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Synthesis and Molecular Structure of $[4][3_4]$(1,2,3,4,5)Ferrocenophane

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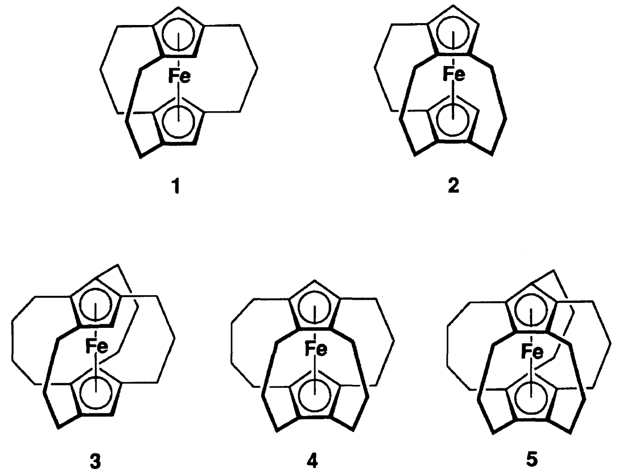
A review of synthetic and structural studies of ferrocenophanes has led to the presumption that the intramolecular substitution of ferrocenophanepropionic acid gives a bridged product when "the distance" between the two carbons to be bridged is greater than 3.20 Å. According to this prediction, the bridging reaction of $[4][3_2]$(1,2,4)ferrocenophane-5-propionic acid ("the distance": ca. 3.5 Å) was carried out, and the expected bridged compound (**13**) was afforded. Subsequently, the construction of fourth and fifth bridges in $[4][3_2]$(1,3,4)ferrocenophane (**16**) was attempted by applying the working hypothesis in order to obtain perbridged $[4][3_4]$(1,2,3,4,5)ferrocenophane (**5**). Both bridging reactions occurred as expected, and the synthesis of **5** was achieved. The absorption spectrum of **5** showed d–d* absorption at an unusually short wavelength ($\lambda_{\max}=345$ nm; ferrocene, 443 nm), which is the shortest value in ferrocene derivatives to our knowledge. The structure of **5** was determined by an X-ray diffraction method. Compound **5** crystallizes in a tetragonal system, space group $I\bar{4}2d$ with unit-cell parameters of $a=14.574(4)$, $c=18.208(4)$ Å and $Z=8$; its R value converged to 0.051 for 1315 reflections. The observed distance between the iron atom and the least-squares aromatic ring of 1.55(9) Å is the smallest among those of all observed multibridged ferrocenophanes. The conformation of the ferrocene moiety is exactly eclipsed, and the dihedral angle of the two rings is small (1.9°).

A number of intramolecularly multibridged ferrocenophanes[1—6] have been prepared[6—8] since the first report concerning ferrocenophane by Rinehart and Curby[9] in 1957. In particular, the synthesis of a $[4_n]$ferrocenophane system ($n=1$—5) bridged with n of tetramethylene chains was completed several years ago,[3,10] and perbridged $[4_5]$(1,2,3,4,5)ferrocenophane was trivially named [4]superferrocenophane.[3,6,10] On the other hand, in a $[3_n]$ferrocenophane system with trimethylene bridges, precursory studies on the synthesis of di- and tribridged compounds containing **1** and **2** (Scheme 1) were carried out by Schlögl[11] and Rinehart[12] and their respective groups before 1963; however, tetra- and pentabridged phanes ($n=4$, 5) have not yet been found in spite of some attempts to synthesize them.[11,13,14] The description of the successful preparation by Schlögl and Peterlik[11] was revised after scrutinizing their synthetic reaction.[15] The product given via an acid-catalyzed cyclization of $[3_3]$(1,2,4)ferrocenophanepropionic acid was assigned to a tetrabridged phane by Vigo;[13] however, Hillman et al.[14,16] proved by an X-ray crystal analysis that this compound was a condensed-ring ferrocenophane produced by homoannular cyclization accompanied by a rearrangement of the existing adjacent bridge. Hillman et al.[14] mentioned that an unusual reaction occurred so as to prevent the introduction of an additional strain due to bridging.



1 **2** **3** **4** **5**

Scheme 1.

It was predicted by a molecular mechanics calculation[17] that pentabridged $[3_5]$ferrocenophane is a spheroidal and highly strained compound, squeezing a metal into a more tight cage than that of $[4_5]$ferrocenophane. Since the project on [4]-superferrocenophane had been completed,[3,18] we next planned to synthesize [3]superferrocenophane, an attractive organometallic cage compound. A different approach from the forced bridging method attempted so

Table 1. Relationship between Bridging Reaction and Molecular Structure in Ferrocenophanealkanoic Acids

Ferrocenophane moiety	Position of $-(CH_2)_mCOOH$ and the number of m		Distance between the two carbons to be bridged		Result of cyclization	
	Position	m	Å	Ref.	Result[a)]	Ref.
Ferrocene	1	2	3.30	20)	B	23)
		3			H	23)
$[3_3](1,2,4)$	3	2	3.15	21)	H	14)
		3			H	24)
$[4][3][4](1,2,4)$	3	2	2.85	b)	H	25)
		3			H	26)
$[4][3][4](1,2,4)$	5	2	3.70	b)	B	25)
		3			H	26)
$[4_3](1,2,4)$	3	2	3.25	22)	B	3)
		3			H	24)
$[4][3_2](1,2,4)$	5	2	3.55	b)	B[c)]	
$[4][3_2](1,3,4)$	2	2	3.35	b)	B[c)]	
$[4][3_3](1,2,3,4)$	5	2	3.60	b)	B[c)]	

a) B, bridging; H, homoannular cyclization. b) The value estimated by inspection with a molecular model. c) Predicted result; the prediction was experimetally proved as described in the text.

far seemed to be required in order to perform the synthesis of a tightly caged compound. Consequently, a concept for introducing bridges into strained ferrocenophanes was presented. Experiments to justify the concept resulted in the establishment of the way to form a trimethylene bridge and to synthesize a new family (**3**—**5**, Scheme 1) of multibridged ferrocenophanes.[19] Moreover, an X-ray crystal analysis of pentabridged compound **5** is described, and the molecular structure of **5**, which is the most strained system in multibridged ferrocenophanes, is discussed.

Results and Discussion

Synthesis. The selectivity in an intramolecularly electrophilic reaction of ferrocenophanealkanoic acid toward bridging or homoannular cyclization is revealed by a consideration of the relationship between the reaction and molecular structure in many ferrocenophanes. As shown in Table 1, the reaction of compounds whose distances between the two carbons to be bridged in the two Cp rings are below 3.15 Å results in the occurrence of only homoannular cyclization in either $m=2$[14,25] or $m=3$;[24,26] the reaction of compounds in which "the distances" are greater than 3.25 Å gave bridged products in $m=2$,[3,23,25] but cyclization products in $m=3$.[23,24,26] That is, although a bridging reaction of butyric acid derivatives does not occur, the types of reactions of propionic acids are apparently affected by "the distance" between the two Cp carbons to be bridged. The boundary of selectivity toward bridging or cyclization seems to be at around 3.20 Å. These facts lead us to the following presumption in contrast to Hillman's suggestion,[14] previously mentioned. The failure of bridge formation in $[3_3](1,2,4)$ferrocenophanepropionic acid is because its intermediary acylium ion cannot enter into the reaction window[27] of the corresponding carbon of the facing Cp ring, due to the short distance between the two Cp carbons (Fig. 1, I).

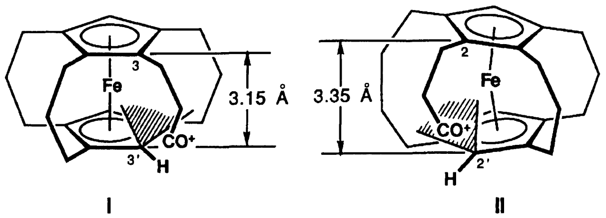
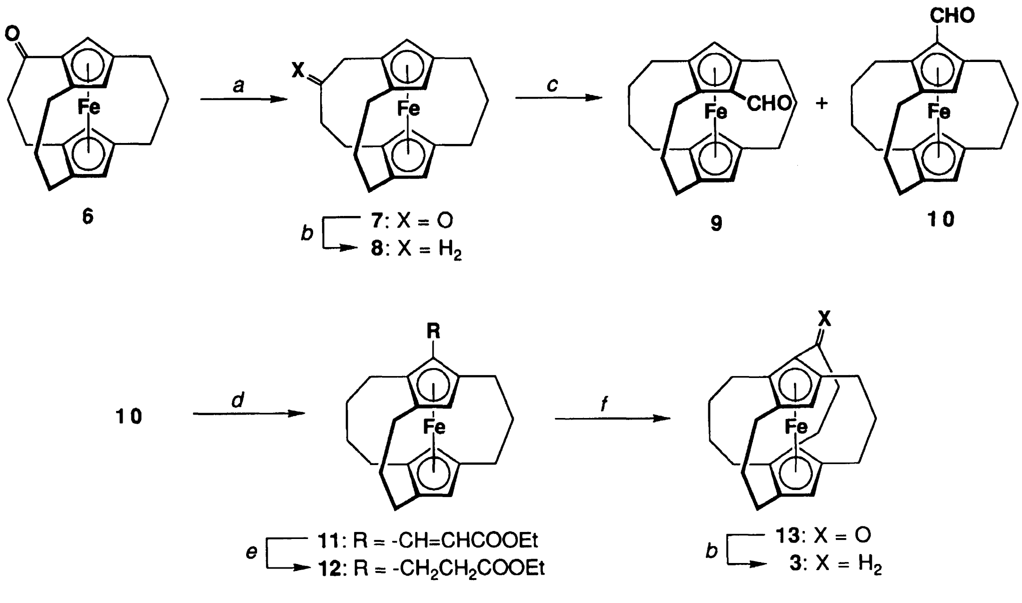


Fig. 1. Geometries of acylium ions of tribridged ferrocenophanes and reaction windows (shaded parts) for the acylium ion center.

If this view is correct, an enlargement of "the distance" should allow the acylium ion center to enter into the reaction window of the desired ring carbon in order to bring about a bridging reaction. According to this consideration, $[3_3](1,2,3)$ferrocenophane-4-propionic acid (a derivative of **2**) can be an appropriate precursor for preparing $[3_4]$ferrocenophane because of the large tilting between the two Cp rings with an opening on the side of the unbridged Cp carbons (the tilting angle of a derivative of **2**: 12.5°[28]). However, the yield of **2**[12] in preparation is too low to be available for the synthetic starting material. Even if $[3_4]$ferrocenophane is prepared by this method, the phane may not be convertible into a perbridged compound by the addition of a trimethylene bridge. We therefore designed the procedure so as to introduce a tetramethylene bridge into the adjacent position to be bridged. "The distance" between the 2- and 2′-carbons adjacent to the tetramethylene bridge in $[4][3_2](1,3,4)$ is 3.35 Å by inspec-



a : CH_2N_2 / CH_3OH *b* : $LiAlH_4$ / $AlCl_3$ *c* : 1) DMF / $POCl_3$, 2) H_2O / NaOH
d : 1) $BrCH_2COOEt$ / Zn, 2) HCl *e* : H_2 / Pd-C *f* : 1) H_2O / NaOH, 2) PPE

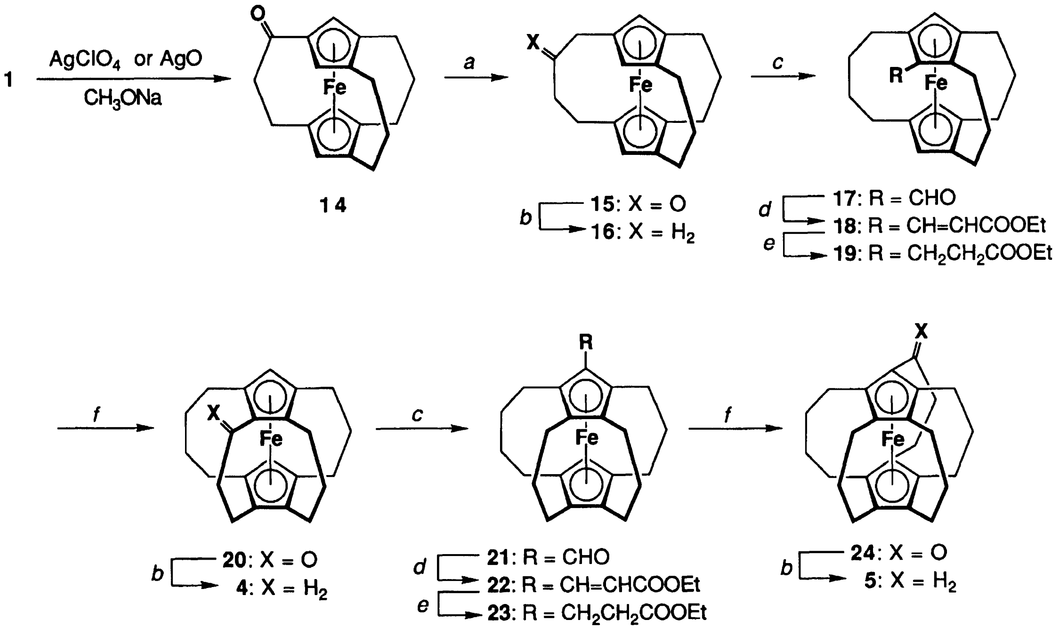
Scheme 2. Synthesis of [4][3_3](1,2,3,5)ferrocenophane (**3**).

tion with a molecular model, and the acylium ion center of the side chain at the 2-position should enter into the reaction window at the 2′-position (Fig. 1, II). The tetramethylene bridge may be able to be contracted to a trimethylene one, for example, by a Wolff rearrangement after bridge formation of the expected position. In order to verify this hypothesis, bridge construction at the 5,5′-positions ("the distance": ca. 3.5 Å) of [4]-[3_2](1,2,4)ferrocenophane (**8**) was first attempted, since **8** could be easily derived from [3_3]ferrocenophane (**6**), which was available by the Rinehart's procedure.[12)]

The results are summarized in Scheme 2. The treatment of **6** with diazomethane afforded a bridge-enlargement product (**7**), which was reduced by $LiAlH_4/AlCl_3$ to give **8** (80% from **6**). Formylation of **8** with *N*,*N*-dimethylformamide (DMF) and phosphoryl chloride yielded two isomers, **9** and **10** (6 and 87%, respectively). 5-Formylferrocenophane (**10**) was converted to **12** by a Reformatsky reaction followed by hydrogenation with Pd–C. A cyclization reaction of propionic acid derived by the hydrolysis of ester (**12**) gave the expected ferrocenophane (**13**) in good yield (81%), despite of formation of a considerably strained system. The ^{1}H and ^{13}C NMR spectra of **3** obtained by the reduction of **13** showed only one singlet of the Cp ring protons (δ=3.62) and eight methylene and five Cp ring carbon signals, respectively; its C_s symmetric structure was confirmed. Further addition of a trimethylene bridge to the 4,4′-position of **3** should be difficult because of its short "distance" between the two carbons to be bridged.

Since our working hypothesis was experimentally justified, the construction of fourth and fifth bridges in [4][3_2](1,3,4)ferrocenophane (**16**) was tried. The reactions are shown in Scheme 3. The selective oxidation of the 4,4′-bridge in **1** was achieved by a treatment with $AgClO_4$/MeONa (a yield of **14**: 54%), which is an oxidant system found by us for the selective oxidation of the α-position of the isolated bridge in [m_n]-ferrocenophanes (m=2—5).[29)] The introduction of a side chain and its conversion reactions were carried out according to the same procedure as those in the preparation of **12**. An intramolecular electrophilic substitution of propionic acids converted by the hydrolysis of **19** and **23** afforded tetra- and pentabridged ferrocenophanes, **20** and **24**, respectively, as expected, though the yield (**20**: 39%; **24**: 49%) was lower than that of **13**. The carbonyl groups of **20** and **24** were reduced to yield **4** and **5**. Only one singlet of the Cp ring protons (δ=3.84) and eight and five carbon signals of the methylenes and Cp rings, respectively, appear in the ^{1}H and ^{13}C NMR spectra of **4**. Although the spectral pattern indicated a [4][3_3]-bridging structure in the C_s symmetric mode in analogy with that of **3**, the chemical shifts of all the signals were different from those of **3**. Those NMR spectral data confirmed that **3** and **4** are isomeric with each other about the positions of the tetramethylene bridge. There are only two isomeric modes of **3** and **4** in [4][3_3]ferrocenophanes, except for asymmetrically bridged phanes.

There is no signal in the region for Cp ring protons in the ^{1}H NMR spectrum of [4][3_4]ferrocenophane (**5**). The ^{13}C NMR showed six and three signals assigned to



Scheme 3. Synthesis of [4][3_3](1,2,3,4)- and [4][3_4](1,2,3,4,5)ferrocenophanes (**4** and **5**). Reaction conditions *a*—*f* are described in Scheme 2.

the methylene carbons and Cp ring carbons, respectively, indicating the presence of C_{2v} symmetry in the molecule.

The color of **5** in the solid state is very light, and in solution almost fades, despite a complex of iron(II); an interesting feature is exhibited in the absorption spectrum in THF. The d–d* absorption band of the iron atom, which appears at 443 nm in ferrocene, is shifted to an unusually short wavelength (345 nm) in **5**. The hypsochromic shift is fairly larger than that of tribridged phane (**1**, 366 nm). The wavelength is the shortest one in all ferrocene derivatives as far as we know.

The absorption of **3** and **4** appears at 365 and 414 nm, respectively. It is interesting that the wavelength of the d–d* absorption of **3** is almost similar to that of **1**. Phane **3** is a compound in which a tetramethylene bridge is added to the framework of **1**. These facts indicate that the energy of the Fe–Cp bond of 1,2,4-tribridged ferrocene with trimethylene chains is little affected by bridging with a tetramethylene chain.

Phane **5** can be a synthetic precursor for symmetric [3_5]ferrocenophane if contraction of the tetramethylene bridge is feasible. Bridge contraction by the selective oxidation of tetramethylene bridge with $AgClO_4$/NaOMe followed by a Wolff rearrangement had already been successful in several compounds involving **4** and **8**.[4] However, the synthesis of [3_5]-ferrocenophane by applying the bridge contraction method to **5** has not yet been achieved.

Table 2. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms with esd's in Parentheses

Atom	x	y	z	B_{eq}[a)]
Fe	0.8088(1)	0.2500(0)	0.1250(0)	2.62(2)
C(1)	0.8910(3)	0.3308(3)	0.1826(2)	4.0(1)
C(2)	0.8351(3)	0.2786(3)	0.2291(2)	4.1(1)
C(3)	0.7407(4)	0.2965(3)	0.2101(3)	5.0(1)
C(4)	0.7399(3)	0.3623(3)	0.1510(3)	4.7(1)
C(5)	0.8346(3)	0.3828(3)	0.1325(3)	4.6(1)
C(6)	0.9930(5)	0.3258(5)	0.1821(4)	7.7(2)
C(7)	1.0377(6)	0.254(3)	0.134(1)	38.5(9)
C(8)	0.8677(5)	0.2077(5)	0.2832(3)	8.6(2)
C(9)	0.8771(5)	0.1056(4)	0.2544(5)	14.2(4)
C(10)	0.8649(5)	0.0600(4)	0.1796(5)	9.0(3)
C(11)	0.6564(4)	0.2459(7)	0.2402(4)	8.7(2)
C(12)	0.6185(5)	0.1580(5)	0.2008(5)	11.0(3)
C(13)	0.6563(4)	0.1064(5)	0.1425(5)	8.8(3)

a) $B_{eq}=4/3\sum_i\sum_j\beta_{ij}a_i\cdot a_j$.

X-Ray Structure Analysis of 5. The molecular structure of **5** was analyzed by an X-ray diffraction method. The positional parameters and equivalent thermal parameters of non-hydrogen atoms are listed in Table 2.[30] Since the iron atom is located on a crystallographic two-fold axis, an asymmetric unit contains one-half of a molecule. A perspective view of the molecule is shown in Fig. 2(a) by an ORTEP drawing with their atomic numbering used in this section.[31] The thermal parameters of the methylene bridge carbons [C(6)–C(13)] possess larger values than those of the ring carbons. Especially, those of the C(7) atom exhibit extraordinary large values among those of the β-carbon atoms [C(7), C(9), and C(12)], the values of which are larger than those of α-carbon atoms [C(6), C(8), C(10), C(11), and C(13)], as shown in Table 2 and Figs. 2(a) and (b). Since molecule **5** comprises a Fe atom, two Cp rings, four trimethylene chains and a tetramethylene chain, the crystallogrphaically required two-fold

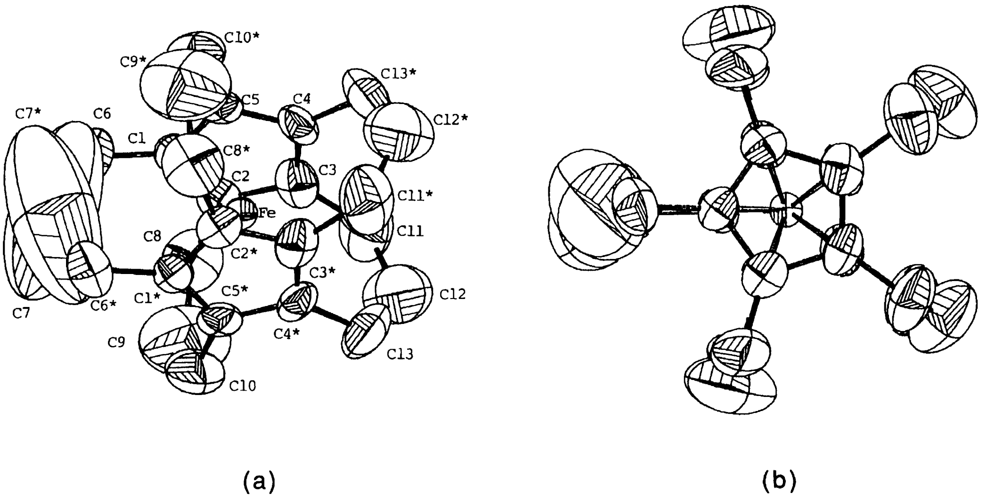


Fig. 2. ORTEP drawing of **5** with thermal ellipsoids at the 50% probability level. H atoms are excluded for clarity. A perspective view and atomic numbering scheme in (a), and a projection of a whole molecule onto the Cp ring plane (b).

axis should pass through the Fe atom and the center of the C(7)–C(7′) bond. Upon repeating the least-squares computation, the C(7) atom gradually moved towards the two-fold axis, and finally C(7) and C(7′) atoms approached each other to be regarded as "one large atom" on an electron density map. However, the size of the C(7) atom, revealed on a Fourier map, was not as large as expected based on its thermal parameters, though its shape was highly anisotropic. Thus, their extraordinary value was caused by the least-squares computation. Though the cause of this unusual behavior of the C(7) cannot be attributed to one of its thermal motion and a certain disorder in the crystal, we exclude the tetramethylene chain from our structural discussion.

Tables 3 and 4 show the selected bond lengths and angles excluding those about the tetramethylene chain. All of the bond lengths and angles about the Cp ring are in the normal range. The least-squares plane of the Cp ring forms a good plane within the calculated esd's (0.1 Å). The two Cp rings are in an exactly eclipsed conformation in relation to each other [see Fig. 2(b)], and are almost parallel; the two least-squares planes are mutually tilted by only 1.9° with an opening on the side of the tetramethylene bridge. The iron-to-ring distance of 1.55(9) Å and the average iron-to-carbon distance of 1.98(9) Å are significantly shorter than the values in ferrocene (Fe–Cp; 1.652, Fe–C; 2.032 Å).[20)]

Table 3. Bond Lengths (in Å) between the Non-Hydrogen Atoms of **5** with esd's in Parentheses

Bond	Length	Bond	Length
Cp-ring		Trimethylene chain	
Fe–C(1)	1.981(5)	C(1)–C(6)	1.490(8)
Fe–C(2)	1.979(5)	C(2)–C(8)	1.504(9)
Fe–C(3)	1.961(6)	C(8)–C(9)	1.58(1)
Fe–C(4)	1.978(5)	C(9)–C(10)	1.53(1)
Fe–C(5)	1.977(6)	C(10)–C(5′)	1.47(1)
C(1)–C(2)	1.399(7)	C(3)–C(11)	1.54(1)
C(2)–C(3)	1.442(7)	C(11)–C(12)	1.57(1)
C(3)–C(4)	1.441(7)	C(12)–C(13)	1.41(1)
C(4)–C(5)	1.453(8)	C(13)–C(4′)	1.52(1)
C(5)–C(1)	1.443(7)		

Table 4. Selected Bond Angles (in Degree) of **5** with esd's in Parentheses

Bond	Angle	Bond	Angle
C(1)–C(2)–C(3)	108.2(4)	C(11)–C(3)–C(2)	126.3(6)
C(2)–C(3)–C(4)	107.9(5)	C(11)–C(3)–C(4)	125.4(6)
C(3)–C(4)–C(5)	107.6(5)	C(10)–C(5′)–C(1′)	127.8(6)
C(4)–C(5)–C(1)	106.6(5)	C(10)–C(5′)–C(4′)	125.4(6)
C(5)–C(1)–C(2)	109.7(4)	C(13)–C(4′)–C(3′)	126.5(5)
C(6)–C(1)–C(2)	124.0(5)	C(13)–C(4′)–C(5′)	125.3(5)
C(6)–C(1)–C(5)	126.1(5)	C(8)–C(9)–C(10)	134.1(9)
C(8)–C(2)–C(1)	125.8(5)	C(11)–C(12)–C(13)	129.8(8)
C(8)–C(2)–C(3)	125.6(5)		

Though taking account of the relatively large esd's, the bond angles around the β-carbons in the trimethylene bridges [C(8)–C(9)–C(10) and C(11)–C(12)–C(13)] are too large for the sp^3 carbons. Also, the α-carbon atoms of the trimethylene bridges fairly deviate from the least-squares planes of the Cp ring (0.13—0.18 Å) to the same side of the iron atom, whereas the α-carbon atoms of the tetramethylene chains are frequently observed to be deviated to the opposite side of the iron atom in other bridged ferrocenophanes.[25,32)] That is, the bonds between the Cp rings and iron atom are compressed by bridging with the trimethylene chains, and the trimethylene bridges are stretched by the ferrocene moiety while opening the bridgehead. The Fe–Cp distance of this compound (1.553 Å) is smaller than that of [3$_3$](1,2,4)ferrocenophane (**1**) (1.573 Å).[21)] This means that compression of the Fe–Cp bond increases with increasing number of trimethylene chains.

The structural results of the present report essentially agree with those of the molecular mechanics calculation (MM2′) of this compound.[17]

The Fe–Cp distance of **5** is shortest in those of ever observed ferrocene derivatives to the best of our knowledge, and its wavelength of d–d* absorbance is also the smallest one, as mentioned above. We have found an approximately linear relationship between the hypsochromic shifts of the d–d* absorption band and the shortening of the Cp–Fe distances in multibridged ferrocenophanes.[6,18,33] This correlation holds for **5**. This compound **5** synthesized in this study is, we think, the ferrocene having the most compressed Cp–Fe–Cp bond and the most strained caged ferrocene among ferrocene derivatives investigated by X-ray structure analysis.

Experimental

All melting points were uncorrected. IR spectra were recorded on a Hitachi Model 215 infrared spectrometer. NMR spectra were measured on a JEOL JNM-FX100 spectrometer, unless otherwise stated. ^{1}H and ^{13}C NMR spectra at 500 and 125.7 MHz, respectively, were obtained on a JEOL JNM-GSX500 spectrometer. The chemical shifts are reported relative to the signal of tetramethylsilane. Mass spectra were obtained with a Hitachi M-80 double-focusing mass spectrometer by electron-impact ionization at 70 eV. The empirical formulas of oily compounds or unstable compounds in solution were determined based on the high-resolution mass spectra, which were analyzed on a Hitachi M-003 data-processing system. UV-visible spectra were recorded with a Hitachi Model 330 spectrophotometer.

General Procedures of Reactions. Bridge Enlargement: A solution of CH_2N_2 in ether (concn ca. 0.2 M, M = mol dm^{-3}) was added to α-oxoferrocenophane in methanol. The mixture was stirred for 12 h at room temperature. After removing the solvent in vacuo, the residue was column-chromatographed on silica gel [elution with benzene/ethyl acetate (20/1)] to afford bridge enlargement product.

Reduction of Ketones: To a suspension of $AlCl_3$ and $LiAlH_4$ in dry ether was added dropwise a solution of α-oxoferrocenophane in dry benzene under a nitrogen atmosphere. The mixture was refluxed for 4 h, and the reaction was quenched with ethyl acetate. After the addition of wet ether, the hydrolysate was extracted with benzene. The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by column chromatography on alumina (elution with benzene) to give reduction product.

Formylation: A solution of ferrocenophane and *N*,*N*-dimethylformamide (DMF) in freshly distilled chloroform was stirred at 0 °C under a nitrogen atmosphere. To the cooled solution was added dropwise $POCl_3$ at 0 °C; the resultant mixture was stirred for 12 h at 50—55 °C under a nitrogen atmosphere. The solvent and DMF was evaporated in vacuo, and the residue was combined with water and then 20% aqueous NaOH. The mixture was stirred for 1 h and extracted with benzene. The organic phase washed with brine and dried over Na_2SO_4. The solvent was evaporated, and the subsequent column chromatography on silica gel [elution with benzene/ethyl acetate (20/1)] gave formyl ferrocenophane.

Condensation by Reformatsky Reaction: To a solution of formylferrocenophane in dry benzene/ether (5/1) was added activated zinc powder, ethyl bromoacetate and a small amount of iodine; the mixture was refluxed for 10 min under a nitrogen atmosphere. The reaction was quenched with water, and zinc was removed by filtration through a short column of celite. The filtrate was combined with concd HCl, and the mixture was extracted with benzene. The benzene phase was washed with saturated aqueous Na_2CO_3 and then with brine, and dried over Na_2SO_4. After removing the solvent in vacuo, the residue was column-chromatographed on silica gel (elution with benzene) to give ferrocenophaneacrylate.

Hydrogenation: A mixture of ferrocenophaneacrylate and 10% Pd–C in ethanol under a hydrogen atmosphere at 1—3 kg cm^{-2} was stirred for 12 h at room temperature. After filtration of the mixture, the solvent was evaporated. The residue was purified by column chromatography on silica gel (elution with benzene) to give ferrocenophanepropionate.

Hydrolysis: Ferrocenophanepropionate was dissolved in ethanol, and 20% aqueous NaOH was added to the solution. The mixture was stirred for 10 min at 80 °C and neutralized with 6% aqueous HCl. The hydrolyzate was extracted with dichloromethane, and the combined extracts were washed with brine and dried over Na_2SO_4. The solvent was evaporated to give propionic acid, which was immediately used for the following bridge-formation reaction without further purification.

Bridge-Formation Reaction: To ethyl polyphosphate ester (PPE), which was prepared in the usual way,[34] was added 1,2-dichloroethane. The mixture was refluxed under an argon atmosphere; ferrocenophanepropionic acid in 1,2-dichloroethane was added dropwise to the refluxed mixture. After refluxing was allowed to continue for 15 min, the reaction mixture was cooled to room temperature and combined with ice-water. Powder of Na_2CO_3 was added to the aqueous mixture. The hydrolyzate was extracted with benzene, and the combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The residue was column-chromatographed on silica gel (elution with benzene) to afford bridged compound.

β-Oxo[4][3₂](1,2,4)ferrocenophane (7). Bridge enlargement of 500 mg (1.56 mmol) of **6**[12] in methanol (150 ml) with an ether solution of CH_2N_2 (150 ml) gave 492 mg (94%) of **7**: Orange prisms, mp 145—146 °C (from ethyl acetate); IR (KBr) 1705 cm^{-1}; ^{1}H NMR (at 500 MHz, $CDCl_3$) δ=1.66, 1.85, 2.21, 2.32, 2.46, 2.62, 2.74 and 2.88 (each 2H, m, CH_2), 3.06 and 3.25 (each 1H, an AX system, J=12.3 Hz, α-CH_2), 3.66, 3.74, 4.06 and 4.07 (each 1H, two pairs of an AX system, J=1.4 Hz Cp H); MS m/z (rel intensity) 334 (100, M$^+$), 306 (62, [M−CO]$^+$).

Found: C, 71.71; H, 6.59%. Calcd for $C_{20}H_{22}OFe$: C, 71.87; H, 6.63%.

[4][3₂](1,2,4)Ferrocenophane (8). Reduction of 450 mg (1.35 mmol) of **7** with $LiAlH_4$ (150 mg, 3.94 mmol) and $AlCl_3$ (450 mg, 3.37 mmol) in ether/benzene (5/3, 80 ml) afforded 430 mg (quant.) of **8**: Orange yellow prisms, 110—111 °C (from ethyl acetate/hexane); ^{1}H NMR (at 500

MHz, $CDCl_3$) δ=1.45—2.35 (20H, m, CH_2), 3.66 and 3.91 (each 2H, an AX system, J=1.35 Hz, Cp H); ^{13}C NMR ($CDCl_3$) δ=21.54, 24.95, 28.51, 28.95, 36.36 and 36.80 (each 2C, methylene C), 69.94 and 73.55 (each 2C, unsubstd. Cp C), 83.29 and 90.21 (4C and 2C, substd. C); MS m/z (rel intensity) 320 (100, M$^+$).

Found: C, 75.00: H, 7.45%. Calcd for $C_{20}H_{24}Fe$: C, 75.01; 7.55%.

3- and 5-Formyl[4][3$_2$](1,2,4)ferrocenophanes (9 and 10). Formylation of 500 mg (1.58 mmol) of **8** with DMF (500 mg, 6.85 mmol) and $POCl_3$ (1.00 g, 6.51 mmol) in chloroform (20 ml) gave two isomeric formylation products. The first eluted band in column chromatography yielded 33 mg (6%) of 3-isomer (**9**): Reddish orange needles, mp 121—123 °C (from ethyl acetate/hexane); IR (KBr) 1665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.40—2.70 (20H, m, CH_2), 3.81 (2H, bs, 3′- and 5′-H), 4.28 (1H, s, 5-H), 10.16 (1H, s, CHO); MS m/z (rel intensity) 348 (100, M$^+$), 319 (5, [M−CHO]$^+$).

Found: M$^+$ m/z 348.1187. Calcd for $C_{21}H_{24}OFe$: M, 348.1175.

The second eluted band yielded 473 mg (86%) of 5-isomer (**10**): Redish orange needles, mp 151—153 °C (from ethyl acetate/hexane); IR (KBr) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20—3.00 (20H, m, CH_2), 3.58 and 4.12 (each 1H, an AX system, J=1.5 Hz, 3′- and 5′-H), 4.07 (1H, s, 3-H); MS m/z (rel intensity) 348 (100, M$^+$), 334 (17, [M−CH_2]$^+$), 319 (10, [M−CHO]$^+$).

Found: M$^+$ m/z 348.1154. Calcd for $C_{21}H_{24}OFe$: M, 348.1175.

Ethyl [4][3$_2$](1,2,4)Ferrocenophane-5-acrylate (11). The Reformatsky reaction of 300 mg (0.86 mmol) of **10** with ethyl bromoacetate (600 mg, 3.59 mmol) and zinc powder (1.0 g) in benzene/ether (5/1, 20 ml) afforded 343 mg (95%) of **11** as a red oil: IR (neat) 1705 and 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.31 (3H, t, J=7 Hz, CH_3), 1.35—2.65 (20H, m, CH_2), 3.56 and 3.84 (each 1H, an AX system, J=1.5 Hz, 3′- and 5′-H), 3.92 (1H, s, 3-H), 4.19 (2H, q, J=7 Hz, OCH_2), 5.95 and 7.70 (each 1H, an AX system, J=16 Hz, alkene H); MS m/z (rel intensity) 418 (100, M$^+$).

Found: M$^+$ m/z 418.1579. Calcd for $C_{25}H_{30}O_2Fe$: M, 418.1593.

Ethyl [4][3$_2$](1,2,4)Ferrocenophane-5-propionate (12). Hydrogenation of 340 mg (0.81 mmol) of **11** with Pd–C (50 mg) in ethanol gave 345 mg (quant.) of **12** as yellow oil: IR (neat) 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.24 (3H, t, J=7 Hz, CH_3), 1.30—2.80 (24H, m, CH_2), 3.56 and 3.60 (1H and 2H, m, Cp H), 4.09 (2H, q, J=7 Hz, OCH_2); MS m/z (rel intensity) 420 (100, M$^+$).

Found. M$^+$ m/z 420.1753. Calcd for $C_{25}H_{32}O_2Fe$: M, 420.1750.

[4]-α-Oxo[3][3$_2$](1,2,3,5)ferrocenophane (13). Hydrolysis of 330 mg (0.79 mmol) of **12** with 20% aqueous NaOH (25 mL) in ethanol (60 ml) gave propionic acid in a quantitative yield. PPE was prepared by using 25 g of P_2O_5. Reaction of the above propionic acid with PPE in 1,2-dichloroethane (300 ml) for 30 min afforded 240 mg (81%) of **13**: Orange plates, mp 267 °C (decomp) (from ethyl acetate/dichloromethane); IR (KBr) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20—3.65 (24H, m, CH_2), 3.72 (1H, s, 4′-H), 3.84 (1H, s, 4-H); MS m/z (rel intensity) 374 (100, M$^+$).

Found: C, 73.48; H, 7.11%. Calcd for $C_{23}H_{26}OFe$: C, 73.80, H, 7.00%.

[4][3$_3$](1,2,3,5)Ferrocenophane (3). Reduction of 140 mg (0.37 mmol) of **13** with $LiAlH_4$ (200 mg, 5.3 mmol) and $AlCl_3$ (500 mg, 3.8 mmol) in ether/benzene (5/3, 20 ml) gave 135 mg (quant.) of **3**: Yellow needles, mp 278—280 °C (from ethyl acetate/dichloromethane); ^{1}H NMR ($CDCl_3$) δ=1.30—2.45 (26H, m, CH_2), 3.62 (2H, s, Cp H); ^{13}C NMR ($CDCl_3$) δ=19.20, 20.81, 22.03, 27.49, 27.83, 38.41, 38.50 and 39.72 (methylene C), 69.99 (unsubstd. Cp C), 82.42, 84.71, 85.73 and 91.82 (substd. Cp C); MS m/z (rel intensity) 360 (100, M$^+$); vis. absorption spectrum (THF) $\lambda_{\max}$ 365 nm (ε=145).

Found: C, 76.29, H, 7.85%. Calcd for $C_{23}H_{28}Fe$: C, 76.67; H, 7.83%.

α-Oxo[3][3$_2$](1,3,4)ferrocenophane (14). To a greenish suspension of 1.47 g (4.80 mmol) of **1** and excess $AgClO_4$ (7.5 g) in methanol (100 ml) was added dropwise a methanol solution of sodium methoxide which was prepared using 4.5 g of Na and 70 ml of methanol. The mixture was stirred for 14 h at room temperature, and then filtered through a short column of alumina (elution with methanol/ether). After concentration of the filtrate, benzene and water were added. The organic layer was washed with brine, dried with Na_2SO_4, and evaporated. The residue was column-chromatographed on silica gel using benzene/ethyl acetate (10/1) as an eluent. The first band yielded 235 mg (15%) of α-hydroxy[3][3$_2$](1,3,4)ferrocenophane, which was converted into ketone **14** by further oxidation under the above mentioned conditions ($AgClO_4/CH_3ONa$). The second band yielded 831 mg (53%) of **14**, which was identical with the authentic sample of **14** prepared by the Rinehart's procedure.[12)] When Ag_2O was used in the place of $AgClO_4$ in the oxidation, **14** was obtained at a yield of 60% with the recovery (26%) of **1**.

β-Oxo[4][3$_2$](1,3,4)ferrocenophane (15). Bridge enlargement of 420 mg (1.31 mmol) of **14** in methanol (150 ml) with an ether solution of CH_2N_2 (150 ml) afforded 405 mg (93%) of **15**: Yellow prisms, mp 185—187 °C (from ethyl acetate); IR (KBr) 1705 cm^{-1}; ^{1}H NMR (at 500 MHz, $CDCl_3$) δ=1.41, 1.59, 2.08 and 2.19 (4H, 2H, 4H and 2H, each m, CH_2 of 3,3′- and 4,4′-bridges), 2.74 (4H, s, γ- and δ-CH_2 of 1,1′-bridge), 3.14 (2H, s, β-CH_2 of 1,1′-bridge), 4.02 and 4.03 (each 2H, s, Cp H); MS m/z (rel intensity) 334 (100, M$^+$), 306 (73, [M−CO]$^+$).

Found: C, 72.13; H, 6.58%. Calcd for $C_{20}H_{22}OFe$: C, 71.87; H, 6.63%.

[4][3$_2$](1,3,4)Ferrocenophane (16). Reduction of 570 mg (1.71 mmol) of **15** with $LiAlH_4$ (240 mg, 6.32 mmol) and $AlCl_3$ (600 mg, 4.49 mmol) in ether/benzene (5/3, 80 ml) gave 518 mg (95%) of **16**: Yellow plates, mp 138—139 °C (from ethyl acetate); ^{1}H NMR (at 500 MHz, $CDCl_3$) δ=1.43 and 1.62 (4H, and 6H, each m, CH_2 of 3,3′- and 4,4′-bridges), 2.07 and 2.18 (each 4H, m, CH_2 of 1,1′-bridge), 3.90 (4H, s, Cp H); ^{13}C NMR ($CDCl_3$) δ=21.30, 30.27, 31.09 and 36.55 (methylene C), 70.28 (unsubstd. Cp C) 85.73 and 89.34 (substd. Cp C); MS m/z (rel intensity) 320 (100, M$^+$).

Found: C, 75.23; H, 7.55%. Calcd for $C_{20}H_{24}Fe$: C, 75.01; H, 7.55%.

2-Formyl[4][3$_2$](1,3,4)ferrocenophane (17). Formylation of 490 mg (1.53 mmol) of **16** with DMF (500 mg, 6.85 mmol) and $POCl_3$ (750 mg, 4.89 mmol) in chloroform (20 ml) gave 486 mg (91%) of **17**: Orange prisms, mp 130—131 °C (from ethyl acetate); IR (KBr) 1655 cm^{-1}; ^{1}H NMR

($CDCl_3$) δ=1.20—2.90 (20 H, m, CH_2), 3.84 and 4.04 (each 1H, an AX system, J=1.3 Hz, 5′- and 2′-H), 4.22 (1H, s, 5-H), 10.32 (1H, s, CHO); MS m/z (rel intensity) 348 (100, M^+), 319 (11, $[M-CHO]^+$).

Found: C, 72.68; H, 7.03%. Calcd for $C_{21}H_{24}OFe$: C, 72.42; H, 6.95%.

Ethyl [4][3_2](1,3,4)Ferrocenophane-2-acrylate (18). Reaction of 480 mg (1.38 mmol) of **17** in benzene/ether (5/1, 25 ml) with ethyl bromoacetate (600 mg, 3.59 mmol) and zinc (2.0 g) gave 559 mg (97%) of **18** as a red oil: IR (neat) 1710 and 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20—2.70 (20H, m, CH_2), 1.32 (3H, t, J=7 Hz, CH_3), 3.80 (2H, s, 2′- and 5′-H), 4.11 (1H, s, 5-H), 4.20 (2H, q, J=7 Hz, OCH_2), 5.97 and 7.73 (each 1H, an AX system, J=16 Hz, alkene H; MS m/z (rel intensity) 418 (100, M^+), 390 (6, $[M-C_2H_4]^+$), 345 (4, $[M-CO_2Et]^+$).

Found: M^+ m/z 418.1581. Calcd for $C_{25}H_{30}O_2Fe$: M, 418.1593.

Ethyl [4][3_2](1,3,4)Ferrocenophane-2-propionate (19). Hydrogenation of 550 mg (1.32 mmol) of **18** with 10% Pd–C (100 mg) in ethanol afforded 551 mg (quant.) of **19** as a yellow oil: IR (neat) 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.10—2.95 (24H, m, CH_2), 1.24 (3H, t, J=7 Hz, CH_3), 3.59 and 3.87 (each 1H, bs, 5′- and 2′-H), 3.84 (1H, s, 5-H), 4.10 (2H, q, J=7 Hz, OCH_2); MS m/z (rel intensity) 420 (100, M^+).

Found: M^+ m/z 420.1734. Calcd for $C_{25}H_{32}O_2Fe$: M, 420.1749.

[4]-α-Oxo[3][3_2](1,2,3,4)ferrocenophane (20). Compound **19** (550 mg, 1.31 mmol) was hydrolyzed with 20% aqueous NaOH (20 ml) in ethanol (50 ml) followed by treatment with PPE (prepared by using 23 g of P_2O_5) in 1,2-dichloroethane. Column chromatographic isolation yielded 189 mg (39%) of **20**: Yellow plates, mp 236—238 °C (from 1,2-dichloroethane); IR (KBr) 1655 cm^{-1}; ^{1}H NMR (at 500 MHz, $CDCl_3$) δ=1.40, 1.56, 1.71, 2.00, 2.15, 2.24, 2.32, 2.54, 2.70, 2.76, 3.09 and 3.46 (1H, 1H, 2H, 3H, 2H, 3H, 1H, 5H, 2H, 1H, 1H, 1H and 1H, each m, CH_2), 3.75 and 4.01 (each 1H, s, Cp H); ^{13}C NMR (at 125.7 Hz, $CDCl_3$) δ=18.30, 18.67, 20.03, 20.12, 27.07, 28.22, 28.63, 28.66, 29.11, 36.65, 39.04 and 49.30 (methylene C), 70.63 and 75.80 (unsubstd. Cp C), 75.03, 84.76, 85.58, 85.83, 87.36, 88.39, 90.30 and 92.36 (substd. Cp C), 212.30 (carbonyl C); MS m/z (rel intensity) 374 (100, M^+).

Found: C, 72.92; H, 6.67%; M^+ m/z 374.1328. Calcd for $C_{23}H_{26}OFe$: C, 73.80; H, 7.00%; M, 374.1331. Calcd for $C_{23}H_{26}OFe\cdot 1/15C_2H_4Cl_2$: C, 72.94; H, 6.95%.

[4][3_3](1,2,3,4)Ferrocenophane (4). Reduction of 170 mg (0.45 mmol) of **20** with $LiAlH_4$, (300 mg, 7.9 mmol) and $AlCl_3$ (700 mg, 5.2 mmol) in ether/benzene (25 ml) gave 150 mg (93%) of **4**: Yellow plates, mp 227—229 °C (from ethyl acetate/dichloromethane); ^{1}H NMR (at 500 MHz, $CDCl_3$) δ=1.52, 1.54, 1.59, 1.73 and 1.85 (2H, 1H, 5H, 2H and 2H, each m, CH_2), 1.96—2.30 (14H, m, CH_2), 3.84 (2H, s, Cp H); ^{13}C NMR ($CDCl_3$) δ=18.18, 18.96, 20.57, 28.71, 29.10, 36.36, 36.50 and 39.57 (methylene C), 71.64 (unsubstd. Cp C), 83.05, 87.48 and 88.70 (2C, 1C, 1C, substd. Cp C); MS m/z (rel intensity) 360 (100, M^+), 332 (10, $[M-C_2H_4]^+$); vis. absorption spectrum (THF) λ_{max} 414 nm (ε=262).

Found: C, 76.87; H, 7.87%. Calcd for $C_{23}H_{28}Fe$: C, 76.67; H, 7.83%.

5-Formyl[4][3_3](1,2,3,4)ferrocenophane (21). Formylation of 180 mg (0.50 mmol) of **4** with DMF (500 mg, 6.85 mmol) and $POCl_3$ (600 mg, 3.91 mmol) in chloroform (10 ml) gave 180 mg (93%) of **21**: Orange prisms, mp 195—196 °C (from ethyl acetate); IR (KBr) 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20—2.95, (26H, m, CH_2), 4.10 (1H, s, Cp H), 10.27 (1H, s, CHO); MS m/z (rel intensity) 388 (100, M^+).

Found: M^+ m/z 388.1461. Calcd for $C_{24}H_{28}OFe$: M, 388.1487.

Ethyl [4][3_3](1,2,3,4)Ferrocenophane-5-acrylate (22). Reaction of 115 mg (0.30 mmol) of **21** with ethyl bromoacetate (300 mg, 1.80 mmol) and zinc (1.0 g) afforded 99 mg (72%) of **22**: Red plates, mp 160—162 °C (from hexane/ethyl acetate); IR (KBr) 1705 and 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.31, (3H, t, J=7 Hz, CH_3), 1.40—2.60 (26H, m, CH_2), 3.48 (1H, s, Cp H), 4.18 (2H, q, J=7 Hz, OCH_2), 5.92 and 7.73 (each 1H, an AX system, J=15 Hz, alkene H); MS m/z (rel intensity) 458 (100, M^+).

Found: M^+ m/z 458.1878. Calcd for $C_{28}H_{34}O_2Fe$: M, 458.1906.

Ethyl [4][3_3](1,2,3,4)Ferrocenophane-5-propionate (23). Hydrogenation of 140 mg (0.31 mmol) of **22** with 10% Pd–C (100 mg) gave 136 mg (95%) of **23**: Yellow plates, mp 110—111 °C; IR (KBr) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.25 (3H, t, J=7 Hz, CH_3), 1.30—2.80 (28H, m, CH_2), 3.63 (1H, s, Cp H), 4.10 (2H, q, J=7 Hz, OCH_2); MS m/z (rel intensity) 460 (100, M^+).

Found: M^+ m/z 460.2080. Calcd for $C_{28}H_{36}O_2Fe$: M, 460.2063.

[4]-α-Oxo[3][3_2](1,2,3,4,5)ferrocenophane (24). Hydrolysis of 140 mg (0.30 mmol) of **23** with aqueous NaOH in ethanol followed by treatment with PPE (prepared by using 20 g of P_2O_5) afforded 60 mg (48%) of **24**: Orange plates, mp 252—253 °C (from ethyl acetate); IR (KBr) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.65—3.20 (30H, m, CH_2); ^{13}C NMR (at 125.7 MHz, $CDCl_3$) δ=17.54, 17.58, 17.83, 18.09, 18.16, 18.36, 25.80, 26.28, 26.75, 26.91, 27.23, 36.86, 37.19, 39.65 and 52.50 (methylene C), 76.60, 84.06, 86.15, 86.54, 86.84, 87.51, 88.00, 88.12, 88.50 and 89.22 (Cp C), 128.32 (carbonyl C); MS m/z (rel intensity) 414 (100, M^+), 386 (10, $[M-CO]^+$).

Found: M^+ m/z 414.1638. Calcd for $C_{26}H_{30}OFe$: M, 414.1644.

[4][3_4](1,2,3,4,5)Ferrocenophane (5). Reduction of 60 mg (0.14 mmol) of **24** with $LiAlH_4$ (70 mg, 1.8 mmol) and $AlCl_3$ (150 mg, 1.1 mmol) in ether/benzene (10 ml) gave 58 mg (quant.) of **5**: Pale yellow prisms, mp 293—294 °C (from ethyl acetate/dichloromethane); ^{1}H NMR ($CDCl_3$) δ=1.60—2.50 (32H, m, CH_2); ^{13}C NMR (at 125.7 MHz, $CDCl_3$) δ=17.97, 18.62, 26.44, 26.97, 37.24 and 29.71 (methylene C), 83.83, 86.58 and 86.87 (Cp C); MS m/z (rel intensity) 400 (100, M^+); vis. absorption spectrum (THF) λ_{max} 345 nm (ε=158).

Found: C, 78.20; H, 8.47%; M^+ m/z 400.1848. Calcd for $C_{26}H_{32}Fe$: C, 78.00; H, 8.06%; M, 400.1851.

Crystal Structure Determination. The pale-yellow crystal used for diffraction analysis was grown from a dichloromethane solution of **5** by vapor-diffusion of diethyl ether. The crystal was mounted on a Rigaku AFC-5 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å). The cell parameters were determined using a least-squares refinement on each 20 accurately centred reflections.

Crystal Data (5): $C_{26}H_{32}Fe$, M_r=400.39, tetragonal, space group $I\bar{4}2d$, a=14.574(4), c=18.208(4) Å, V=3867(1) Å^3, Z=8, $F(000)$=1712, D_o=1.36, D_x=1.375 Mg m^{-3}, μ(Mo $K\alpha$)=0.80 mm^{-1}.

The intensities were measured by the θ–2θ scan technique at a scan speed of 4 ° min^{-1} in θ. A scan width of $(1.0+0.35\tan\theta)^\circ$ in θ was set with a background counting time of 5 s. Three standard reflections were monitored every 100 reflections. Reflections with $F_o>3\sigma(F_o)$ were considered to be observed. The intensities were corrected for Lorentz and polarization effects, but not for absorption. At the final cycles of the refinement, two reflections, (112) and (200), were omitted for the extinction effect. Summaries of the data collection and processing parameters are given in Table 5.

The structure was solved, and all the non-hydrogen atoms were located by a direct method (MULTAN 84).[35] After several cycles of a block-diagonal least-squares refinement, all of the positional parameters of the H atoms were calculated. In the final cycle of the refinement, the positional parameters of all the atoms and the anisotropic thermal parameters for non-hydrogen atoms were included. Also, the constant isotropic thermal parameter, B=4.0 Å^2, was given for H atoms. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$. Scattering factors with anomalous dispersion of Fe were taken from International Tables for X-Ray Crystallography.[36] Computations were performed using a Panafacom U-1200 IIA with the Rigaku RASA-5P program package system and a HITAC M-680H at the Computer Centre of the University of Tokyo with UNICS program system (local-version).[37]

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Table 5. Summary of Data Collection and Structure Refinement for **5**

Crystal size/mm	0.5×0.5×0.5
Unit cell determination	
2θ range/°	27.67—31.97
Data collection	
2θ range/°	4—60
Index range	
h	0—20
k	0—20
l	0—25
Standard reflections	
Indices	0,10,2; −10,−2,2; 10,−2,2
Fluctuations	± 2% in F
No. of reflections	
Measured	3117
Observed(final)	1317(1315)
Refined parameters	187
Final R	0.051
wR	0.052
S	1.035
Weighting scheme	$[\sigma^2(F)+0.0001\|F_o\|^2]^{-1}$
Maximum and mean Δ/σ	0.43, 0.092
Maximum and	1.0
Minimum $\Delta\rho$/eÅ^3	−0.4

References

1) The nomenclature of the ferrocenophanes in paper published by the authors[2—4] was a modification of that proposed by Vögtle and Neumann.[5] The modified numbering system is also adopted for the compounds mentioned in this paper, because these are closely connected with the ferrocenophanes reported in a series of studies concerning multibridged ferrocenophanes.[2—4,6]

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