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Prismatic and Antiprismatic [4_2]Ferrocenophanes ([4](1,1′)[4](3,3′)- and [4](1,1′)[4](3,4′)Ferrocenophanes)

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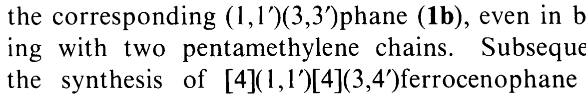
[4](1,1′)[4](3,4′)Ferrocenophane (**2a**), also trivially called antiprismatic [4_2]ferrocenophane, which possesses a C_2 symmetric configuration has been synthesized via intramolecular oxidative coupling of the dienolate ion derived from 3,4′-diacetyl[4](1,1′)ferrocenophane. The antiprismatic phane (**2a**) and the corresponding prismatic [4](1,1′)[4](3,3′)ferrocenophane (**1a**), which is bridged by a C_{2v} symmetric mode, has been characterized by X-ray analysis and ^{1}H NMR and electronic spectrometries. The crystal data of the phanes are as follows: **1a**, orthorhombic, $Pbca$, a=18.469(4), b=19.994(4), c=7.610(2) Å; Z=8; **2a**, triclinic, $P\bar{1}$, a=7.547(1), b=8.540(1), c=5.886(1) Å, α=96.60(1), β=107.10(1), γ=101.71(1)°, Z=1. Antiprismatic phane **2a** has a completely staggered conformation about the two cyclopentadienyl (Cp) rings, while prismatic **1a** has an intermediary conformation of eclipsed and staggered forms. The Cp–Fe–Cp distance of **2a** (3.260 Å) is shorter than that of **1a** (3.275 Å). The hypsochromic shift of the d–d* absorption band of **2a** in the electronic spectrum is more remarkable than that of **1a** (ferrocene, 443 nm; **1a**, 420 nm; **2a**, 403 nm in THF). Those results reveal that an antiprismatic bridging mode with tetramethylene chains brings about a higher strain in the molecule compared with a prismatic one.

A number of ferrocenophanes have been synthesized and their synthetic methods and molecular structures have been discussed.[1–4)] The reaction of ferrocene- or ferrocenophane-propanoic acids with dehydration reagents generally gives heteroannular cyclization products, bridged between the two cyclopentadienyl (Cp) rings, in preference to homoannular ones. Accordingly, the intramolecular electrophilic substitution is the most convenient procedure for the preparation of ferrocenophanes involving multibridged phanes. Dibridged [m_2]ferrocenophanes ($3 \leq m \leq 5$) linked at the 1,3-positions[5–8)] were also prepared via cyclization of [m](1,1′)ferrocenophane-3-propanoic acids. Interestingly, this cyclization yields only 3′-bridged compounds, which are dibridged ferrocenophanes linked at the symmetrical positions of the two Cp rings, but no 4′-bridged one. On the other hand, Astruc et al.[9)] found that two dibridged ferrocenophanes linked with the 1,3-positions of cyclopentane rings were produced by the treatment of ferrocene with $AlCl_3$ under drastic reaction conditions, and that both were (1,1′)(3,3′)-bridged compounds. The introduction of a larger strain into the molecule in a (1,1′)(3,4′)bridging mode, compared with that in the (1,1′)(3,3′)bridging, would result in these reaction behaviors. However, a comparison between (1,1′)(3,3′)- and (1,1′)(3,4′)ferrocenophanes regarding molecular structure has not been made, since there has been no structurally characterized (1,1′)(3,4′)phane. Although a [5_2]ferrocenophane derivative was described by Nesmeyanov et al.[10)] as an example of a (1,1′)(3,4′)-dibridged phane, its configuration has not been ascertained. We recently demonstrated that [5](1,1′)[5](3,4′)ferrocenophane (**2b**) could be prepared via a base-catalyzed intramolecular condensation of 3,4′-diacyl[5](1,1′)ferrocenophane,[11)] and that the (1,1′)(3,4′)phane (**2b**) was more strained in a spectroscopic meaning than the corresponding (1,1′)(3,3′)phane (**1b**), even in bridging with two pentamethylene chains. Subsequently, the synthesis of [4](1,1′)[4](3,4′)ferrocenophane (**2a**) bridged with two tetramethylene chains that should bring about a larger strain to the molecule than with pentamethylene ones was attempted by a condensation method. We obtained the expected dibridged phane, and the molecular structure of **2a** has been characterized by X-ray analysis and spectrometry. Furthermore, the crystal structure of [4](1,1′)[4](3,3′)-ferrocenophane (**1a**)[6,7)] has also been analyzed, and the molecular features of the two phanes are discussed while comparing them.

The isomeric phanes, **1b** and **2b**, were named prismatic and antiprismatic [5_2]ferrocenophanes, respectively, according to a suggestion by Watts[1)] in a previous paper.[11)] The trivial name is also used in this report, that is, **1a** and **2a** are called prismatic and antiprismatic [4_2]ferrocenophanes, respectively.



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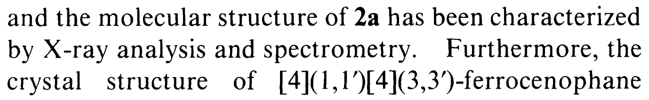

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Results and Discussion

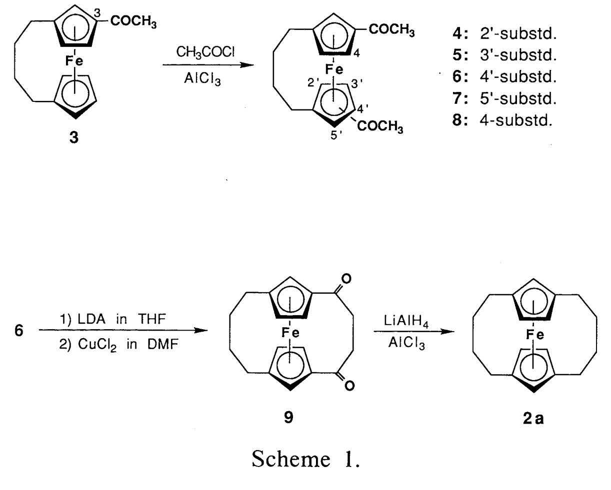
Synthesis of 2a. The acylation of 3-acyl[*m*](1,1′)-ferrocenophanes predominantly yields the corresponding 4′-substituted product.[11,13] On the other hand, Saegusa et al.[12] reported a facile method for constructing a tetracarbon bridge to ferrocene by intramolecular oxidative coupling between two acetyl groups on the Cp rings. Therefore, 3,4′-diacetyl[4]ferrocenophane (**6**) was first prepared and the application of Saegusa's procedure to **6** was examined to form the second (3,4′)bridge.

The preparation of **6** was carried out by acetylation of 3-acetyl[4]ferrocenophane (**3**)[14] with acetyl chloride and aluminum chloride. Four isomeric diacetyl compounds were produced in the reaction; the *β*′-acetylated product (**5** or **6**) (43%) was easily distinguishable from the other isomers (**4**, 12%; **7**, 21%; **8**, 2%) on the basis of the appearance of a triplet signal (δ=4.68) with a meta coupling constant (J=1.3 Hz) of the Cp rings in the ^{1}H NMR spectrum. The spectra of *α*′- (**4** and **7**) and 4-acetyl (**8**) compounds showed a triplet signal with an ortho coupling constant (J=2.7 Hz) and a singlet signal, respectively, in the region of the Cp ring protons (δ= 4—5).

3,4′-Diacetyl configuration of the *β*′-acyl compound had been predicted, since the 3′-position of 3-acylferrocenophanes is generally scarcely acetylated,[11,13] though this prediction alone is insufficient to establish the configuration. In a previous report,[11] the antiprismatic structure of [5$_2$]ferrocenophane-1,5-dione was evidenced by a measurement of the ^{1}H NMR spectrum in the presence of a chiral shift reagent. This technique was applied to determine the substitution mode of the *β*′-acyl compound. The desired 3,4′-diacetyl[4]ferrocenophane (**6**) is a racemic mixture of two chiral compounds, while the corresponding isomeric 3,3′-diacetyl phane (**5**) ia a *meso* compound possessing a symmetric plane through the central iron atom. Accordingly, each proton signal of the former in the ^{1}H NMR spectrum in the presence of a chiral shift reagent should split into two signals, but that of the latter does not. The actual spectrum of the *β*′-acyl compound in CDCl$_3$ containing Eu(tfmc),[15] a chiral shift reagent, showed splittings of the signals due to diastereomeric interactions between a pair of enantiomers and the reagent. It is thus estimated that the *β*′-acyl product is 3,4′-diacetylferrocenophane (**6**), as previously predicted. No isomeric diacyl compound **5** was produced in that acetylation.

The treatment of **6** with lithium diisopropylamide (LDA) followed by oxidation with CuCl$_2$, according to a procedure by Saegusa et al.,[12] gave the expected dibridged diketone **9** in low yield (14%). Antiprismatic [4$_2$]ferrocenophane (**2a**) was obtained by the reduction of **9**. The spectra and the melting point of **2a** (mp 153—154 °C) were different from those of prismatic [4$_2$]ferrocenophane (**1a**) (mp 117 °C[7]), which was previously synthesized and characterized. The ^{1}H and ^{13}C NMR spectra of **2a** showed a set of AX$_2$ system signals of the Cp ring protons at δ=3.89 (2H, t) and 4.07 (4H, d) [**1a**: δ=3.97 (4H, d) and 4.05 (2H, t)], and three carbon signals of the Cp rings at δ=67.94, 70.22 and 86.33 [**1a**: δ=67.60, 68.77 and 87.13], respectively.

Molecular Structures of 1a and 2a. The X-ray structure analyses of the phanes, antiprismatic [4$_2$]ferrocenophane (**2a**) as well as prismatic phane **1a**, were carried out in order to examine the influence of their



Scheme 1.

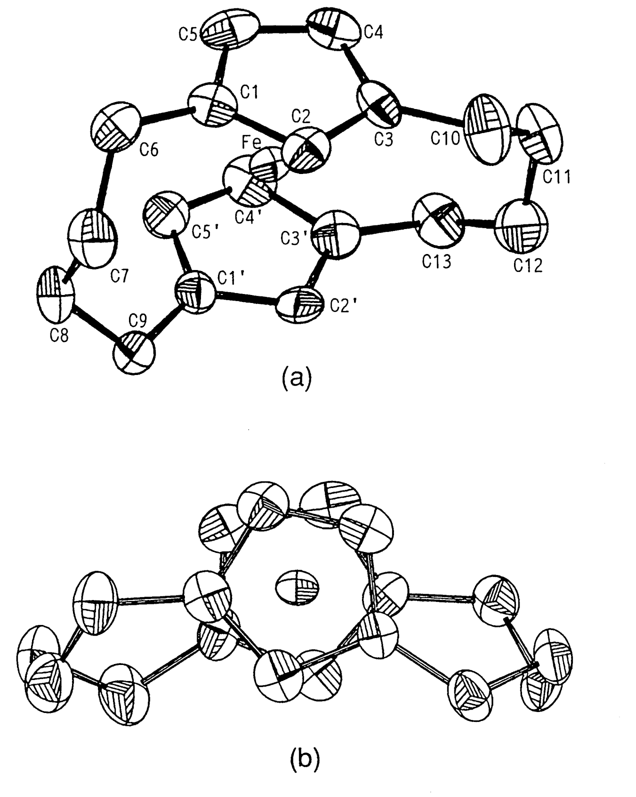


Fig. 1. ORTEP drawing of **1a** with thermal ellipsoids at the 50% probability level. H atoms are excluded for clarity. A perspective view and atomic numbering scheme in (a), and a projection of a whole molecule onto the Cp plane (b).

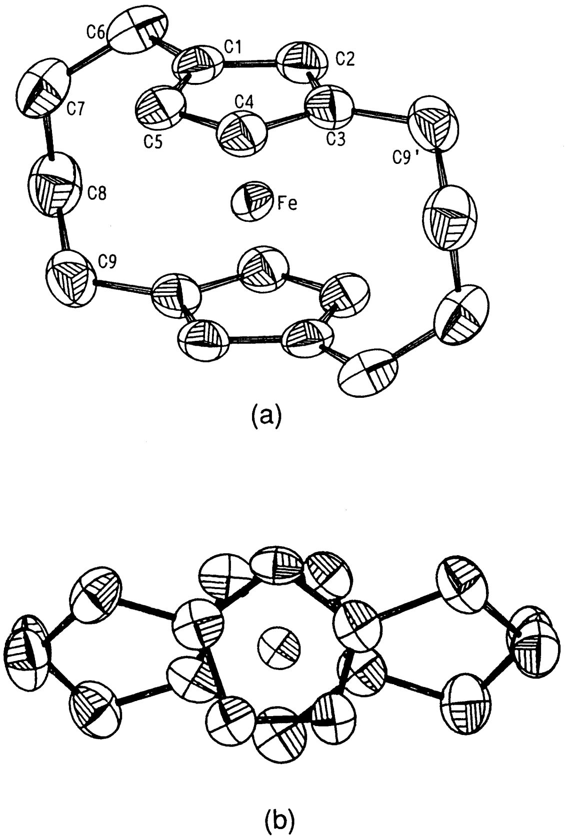


Fig. 2. ORTEP drawing of **2a** with thermal ellipsoids at the 50% probability level. H atoms are excluded for clarity. A perspective view and atomic numbering scheme in (a), and a projection of a whole molecule onto the Cp plane (b).

bridging mode on the molecular structure. Perspective views of both molecules are shown in Figs. 1 and 2 by ORTEP drawing with their atomic numbering scheme.[16] The Fe atom of **2a** occupies the center of symmetry in the crystal lattice, as opposed to **1a** which possesses no crystallographical symmetry in the molecule. As shown in Tables 1 and 2, the bond lengths and angles of both phanes are in the normal ranges, compared with other multibridged ferrocenophanes.[4,17]

Each of the Cp rings shows good planarity, as described by the least-squares plane calculations provided in Table 3. Since the **2a** molecule possesses a center of symmetry, as stated above, the two Cp rings are completely parallel and are exactly staggered in relation to each other [see Fig. 2(b)]. Moreover, since the bond lengths of C(1)–C(6) and C(3′)–C(9) [same as C(3)–(9′)] are equal within esd's, the entired molecule of **2a** is almost in a C_2 symmetric conformation, even in the crystalline state. On the other hand, the observed structure of **1a** largely deviates from a prismatic (eclipsed) form that is presumably expected due to its C_{2v} bridging mode. The two Cp rings of **1a** are rotated

Table 2. Selected Bond Angles (in Degree) of **1a** and **2a** with Estimated Standard Deviations in Parentheses

	Bond	Angle	Bond	Angle
1a	C(5)–C(1)–C(2)	106.0(4)	C(6)–C(7)–C(8)	116.9(5)
	C(1)–C(2)–C(3)	110.1(4)	C(7)–C(8)–C(9)	117.3(5)
	C(2)–C(3)–C(4)	105.7(4)	C(8)–C(9)–C(1′)	117.1(5)
	C(3)–C(4)–C(5)	109.1(5)	C(9)–C(1′)–C(2′)	125.2(4)
	C(4)–C(5)–C(1)	109.0(5)	C(9)–C(1′)–C(5′)	124.9(5)
	C(5′)–C(1′)–C(2′)	107.9(5)	C(2)–C(3)–C(10)	125.5(4)
	C(1′)–C(2′)–C(3′)	108.7(4)	C(4)–C(3)–C(10)	128.7(5)
	C(2′)–C(3′)–C(4′)	106.9(4)	C(3)–C(10)–C(11)	115.3(5)
	C(3′)–C(4′)–C(5′)	108.9(5)	C(10)–C(11)–C(12)	116.9(5)
	C(4′)–C(5′)–C(1′)	107.7(5)	C(11)–C(12)–C(13)	116.3(5)
	C(2)–C(1)–C(6)	128.9(5)	C(12)–C(13)–C(3′)	115.7(5)
	C(5)–C(1)–C(6)	125.1(5)	C(13)–C(3′)–C(2′)	127.8(5)
	C(1)–C(6)–C(7)	117.0(5)	C(13)–C(3′)–C(4′)	125.2(5)
2a	C(5)–C(1)–C(2)	107.5(2)	C(1)–C(6)–C(7)	116.2(2)
	C(1)–C(2)–C(3)	108.6(2)	C(6)–C(7)–C(8)	117.7(3)
	C(2)–C(3)–C(4)	107.5(2)	C(7)–C(8)–C(9)	117.8(3)
	C(3)–C(4)–C(5)	108.5(2)	C(8)–C(9)–C(3′)	116.0(2)
	C(4)–C(5)–C(1)	107.8(2)	C(2)–C(3)–C(9′)	126.5(2)
	C(2)–C(1)–C(6)	126.5(2)	C(4)–C(3)–C(9′)	126.0(2)
	C(5)–C(1)–C(6)	126.0(2)		

Table 1. Bond Lengths (in Å) between the Heavier Atoms of **1a** and **2a** with Estimated Standard Deviations in Parentheses

	Bond	Length	Bond	Length	Bond	Length
1a	Fe–C(1)	2.033(5)	C(1)–C(2)	1.422(7)	C(1)–C(6)	1.496(8)
	Fe–C(2)	2.032(5)	C(2)–C(3)	1.435(7)	C(6)–C(7)	1.518(9)
	Fe–C(3)	2.038(5)	C(3)–C(4)	1.429(7)	C(7)–C(8)	1.534(9)
	Fe–C(4)	2.037(5)	C(4)–C(5)	1.407(7)	C(8)–C(9)	1.524(9)
	Fe–C(5)	2.036(5)	C(5)–C(1)	1.431(7)	C(9)–C(1′)	1.507(8)
	Fe–C(1′)	2.035(5)	C(1′)–C(2′)	1.428(7)	C(3)–C(10)	1.508(8)
	Fe–C(2′)	2.037(5)	C(2′)–C(3′)	1.423(7)	C(10)–C(11)	1.533(9)
	Fe–C(3′)	2.039(5)	C(3′)–C(4′)	1.422(8)	C(11)–C(12)	1.529(8)
	Fe–C(4′)	2.038(6)	C(4′)–C(5′)	1.425(8)	C(12)–C(13)	1.545(8)
	Fe–C(5′)	2.040(5)	C(5′)–C(1′)	1.415(8)	C(13)–C(3′)	1.496(7)
2a	Fe–C(1)	2.018(2)	C(1)–C(2)	1.426(3)	C(1)–C(6)	1.511(4)
	Fe–C(2)	2.021(2)	C(2)–C(3)	1.427(3)	C(6)–C(7)	1.537(4)
	Fe–C(3)	2.027(2)	C(3)–C(4)	1.410(3)	C(7)–C(8)	1.543(4)
	Fe–C(4)	2.041(2)	C(4)–C(5)	1.436(3)	C(8)–C(9)	1.527(4)
	Fe–C(5)	2.045(2)	C(5)–C(1)	1.420(3)	C(9)–C(3′)	1.513(4)

Table 3. Least-Squares Planes through the Cp Rings and Deviations of Atoms (in Å) from the Planes

1a: Plane 1					
$-0.32366X+0.61294Y+0.72080Z+0.51741=0$					
C(1)	−0.016	C(2)	0.013	C(3)	−0.008
C(4)	0.007	C(5)	0.005		
C(6)*	−0.012	C(10)*	0.027	Fe*	−1.635
Plane 2					
$-0.33216X+0.60202Y+0.72612Z+3.91399=0$					
C(1′)	0.003	C(2′)	−0.006	C(3′)	0.007
C(4′)	−0.004	C(5′)	0.001		
C(9)*	−0.035	C(13)*	−0.012	Fe*	1.640
Dihedral angle of Plane 1 and Plane 2: 0.85°					
2a: Plane 3					
$0.73219X-0.57204Y+0.36968Z+1.62981=0$					
C(1)	0.011	C(2)	−0.011	C(3)	0.007
C(4)	−0.001	C(5)	−0.006		
C(6)*	0.063	C(9)*	0.062	Fe*	1.630

X, Y, and Z are orthogonal coordinates (in Å) given by the following equation:

$$\begin{pmatrix}X\\Y\\Z\end{pmatrix}=\begin{pmatrix}a & b\cos\gamma & c\cos\beta\\ 0 & b\sin\gamma & -c\sin\beta\cos\alpha^*\\ 0 & 0 & c\sin\beta\sin\alpha^*\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix}$$

The atoms marked with asterisks were excluded for the least-squares plane calculation.

by ca. 26° about each other, as shown in Fig. 1(b). The rotational angle is large, even when compared with ferrocene (12°).[18] This additional rotation of **1a** may be caused by a situation in which the two tetramethylene chains are slightly too long to link between the symmetric position of the two Cp rings. The two Cp rings of **1a** are almost parallel (dihedral angle, 0.85°).

The Cp–Fe–Cp distance of **2a** is shorter (3.260 Å) than that of **1a** (3.275 Å; ferrocene, 3.304 Å[18]). Compression between the two Cp rings in ferrocenophanes generally reflects the magnitude of strain which is brought about by bridging with short chains or multilinking.[3,4] Furthermore, all of the α-carbon atoms (6- and 9-carbons) of the bridge head in **2a** fairly deviate from the least-squares planes of the Cp rings in the direction of the Fe atom (ca. 0.06 Å), while the deviations of the α-carbons in **1a** are inconsistent. These results reveal that antiprismatic dibridging of ferrocene with the tetramethylene chains results in strong tension to the entired molecule, compared with prismatic linking. This molecular feature was supported by an inspection with a molecular model and ^{1}H NMR spectrometry. The construction of molecules of **2a** using a Dreiding molecular model is possible only in a C_2 symmetric conformation that is similar to the X-ray crystal structure. The conformation is rigid; the deformation of the zigzag form of the methylene chains is difficult without a cleavage of the model. The structure of **1a** is more relaxed than that of **2a**, and the conformation of the methylene chains can be changed with a slight deformation of the ferrocene moiety.

The ^{1}H NMR spectral behaviors of the two phanes reflect the charasterics of their structures. The methylene proton signals of **2a** appear as four sharp peaks having fine structures at δ=1.61, 2.00, 2.22, and 2.81. The signal patterns in pyridine-d_5 were almost unchanged, even at 160 °C. The methylene signals of **1a** at room temperature comprise two broad peaks at δ=1.77 ($W_{h/2}$=14.5 Hz) and 2.39 ($W_{h/2}$=12.5 Hz), in contrast with those of **2a**. This spectrum would indicate conformational thermal motions of the methylene bridges of **1a** at a moderately fast rate on the ^{1}H NMR time scale at room temperature.

In the visible absorption spectrum of **2a** in THF, the band assigned to the d–d* transition of the iron (ferrocene: 443 nm[19]) shows a pronouncedly hypsochromic shift (403 nm), compared with that of **1a** (420 nm). We have found a linear relationship between the hypsochromic shifts of the d–d* absorption and a shortening of the Cp–Fe–Cp distance in multibridged ferrocenophanes.[3,4,19] This correlation also holds for the two phanes under consideration. A compression of the bond between the Cp rings and metal in metallocene causes an elevation of the LUMO (e_{1g}*)[20] and consequently results in a hypsochromic shift of the d–d* absorption.

The existence of (1,1′)(3,4′)phanes was suggested by Schlögl and Seiler[21] but has not been evidenced thus far. By the present work, the molecular structure of one of (1,1′)(3,4′)phanes has first been confirmed, and it has been revealed that (1,1′)(3,4′)phane is more strained than that of the corresponding (1,1′)(3,3′)phane. This conclusion gives a suggestion for reasoning the behavior in cyclization of [*m*](1,1′)ferrocenophane-3-propanoic acids, although **2a** has not the same chemical structure as the product in the cyclization. (1,1′)(3,4′)Bridging mode may introduce a remarkably larger strain into the molecule compared with (1,1′)(3,3′)bridging so that the reaction gives no 4′-bridged product.

Experimental

Melting points were uncorrected. IR spectra were measured by using a Hitachi 215 grating infrared spectrometer. NMR spectra were measured on a JEOL JNM-GSX500 spectrometer relative to tetramethylsilane as an internal standard. Mass spectra were obtained with a Hitachi M-80 double-focusing mass spectrometer by electron impact (EI) ionizing technique at 70 eV. High-resolution mass spectra were analyzed on a Hitachi M-003 data processing system. Electronic spectra were recorded on a Hitachi 323 spectrophotometer in THF.

3,4′-Diacetyl[4](1,1′)ferrocenophane (6). Acetyl chloride (1.10 g, 14.0 mmol) was added dropwise to a suspension of **3** (3.25 g, 11.5 mmol) and $AlCl_3$ (3.87 g, 29.0 mmol) in dichloromethane (150 ml) under N_2 atmosphere. The reaction mixture was stirred at room temperature for 2 h, and then ice-water containing ascorbic acid was added. The hydrolyzate was extracted with dichloromethane, and the extracts were washed with saturated aq Na_2CO_3 and saturated aq NaCl, dried over $CaCl_2$ and evaporated. The residue was column-chromatographed over silica gel with hexane/ethyl acetate

(10/1—3/1) to be separated into many bands. The third band yielded 3,4-diacetyl[4](1,1′)ferrocenophane (**8**) (0.088 g, 2%), which was recrystallized from hexane/ethyl acetate to give reddish orange plates; mp 91.5—93 °C. IR (KBr) 1660, 1640 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.82, 1.90, 2.37, and 2.54 (each 2H, m, -CH$_2$-), 2.50 (6H, s, -COCH$_3$), 4.17 and 4.25 (each 2H, AA′XX′ system, 2′-, 3′-, 4′-, and 5′-H of Cp), 4.88 (2H, s, 2- and 5-H of Cp).

Found: C, 66.73; H, 6.26%. Calcd for $C_{18}H_{20}O_2Fe$: C, 66.69; H, 6.22%.

The fourth band yielded 3,5′-diacetyl[4](1,1′)ferrocenophane (**7**) (0.771 g, 21%), which was recrystallized from hexane/ethyl acetate to give reddish orange plates; mp 101—102 °C. IR (KBr) 1655 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.82, 1.93, 2.10, 2.34, 2.45, and 3.22 (2H, 1H, 1H, 1H, 2H, and 1H, each m, -CH$_2$-), 2.31 and 2.37 (each 3H, s, -COCH$_3$), 4.37 and 4.40 (2H and 1H, each m, 5-, 2′-, and 4′-H of Cp), 4.48 (1H, t, *J*=2.7 Hz, 3′-H of Cp), 4.56 (1H, t, *J*=1.4 Hz, 2-H of Cp), 4.64 (1H, dd, *J*=1.4, 2.6 Hz, 4-H of Cp).

Found: C, 66.56; H, 6.22%. Calcd for $C_{18}H_{20}O_2Fe$: C, 66.69; H, 6.22%.

The fifth band yielded 3,2′-diacetyl[4](1,1′)ferrocenophane (**4**) (0.444 g, 12%), which was recrystallized from hexane/ethyl acetate to give reddish orange plates; mp 111—111.5 °C. IR (KBr) 1660 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.90, 1.97, 2.38, 2.45, and 3.13 (3H, 1H, 1H, 2H, and 1H, each m, -CH$_2$-), 2.36 and 2.43 (each 3H, s, -COCH$_3$), 4.14 (1H, t, *J*=2.7 Hz, 4′-H of Cp), 4.22 (1H, dd, *J*=1.5, 2.7 Hz, 5′-H of Cp), 4.63 (1H, t, *J*=1.4 Hz, 2-H of Cp), 4.68 (1H, dd, *J*=1.4, 2.5 Hz, 5-H of Cp), 4.70 (1H, dd, *J*=1.5, 2.7 Hz, 3′-H of Cp), 4.79 (1H, dd, *J*=1.4, 2.5 Hz, 4-H of Cp).

Found: C, 66.63; H, 6.28%. Calcd for $C_{28}H_{20}O_2Fe$: C, 66.69; H, 6.22%.

The sixth band yielded 3,4′-diacetyl[4](1,1′)ferrocenophane (**6**) (1.62 g, 43%), which was recrystallized from hexane/ethyl acetate to give reddish orange plates; mp 119—120 °C. IR (KBr) 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.87 and 2.47 (each 4H, m, -CH$_2$-), 2.36 (6H, s, -COCH$_3$), 4.46 (2H, dd, *J*=1.3, 2.6 Hz, 5- and 2′-H of Cp), 4.53 (2H, dd, *J*=1.3, 2.6 Hz, 4- and 3′-H of Cp), 4.68 (2H, t, *J*=1.3 Hz, 2- and 5′-H of Cp).

Found: C, 66.52; H, 6.22%. Calcd for $C_{18}H_{20}O_2Fe$: C, 66.69; H, 6.22%.

[4](1,1′)[4](3,4′)Ferrocenophane-1,4-dione (9). LDA in THF (6 ml) was prepared from diisopropylamine (2.00 ml, 14.1 mmol) and butyllithium in hexane (1.6 M concn, 8.90 ml, 14.1 mmol) according to the usual procedure. To the LDA solution was added dropwise a solution of 3,4′-diacetyl[4]ferrocenophane (**6**) (2.00 g, 6.21 mmol) in THF (90 ml) at −78 °C under argon atmosphere. The resulting reaction mixture was stirred at −78 °C for 30 min, and then a solution of well-dried anhydrous CuCl$_2$ (3.10 g, 22.4 mmol) in DMF (90 ml), which was previously cooled to −78 °C, was added all at once. After being stirred at −78 °C, the mixture was quenched with water and extracted with dichloromethane. The extracts were washed with 3% HCl and saturated aq NaCl, dried over CaCl$_2$ and evaporated. Column chromatographic separation of the residue over silica gel with hexane/ethyl acetate (10/1—3/1) gave a number of eluted band. The sixth band eluted with hexane/ethyl acetate (3/1) yielded the desired diketone **9**. The lastly eluted portion of the band was purified on thin-layer chromatography over silica gel, because the part was contaminated with the following eluted band, the starting material (**6**). The combined diketone **9** (0.271 g, 14%) was recrystallized from ethyl acetate to give orange-yellow needles; mp 257—259 °C. IR (KBr) 1685 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.53, 2.02, 2.20, and 2.74 (each 2H, m, -CH$_2$- of 1,1′-bridge), 2.53 and 3.35 (each 2H, AA′XX′ system, -CH$_2$- of 3,4′-bridge), 4.62 (2H, dd, *J*=1.5, 2.7 Hz, 4- and 3′-H of Cp), 4.77 (2H, t, *J*=1.5 Hz, 2- and 5′-H of Cp), 4.84 (2H, dd, *J*=1.5, 2.7 Hz, 5- and 2′-H of Cp); ^{13}C NMR (CDCl$_3$) δ=27.62, 31.35, and 38.14 (-CH$_2$-), 70.86, 75.75, 76.22, 78.42, and 93.27 (Cp-C), 203.82 (C=O); MS *m/z* 322 (M$^+$).

Found: C, 66.93; H, 5.70%. Calcd for $C_{18}H_{18}O_2Fe$: C, 67.10; H, 5.63%.

[4](1,1′)[4](3,4′)Ferrocenophane (2a). Diketone **9** (0.200 g, 6.21 mmol) in ether (60 ml) was added dropwise to a suspension of LiAlH$_4$ (0.140 g, 3.70 mmol) and AlCl$_3$ (0.830 g, 6.20 mmol) in ether (60 ml). The mixture was stirred at room temperature under argon atmosphere for 2 h. After the reagents was decomposed with wet ether, the product was extracted with ether. The extracts were washed with saturated aq NaCl, dried over Na$_2$SO$_4$ and evaporated. The residue was eluted through a short column of silica gel with benzene to yield [4$_2$]ferrocenophane **2a** (0.148 g, 81%), which was recrystallized from ethyl acetate to give yellow plates; mp 153—154 °C. ^{1}H NMR (CDCl$_3$) δ=1.61, 2.00, 2.22, and 2.81 (each 4H, m, -CH$_2$-), 3.89 (2H, t, *J*=1.5 Hz, 2- and 5-H of Cp), 4.07 (4H, d, *J*=1.5 Hz, 4-, 5-, 2′-, and 3′-H of Cp); ^{13}C NMR (CDCl$_3$) δ=28.45 and 31.67 (-CH$_2$-), 67.94, 70.22, and 86.33 (Cp-C); λ_{max} (THF) 403 nm (ε=121).

Found: C, 73.40; H, 7.57%; *m/z* 294.1075. Calcd for $C_{18}H_{22}Fe$: C, 73.48; H, 7.54%; M$^+$, 294.1070.

Spectra of [4](1,1′)[4](3,3′)Ferrocenophane (1a). The NMR and electronic spectra of **1a** (mp 117 °C)[7] were also measured on the same instruments in order to compare with those of **2a**. ^{1}H NMR (CDCl$_3$) δ=1.77 and 2.39 (each 8H, m, -CH$_2$-), 3.97 (4H, d, *J*=1.5 Hz, 4-, 5-, 4′-, and 5′-H of Cp), 4.05 (2H, t, *J*=1.5 Hz, 2- and 2′-H of Cp); ^{13}C NMR (CDCl$_3$) δ=27.49 and 30.27 (-CH$_2$-), 67.60, 68.77, and 87.13 (Cp-C); λ_{max} (THF) 420 nm (ε=106).

Crystal Structure Determination. The crystals were mounted on a Rigaku AFC-5 diffractometer using a graphite-monochromatized Mo *K*α radiation (λ=0.71073 Å). Cell parameters were determined using least-squares refinement on each 20 accurately centered reflections.

Crystal Data (**1a**): $C_{18}H_{22}Fe$, M_r=294.20, orthorhombic, space group *Pbca*, a=18.469(4), b=19.994(4), c=7.610(2) Å, V=2810(1) Å^3, Z=8, F(000)=1248, D_x=1.391 Mg m^{-3}, μ(Mo *K*α)=1.09 mm^{-1}. (**2a**): $C_{18}H_{22}Fe$, M_r=294.20, triclinic, space group $P\bar{1}$, a=7.547(1), b=8.540(1), c=5.886(1) Å, α=96.60(1), β=107.10(1), γ=101.71(1)°, V=348.8(1) Å^3, Z=1, F(000)=156, D_x=1.401 Mg m^{-3}, μ(Mo *K*α)=1.09 mm^{-1}.

Intensities were measured with θ-2θ scan technique and scan speed 4° min^{-1} in θ. Scan width of $(1.0+0.35 \tan\theta)°$ in θ was set with background counting time of 5 s. Three standard reflections were monitored every 100 reflections. Observation range was adopted as $2\theta<60°$. Reflections with $F_o \geq 3\sigma(F_o)$ were considered to be observed. Intensities were corrected for Lorentz and polarization effect, but not for absorption. At the final cycles of the refinement, four reflections, (040), (200), (210), and (600) for **1a**, and three reflections, (001), $(1\bar{1}\bar{1})$, and $(10\bar{1})$ for **2a**, were omitted for the extinction effect. Summary of data collection and processing parameters are given in Table 4.

The structure was solved and all the non-H atoms were located by the direct method (MULTAN84).[22] After several

Table 4. Summary of Data Collection and Structure Refinement for **1a** and **2a**

	1a	**2a**
Crystal size (mm)	0.45×0.40×0.15	0.50×0.40×0.25
Unit cell determination		
2θ range/°	25.64—30.44	28.49—31.49
Data collection		
2θ range/°	4—60	4—60
Index range		
h	0—26	−10—10
k	0—28	−12—12
l	0—11	0—8
Standard reflections		
Indices	0, 14, 0; $\bar{8}$, 11, 0; 8, 11, 0	$\bar{4}$, $\bar{2}$, 0; 4, 1, 1; $\bar{4}$, $\bar{3}$, 1
Fluctuations	±2% in F	±1% in F
No. of reflections		
Measured	4621	2229
Observed (final)	2313 (2309)	1961 (1958)
Refined parameters	238	121
Final R	0.080	0.050
wR	0.063	0.035
S	1.576	0.506
Weighting scheme	$[\sigma^2(F)+0.0004\|F_o\|^2]^{-1}$	$[\sigma^2(F)]^{-1}$
Maximum and mean Δ/σ	0.31, 0.032	0.22, 0.03
Maximum and minimum $\Delta\rho$/eÅ^3	0.7 −0.7	1.5 −0.9

Table 5. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms of **1a** and **2a**, with esd's in Parentheses

$$B_{eq}=4/3\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$$

		x	y	z	B_{eq}
1a	Fe	0.65749(3)	0.10357(3)	0.09276(8)	2.31(1)
	C1	0.6916(3)	0.1602(2)	0.2986(7)	3.2(1)
	C2	0.6545(3)	0.2004(2)	0.1735(7)	3.1(1)
	C3	0.5825(2)	0.1754(2)	0.1471(6)	2.7(1)
	C4	0.5750(3)	0.1202(2)	0.2650(7)	3.4(1)
	C5	0.6405(3)	0.1111(3)	0.3564(6)	3.7(1)
	C1′	0.7454(3)	0.0815(3)	−0.0577(6)	3.1(1)
	C2′	0.6855(3)	0.0999(2)	−0.1660(6)	3.1(1)
	C3′	0.6271(3)	0.0554(2)	−0.1316(6)	2.8(1)
	C4′	0.6520(3)	0.0087(2)	−0.0042(7)	3.4(1)
	C5′	0.7247(3)	0.0249(2)	0.0421(7)	3.5(2)
	C6	0.7673(3)	0.1672(3)	0.3661(7)	4.3(2)
	C7	0.8255(3)	0.1845(3)	0.2327(9)	4.7(2)
	C8	0.8543(3)	0.1270(3)	0.1191(8)	4.7(2)
	C9	0.8181(3)	0.1157(3)	−0.0584(7)	4.8(2)
	C10	0.5267(3)	0.2054(2)	0.0257(8)	3.6(2)
	C11	0.4820(3)	0.1548(3)	−0.0799(8)	4.2(2)
	C12	0.5182(3)	0.1240(3)	−0.2414(8)	4.2(2)
	C13	0.5538(3)	0.0548(3)	−0.2151(7)	3.7(2)
2a	Fe	0.0	0.0	0.0	2.79(1)
	C1	−0.0352(3)	0.2108(3)	−0.1081(4)	3.47(7)
	C2	−0.1393(3)	0.0757(3)	−0.2999(4)	3.58(8)
	C3	−0.2719(3)	−0.0305(3)	−0.2214(4)	3.44(7)
	C4	−0.2539(3)	0.0410(3)	0.0151(4)	3.43(7)
	C5	−0.1082(3)	0.1911(3)	0.0862(4)	3.49(8)
	C6	0.1255(3)	0.3488(3)	−0.1086(5)	4.65(9)
	C7	0.2858(4)	0.4183(3)	0.1347(5)	5.22(10)
	C8	0.4402(3)	0.3236(3)	0.2141(5)	5.17(10)
	C9	0.4042(3)	0.1925(3)	0.3626(5)	4.68(9)

cycles of block-diagonal least-squares refinement, all the positional parameters of H atoms (except for 5 atoms of **1a**, which were located on the D map) were calculated. In the final cycle of the refinement, the positional parameters of all the atoms and anisotropic thermal parameters for non-H atoms were included. And 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.[23] 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 Center of the University of Tokyo with UNICS program system (local-version).[24] The positional parameters and equivalent thermal parameters of non-H atoms of **1a** and **2a** are listed in Table 5.[25]

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25) Lists of anisotropic thermal parameters, H-atom parameters, and observed and calculated structure factors have been deposited as Document No. 9044 at the Office of the Editor of Bull. Chem. Soc. Jpn.