)	122(13)	196(9)	
C8	1297(9)	734(13)	5223(8)	4.3	H14	73(11)	−167(20)	160(13)	
C9	578(8)	1354(13)	4510(8)	4.0	H14′	−2(9)	−101(15)	191(10)	
C10	447(8)	708(13)	3631(9)	4.6	H15	106(7)	−222(12)	322(8)	
C11	2371(11)	900(15)	2519(10)	5.6	H15′	177(9)	−130(16)	310(10)	
C12	1583(10)	765(17)	1572(10)	6.2	H16	404(8)	109(14)	549(9)	
C13	716(11)	366(17)	1602(9)	6.9	H16′	409(8)	159(15)	425(9)	
C14	608(11)	−993(15)	1990(10)	7.3	H20	245(9)	−198(16)	471(10)	
C15	1152(10)	−1305(13)	3030(11)	6.2	H20′	213(8)	−183(14)	572(9)	
C16	3761(9)	1221(16)	4646(11)	6.2	H21	351(9)	451(16)	553(10)	
C17	3720(14)	−448(21)	4558(14)	10.7	H21′	369(10)	298(18)	595(12)	
C18	3925(10)	−1057(17)	5523(10)	6.5	H25	177(9)	0(15)	657(10)	
C19	3189(12)	−1001(25)	5797(19)	13.6	H25′	108(8)	135(14)	644(9)	
C20	2310(9)	−1355(15)	5284(11)	5.8	H26	162(7)	570(11)	402(8)	
C21	3176(9)	3623(16)	5638(9)	6.1	H26′	135(9)	475(15)	476(9)	
C22	2831(12)	3941(32)	6337(11)	14.9	H27	28(8)	573(14)	370(9)	
C23	2064(9)	3381(17)	6412(9)	5.9	H27′	50(10)	530(17)	273(10)	
C24	2180(20)	2025(22)	6778(11)	16.3	H28	9(8)	304(13)	293(8)	
C25	1598(11)	917(17)	6295(10)	7.0	H28′	−57(8)	431(14)	270(9)	
C26	1354(8)	4790(13)	4081(9)	4.5	H29	−72(7)	413(12)	422(8)	
C27	449(9)	5013(15)	3378(11)	5.9	H29′	−98(10)	267(18)	356(11)	
C28	−217(8)	3851(15)	3180(10)	5.7	H30	46(15)	307(26)	517(17)	
C29	−498(12)	3305(20)	3926(13)	9.0	H30′	−32(8)	184(14)	502(9)	
C30	10(9)	2420(17)	4660(10)	5.9					

Table 2. Bond Lengths (in Å) between the Heavier Atoms of **2** with Estimated Standard Deviations in Parentheses

Bond	Length	Bond	Length	Bond	Length	Bond	Length
Fe-C1	2.052(15)	C1-C5	1.401(18)	C7-C8	1.469(20)	C17-C18	1.501(26)
Fe-C2	2.053(14)	C1-C11	1.485(21)	C7-C20	1.503(18)	C18-C19	1.442(32)
Fe-C3	2.082(11)	C2-C3	1.433(18)	C8-C9	1.414(15)	C19-C20	1.418(22)
Fe-C4	2.055(13)	C2-C16	1.535(18)	C8-C25	1.525(19)	C21-C22	1.426(27)
Fe-C5	2.032(13)	C3-C4	1.423(15)	C9-C10	1.423(19)	C22-C23	1.438(28)
Fe-C6	2.050(13)	C3-C21	1.555(16)	C9-C30	1.490(21)	C23-C24	1.432(26)
Fe-C7	2.066(13)	C4-C5	1.413(17)	C11-C12	1.544(18)	C24-C25	1.460(28)
Fe-C8	2.097(15)	C4-C26	1.484(19)	C12-C13	1.517(25)	C26-C27	1.497(17)
Fe-C9	2.080(14)	C6-C7	1.438(16)	C13-C14	1.502(23)	C27-C28	1.544(20)
Fe-C10	2.046(13)	C6-C10	1.406(19)	C14-C15	1.528(20)	C28-C29	1.487(28)
C1-C2	1.415(15)	C6-C15	1.552(22)	C16-C17	1.650(26)	C29-C30	1.416(22)

manner as the γ-methylene group approaches to the ferrocene moiety. The chains C1···C6 and C4···C9 can take such a conformation, because there is no substituent at the 5- and 10 positions. However, the chains C2···C7 and C3···C8 which are surrounded with the two bridges cannot take a boat form. Therefore, the two chains are forced to have a zigzag-like conformation to avoid steric effect of the bridges in both sides.

The β- and β'-carbon atoms C17, C19, C22, and C24 of the methylene bridges undergo large thermal vibrations. The root-mean-square displacement of these atoms along the thermal ellipsoid principal axes are listed in Table 4. Most of the largest axes lie nearly along the line bisecting the bonds linking the methylene carbon atoms. This is probably due to the disorder of these bridging carbon atoms. Apparent torsion angles along each chain are listed in Table 5 which were calculated by assuming the methylene carbon atoms situated at their mean position (Table 1). It is clear that the bridging methylene chains C1···C6 and C4···C9 are much more relieved situation since there is no bridge in the neighboring position

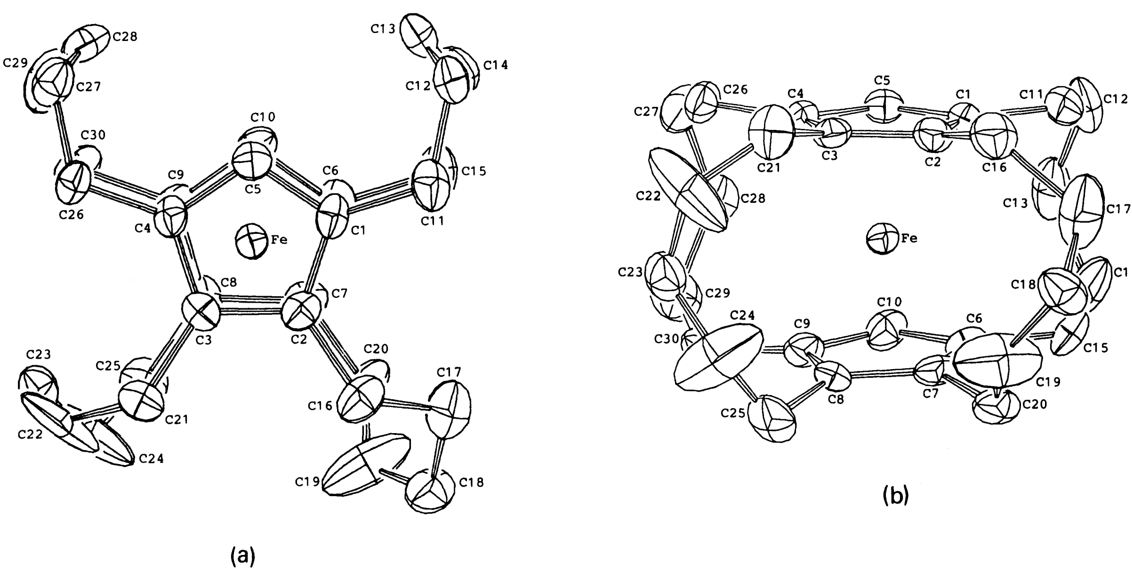


Fig. 1. (a) An ORTEP drawing[18] of the molecule viewed perpendicular to the plane formed by the two lines C1-C4 and C3-C5. The thermal ellipsoid encloses the region where the center of each atom will be found with probability 30%. Hydrogen atoms are omitted. (b) Same as (a) but rotated 90° about the horizontal line through C1 and C4.

Table 3. Bond Angles (in Degree) of **2** with Estimated Standard Deviations in Parentheses

Bond	Angle	Bond	Angle	Bond	Angle	Bond	Angle
C2-C1-C5	106.0(11)	C1-C5-C4	111.4(11)	C8-C9C-30	126.2(12)	C22-C21-C3	122.8(15)
C2-C1-C11	125.8(12)	C7-C6-C10	108.8(12)	C6-C10-C9	109.1(12)	C23-C22-C21	126.9(19)
C5-C1-C11	127.9(12)	C7-C6-C15	124.6(12)	C12-C11-C1	117.5(13)	C24-C23-C22	113.4(17)
C3-C2-C1	108.8(11)	C10-C6-C15	126.6(13)	C13-C12-C11	118.5(13)	C25-C24-C23	122.5(20)
C3-C2-C16	123.7(11)	C8-C7-C6	106.0(11)	C14-C13-C12	120.1(14)	C8-C25-C24	120.8(16)
C1-C2-C16	126.6(12)	C8-C7-C20	125.7(12)	C15-C14-C13	118.3(14)	C27-C26-C4	118.5(12)
C4-C3-C2	107.8(11)	C6-C7-C20	127.2(12)	C6-C15-C14	117.2(13)	C28-C27-C26	119.0(12)
C4-C3-C21	127.5(11)	C9-C8-C7	108.0(11)	C17-C16-C2	115.0(13)	C29-C28-C27	122.2(14)
C2-C3-C21	124.1(11)	C9-C8-C25	127.5(12)	C18-C17-C16	109.4(16)	C30-C29-C28	123.9(16)
C5-C4-C3	105.9(11)	C7-C8-C25	123.8(12)	C19-C18-C17	111.6(17)	C9-C30-C29	122.5(14)
C5-C4-C26	126.2(12)	C10-C9-C8	108.1(11)	C20-C19-C18	130.3(20)		
C3-C4-C26	127.3(11)	C10-C9-C30	125.6(12)	C7-C20-C19	122.0(15)		

Table 4. The Root-Mean-Square Displacements (in Å) of Atoms along the Three Principal Axes of the Thermal Ellipsoid. $U1$, $U2$, and $U3$ are Arranged in Order of the Magnitudes

	$U1$	$U2$	$U3$
C17	0.460	0.352	0.264
C19	0.598	0.321	0.240
C22	0.680	0.280	0.157
C24	0.704	0.296	0.189

(C5···C10) and the torsion angles along these chains are more close to those of the normal gauche conformation. Apparent shortening by oscillatory motions[20] of atoms is clearly seen in the bond lengths between the central two carbon atoms for each methylene chain (see Table 2).

Table 6 shows the planarity of the Cp rings and the deviations of atoms from the planes. The deviations of the α-methylene carbons linked directly to the Cp rings are in a direction expanding the ferrocene cage and the magnitude of the deviation is less remarkable for the above mentioned two relieved methylene chains. Based on these facts it may be clear that the pentamethylene chains are too long to accommodate between the two Cp rings, and that the chains in a boat conformation can link the ferrocene nucleus with less strain than that in a zigzag form.

The conformation of the ferrocene moiety is almost similar to that of tribridged phane **1**.[19] The two Cp rings are in an eclipsed conformation about the Cp-Fe-Cp axis. The Cp rings show a good planarity and the average value of the atomic deviations from its

Table 5. Torsion Angles (in Degree) along the Bridge Methylene Chain with Estimated Standard Deviations in Parentheses

Bond	Angle	Bond	Angle
C1-C11-C12-C13	−55.1(16)	C3-C21-C22-C23	23.2(28)
C11-C12-C13-C14	−63.3(17)	C21-C22-C23-C24	75.3(16)
C12-C13-C14-C15	62.6(16)	C22-C23-C24-C25	−127.8(19)
C13-C14-C15-C6	56.5(16)	C23-C24-C25-C8	44.0(20)
C2-C16-C17-C18	−110.6(13)	C4-C26-C27-C28	51.8(15)
C16-C17-C18-C19	78.8(16)	C26-C27-C28-C29	63.3(17)
C17-C18-C19-C20	47.3(29)	C27-C28-C29-C30	−76.5(20)
C18-C19-C20-C7	−97.5(10)	C28-C29-C30-C9	−35.9(20)

Table 6. The Least-Squares Planes of the Two Cp Rings of **2** and Deviations of Atoms (in Å) from the Planes with Estimated Standard Deviations in Parentheses

$0.5443X+0.6478Y-0.5329Z=1.233$			
C1	−0.004(11)	C11	0.093(13)
C2	−0.006(11)	C16	0.209(13)
C3	0.013(11)	C21	0.248(12)
C4	0.015(11)	C26	0.109(12)
C5	0.012(11)	Fe	−1.664(8)
$0.6036X+0.6676Y-0.4358Z=-1.409$			
C6	−0.009(12)	C15	−0.070(13)
C7	0.011(12)	C20	−0.199(13)
C8	−0.009(12)	C25	−0.236(14)
C9	0.003(11)	C30	−0.081(13)
C10	0.004(12)	Fe	1.672(8)

own least-squares plane is about 0.009 Å (root mean square). The distance between the two Cp rings through the Fe atom (3.336(16) Å) is slightly extended in comparison with that of **1** (3.293(2) Å). It is reasonable that addition of a pentamethylene chain which is too long to link between the two Cp rings results in the extension of the Cp ring distance.

Electronic Spectrum. The electronic spectrum of **2** exhibits a fairly large bathochromic shift of the d-d* absorption band in the visible region (460 nm). We have observed a linear relationship between the wavelength of the d-d* absorption and the number of tetramethylene bridges in [4_n]ferrocenophanes (n=0—5),[11,21,22] but there is no analogous relation in [5_n]ferrocenophanes. The wavelengths of the bands in mono-, di-, and tribridged phanes with pentamethylene chains are almost similar to that of ferrocene (443, 447, 446, 444, and 442 nm for ferrocene, [5]-, [5_2](1,2)-, [5_2](1,3)-, and [5_3](1,2,4)ferrocenophanes, respectively), but that of tetrabridged phane **2** is 18 nm higher than the same band of **1**. A linear relationship between the hypsochromic shift of the d-d* band and the compression of the Cp–Fe–Cp distance has been found in the study on the electronic spectra of various multibridged ferrocenophanes.[21] If the relation also holds for [5_n]ferrocenophanes, the slight elongation of the Cp–Fe–Cp distance in **2** as compared with that of **1** should result in a bathochromic shift of the band in **2**. However, we have not yet found a definitive explanation for the cause of the unusual shift in compound **2**.

The successive hypsochromic shift with the decrease of the methylene group of the 3,3′-bridge was shown in tetrabridged phanes (460, 454, and 447 nm for **2**, **11**, and **7**, respectively). Barr and Watts[23] reported that the d-d* band responded to a ring tilt deformation of the ferrocene nucleus and shifted to a long wavelength with increasing dihedral angle between the two Cp rings in ferrocenophanes. Accordingly, the shift behavior in tetrabridged phane would be reasonably explained by the "tilting effect," because the tiltings of the phanes presumably increase with the decrease of the length of the bridge at the 3,3′-position though the dihedral angles are not confirmed by structural analysis.

Experimental

All melting points were uncorrected. IR spectra were measured using a Hitachi model 215 grating infrared spectrometer. NMR spectra were measured on a JEOL JNM-FX100 spectrometer relative to tetramethylsilane as an internal standard. The figures in the parentheses of ^{13}C NMR spectral data represent the number of the peaks overlapping each other. Mass spectra were obtained with a Hitachi RMU-7M or a Hitachi M-80 double focusing mass spectrometer by electron impact ionizing technique at 70 eV. High-resolution mass spectra were analyzed on a Hitachi M-003 data processing system. Electronic spectra were measured on a Hitachi 330 spectrometer in tetrahydrofuran.

3-Formyl[5_3](1,2,4)ferrocenophane (3). A solution of [5_3](1,2,4)ferrocenophane (**1**)[13] (348 mg) and *N*,*N*-dimethylformamide (525 mg) in freshly distilled chloroform (15 ml) was stirred at 0 °C. To the cooled solution phosphoryl chloride (1.11 g) was added dropwise under a nitrogen atmosphere. The reaction mixture was stirred at 55 °C for 17 h, and then evaporated to dryness. Water was added to the residue, and the aqueous mixture was neutralized with aq. 20% NaOH. The mixture was extracted with benzene several times, and the extracts were washed with saturated aq. NaCl, dried over Na_2SO_4, and evaporated. The residue was column-chromatographed over alumina to be separated into two bands. The first band eluted with benzene yielded the starting material (44 mg, 13%). The second band eluted with benzene–ethyl acetate (20:1) yielded aldehyde **3** (320 mg, 86%), which was recrystallized from ethyl acetate to give orange-red prisms; mp 145—148 °C. IR (KBr) 1670 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$); δ=1.40—3.30 (30H, m, $-CH_2-$), 3.65 and 3.84 (each 1H, an AX system, J=1.6 Hz, 3′- and 5′-H), 4.16 (1H, s, 5-H), 10.33 (1H, s, -CHO); MS m/z (rel intensity), 418 (100, M$^+$), 389 (7), 388 (5).

Found: C, 74.70; H, 8.29%; m/z 418.1936. Calcd for $C_{26}H_{34}OFe$: C, 74.64; H, 8.19%; M, 418.1956.

Ethyl [5$_3$](1,2,4)Ferrocenophane-3-acrylate (4). To a solution of aldehyde **3** (100 mg) in dry benzene–ether (5:1, 6 ml) was added activated zinc (313 mg) and a small amount of iodine, and the mixture was stirred at room temperature under a nitrogen atmosphere. Ethyl bromoacetate (160 mg) was added dropwise to the suspension. The reaction mixture was refluxed on an oil bath at 110 °C for 10 min. After water was added, the mixture was extracted with benzene. The extracts were treated with concd HCl and then with aq. Na_2CO_3 containing ascorbic acid. The organic layer was washed with saturated aq. NaCl, dried over Na_2SO_4, and evaporated. The residue was eluted through a column of silica gel with benzene to yield acrylate **4** (120 mg, quant.), which was recrystallized from ethyl acetate to give red-violet flakes; mp 114—116 °C. IR (KBr) 1715 and 1625 (C=O and C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.40—3.00 (30H, m, $-CH_2-$), 1.34 (3H, t, J=7 Hz, $-CH_3$), 3.49 and 3.59 (each 1H, an AX system, J=1.6 Hz, 3′- and 5′-H), 4.02 (1H, s, 5-H), 4.27 (2H, q, J=7 Hz, $-OCH_2-$), 6.08 and 7.87 (each 1H, an AX system, J=16 Hz, olefin-H); MS m/z (rel intensity) 488 (100, M$^+$), 460 (2).

Found: C, 73.46; H, 8.33%; m/z 488.2396. Calcd for $C_{30}H_{40}O_2Fe$: C, 73.76; H, 8.25%; M, 488.2376.

Ethyl [5$_3$](1,2,4)Ferrocenophane-3-propionate (5). Acrylate **4** (1.16 g) was reduced with H_2 gas (1 atm) and 10% Pd–C (350 mg) in acetone (80 mg) at room temperature for 24 h. The reaction mixture was evaporated and the residue was eluted through a short column of silica gel with benzene–ethyl acetate (3:1). The eluted propionate **5** (1.20 g, quant.) was recrystallized from ethyl acetate to give yellow prisms; mp 91.5—95 °C. IR (KBr) 1740 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.40—3.00 (34H, m, $-CH_2-$), 1.27 (3H, t, J=7.5 Hz, $-CH_3$), 3.27 (1H, bs, 5-H), 3.62 (2H, bs, 3′- and 5′-H), 4.11 (2H, q, J=7.5 Hz, $-OCH_2-$); MS m/z (rel intensity) 490 (100, M$^+$), 4.76 (2), 461 (3), 417 (2), 388 (3).

Found: C, 73.46; H, 8.70%; m/z 490.2526. Calcd for $C_{30}H_{42}O_2Fe$: C, 73.46; H, 8.63%; M, 490.2532.

[5$_2$]-α-Oxo[3][5](1,2,3,4)ferrocenophane (6). Propionate **5** (100 mg) was dissolved into ethanol (20 ml) and the solution was added dropwise to 20% aq. NaOH (20 ml) which was heated at 90 °C. The reaction mixture was stirred at 90 °C for 10 min, and then neutralized with concd HCl. The mixture was extracted with benzene. The extracts were washed with saturated aq. NaCl, dried over Na_2SO_4, and evaporated. The residue, which was crude [5$_3$](1,2,4)ferrocenophane-3-propionic acid, was immediately used for the following reaction without further purification, because the acid was very sensitive to air.

The crude acid was dissolved into 1,2-dichloroethane, and oxygen in the solution was removed as much as possible by ultrasonic vibration. 1,2-Dichloroethane (25 ml) was added to 50% polyphosphoric acid ethyl ester (PPE) prepared in the usual way,[24] and the mixture was refluxed under an argon atmosphere for 1 h to remove oxygen in the reagent. The above solution of the acid was added dropwise to the refluxing solution of PPE, and the reaction mixture was refluxed on an oil bath at 80 °C under an argon atmosphere for 30 min. After 20% aq. NaOH containing ascorbic acid were added to be neutralized, the mixture was stirred at room temperature for 1 h and extracted with 1,2-dichloroethane. The extracts were washed with saturated aq. NaCl, dried over Na_2SO_4, and evaporated. To a solution of the residue in benzene was added a solution of diazomethane in ether. The mixture was stirred and evaporated, and the residue was dissolved into benzene again. Alumina was added to the benzene solution. The suspension was placed in a column packed with silica gel and eluted with benzene. The orange band yielded bridged product **6** (91 mg, quant.), which was recrystallized from ethyl acetate to give orange prisms; mp 225—228 °C. IR (KBr) 1665 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30—3.70 (34H, m, $-CH_2-$), 3.63 (1H, s, 5-H), 3.68 (1H, s, 5′-H); ^{13}C NMR ($CDCl_3$) δ=20.65, 21.24, 21.94, 22.06, 22.29, 22.41, 22.58, 23.17, 24.16, 24.34, 25.98 (3C), 26.21, 26.79, 33.35, and 47.80 (methylene-C), 70.67 and 73.30 (unsubstd. Cp-C), 70.26, 79.39, 83.54, 86.00, 86.12, 90.39, 90.68, and 93.02 (substd. Cp-C), 213.48 (C=O); MS m/z (rel intensity) 444 (100, M$^+$), 416 (24).

Found: C, 75.70; H, 8.13%; m/z 444.2093. Calcd for $C_{28}H_{36}OFe$: C, 75.71; H, 8.17%; M, 444.2112.

[5$_2$][3][5](1,2,3,4)Ferrocenophane (7). A solution of ketone **6** (100 mg) in absolute ether (10 ml) was added to a suspension of $LiAlH_4$ (100 mg) and $AlCl_3$ (200 mg) in ether (10 ml). The reaction mixture was stirred at room temperature for 3 h. Saturated aq. NH_4Cl was added to the mixture and the hydrolyzate was extracted with benzene. The extracts were washed with saturated aq. NaCl, dried over Na_2SO_4, and evaporated. Column chromatographic purification of the residue over alumina gave compound **7** (97 mg, quant.), which was recrystallized from ethyl acetate to give yellow prisms; mp 212—214 °C. ^{1}H NMR ($CDCl_3$) δ=1.20—3.20 (36H, m, $-CH_2-$), 3.56 (2H, s, Cp-H); ^{13}C NMR ($CDCl_3$) δ=18.81, 20.57, 21.05, 21.83, 22.61, 22.91, 24.61, 25.83, 26.07, 32.22, and 33.87 (methylene-C), 70.18 (unsubstd. Cp-C), 82.81, 86.41, and 91.53(2C) (substd. Cp-C); λ_{max} (THF)=447 nm (ε=245); MS m/z (rel intensity) 430 (100, M$^+$).

Found: C, 78.14; H, 8.88; m/z 430.2320. Calcd for $C_{28}H_{38}Fe$: C, 78.17; H, 8.90; M, 430.2320.

[5$_2$]-α-Oxo[4][5]- and [5$_2$]-α-Oxo[5][5](1,2,3,4)ferrocenophanes (9 and 10). Ketone **6** (500 mg) was dissolved into dry benzene (50 ml) and BF_3 etherate (0.7 ml) was added to the solution under a nitrogen atmosphere. The mixture was cooled on an ice-water bath. To the vigorously stirring solution of the complex was rapidly added an ether solution of alcohol-free diazomethane (50 ml), which had been prepared in the usual way[13] and stored over KOH. Water containing ascorbic acid and then 20% aq. NaOH was added and the mixture was extracted with benzene. 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. The first band yielded [5$_2$]-β-oxo[4][5](1,2,3,4)ferrocenophane (**8**) (180 mg, 35%). IR (KBr) 1700 (C=O) cm^{-1}. The ketone **8** was contaminated with further enlarged products, which could not be removed by means of various methods for purification.

The second band yielded ketone **10** (160 mg, 30%), which was recrystallized from ethyl acetate to give orange prisms; mp>300 °C. IR (KBr) 1650 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.60—3.00 (38H, m, $-CH_2-$), 3.69 (1H, s, 5-H), 4.00 (1H, s, 5′-H); ^{13}C NMR ($CDCl_3$) δ=21.70, 22.00, 22.52, 22.70 (3C), 22.93 (3C), 24.63, 24.75, 25.16(2C), 25.57, 25.68, 25.80, 26.68, 28.37, and 39.84 (methylene-C), 69.68 and 73.07 (unsubstd. Cp-C), 81.03, 82.78, 85.47, 86.06, 87.52, 88.51, 88.92, and 89.10 (substd. Cp-C), 210.84 (C=O); MS *m/z* (rel intensity) 472 (100, M^+), 458 (7), 444 (15).

Found: C, 76.13; H, 8.29%; *m/z* 472.2420. Calcd for $C_{30}H_{40}OFe$: C, 76.30; H, 8.54%; M, 472.2426.

The third band yielded ketone **9** (170 mg, 33%), which was recrystallized from ethyl acetate to give orange prisms; mp 258—261 °C. IR (KBr) 1660 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40—3.00 (36H, m, $-CH_2-$), 3.68 (1H, s, 5-H), 3.91 (1H, s, 5′-H); ^{13}C NMR ($CDCl_3$) δ=21.41, 21.82, 22.23, 22.46, 22.64, 22.87, 23.05, 23.34, 23.64, 24.22, 24.45, 25.62, 25.74(2C), 26.09, 30.13, 31.01, and 43.29 (methylene-C), 69.21 and 73.25 (unsubstd. Cp-C), 79.97, 82.90, 85.12, 85.53, 86.88, 89.16(2C), and 89.74 (substd. Cp-C), 210.08 (C=O); *m/z* (rel intensity) 458 (100, M^+).

Found: C, 75.90; H, 8.21; *m/z* 458.2271. Calcd. for $C_{29}H_{38}OFe$: C, 76.01; H, 8.36; M, 458.2270.

The ketone **9** (100 mg) was converted into the desired ketone **10** (45 mg, 42%) by bridge enlargement in benzene (20 ml) with BF_3 etherate (0.14 ml) and diazomethane (ether solution 10 ml), according to the same procedure as the reaction of **6**.

[5_2][4][5](1,2,3,4)Ferrocenophane (11). Reduction of ketone **9** (100 mg) with $LiAlH_4$ (100 mg) and $AlCl_3$ (200 mg) in ether (20 ml) was carried out according to the same procedure as in the preparation of **7**. The crude product **11** (84 mg, 87%) was recrystallized from ethyl acetate to give yellow prisms; mp 242—243 °C. ^1H NMR ($CDCl_3$) δ=1.30—2.90 (38H, m, $-CH_2-$), 3.63 (2H, s, Cp-H); ^{13}C NMR ($CDCl_3$) δ=21.20, 21.69, 22.47, 22.86, 23.10, 24.32, 25.64, 26.17(2C), 27.24, and 27.78 (methylene-C), 68.67 (unsubstd. Cp-C), 81.59, 81.78, 85.83, and 87.58 (substd. Cp-C); λ_{max}(THF)=454 nm (ε=130); MS *m/z* (rel intensity) 444 (100, M^+).

Found: C, 78.34; H, 9.04%; *m/z* 444.2467. Calcd for $C_{29}H_{40}Fe$: C, 78.37; H, 9.07%; M, 444.2470.

[5_4](1,2,3,4)Ferrocenophane (2). Reduction of ketone **10** (290 mg) with $LiAlH_4$ (233 mg) and $AlCl_3$ (490 mg) in ether (10 ml) was carried out according to the same procedure as in the preparation of **7**. The crude product **2** (223 mg, 80%) was recrystallized from ethyl acetate to give yellow prisms; mp 245 °C (decomp). ^1H NMR ($CDCl_3$) δ=1.30—2.90 (40H, m, $-CH_2-$), 3.70 (2H, s, Cp-H); ^{13}C NMR ($CDCl_3$) δ=21.88, 22.76, 22.96, 25.20, 25.29, and 28.22 (methylene-C), 68.43 (unsubstd. Cp-C), 83.39 and 87.09 (substd. Cp-C); λ_{max}(THF)=460 nm (ε=124); MS *m/z* (rel intensity) 458 (100, M^+).

Found: C, 78.88; H, 9.23%; *m/z* 458.2613. Calcd for $C_{30}H_{42}Fe$: C, 78.59; H, 9.23%; M, 458.2633.

X-Ray Crystallographic Analysis of 2. Crystals of **2** were grown in a dichloromethane–hexane solution as pale orange prisms elongated along the c axis. A specimen with approximate dimensions 0.5×0.1×0.05 mm was chosen for X-ray diffraction measurement. Crystal data and intensity data were collected on a Philips PW 1100 diffractometer using graphite monochromated Mo *Kα* radiation.

Crystal data: [5_4](1,2,3,4)Ferrocenophane, $C_{30}H_{42}Fe$, MW=458.5. Monoclinic, space group $P2_1/n$, Z=4, D_{cal}=1.314 g cm^{-3}. Lattice constants, a=16.691(10), b=9.858(5), c=15.237(8) Å, β=112.43(6)°, U=2317 $Å^3$. μ for Mo $K\alpha$=6.6 cm^{-1}.

Intensities of 1710 reflections were measured as above the $2\sigma(I)$ level out of 3737 independent reflections within the 2θ angle range 6° through 50°. No absorption correction was applied.

The crystal structure was solved by the heavy atom method and refined by the block-diagonal-matrix least-squares calculations including 30 hydrogen atoms with isotropic temperature factors and dispersion terms of the atomic scattering factor of Fe for Mo *Kα* radiation.$^{25)}$ Twelve hydrogen atoms attached to C17, C18, C19, C22, C23, and C24 were not included because these were not found on the diffraction electron-density map due to the disorders described in results and discussion. The final *R* value was 0.085 for 1710 reflections. Bond lengths and bond angles calculated from the refined atomic coordinates (Table 1) are listed in Tables 2 and 3.[††]

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