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[2]Metacyclo- and [2]Paracyclo[2](1,3)ferrocenophanes[1)]

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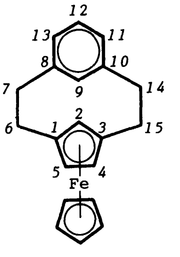
[2]Metacyclo- and [2]paracyclo[2](1,3)ferrocenophanes (**1** and **2**) have been synthesized and characterized by means of X-ray diffraction and spectroscopy. The crystal data of the phanes were determined as follows: **1**, monoclinic, $P2_1$, a=8.851(4), b=15.742(8), c=5.963(3) Å, β=109.76(5)°, Z=2; **2**, orthorhombic, $Pbca$, a=15.308(8), b=24.716(12), c=8.034(4) Å, Z=8. The benzene rings of the both phanes are distorted in a similar manner to [2.2]cyclophanes but the planarities of the cyclopentadienyl (Cp) rings are maintained. The distance between the substituted Cp ring and the iron atom in **1** is considerably extended (1.678(4) Å) in comparison with ferrocene, whereas that of **2** (1.659(3) Å) is not. The 2-hydrogen of the Cp ring and the 9-hydrogen of the benzene ring in **1** are situated right above each other's rings. In the ^{1}H NMR spectrum of **1**, the 2- and 9-protons shifted to highfield to a considerable extent (δ 1.18 and 5.34, respectively) due to the diamagnetic anisotropic effects of the benzene and Cp rings. The electronic spectra of both phanes exhibited bathochromic shifts of the d-d absorption band of the iron (**1**, 451 nm, **2**, 447 nm) as compared to [3]metacyclo- and [3]paracyclo[3](1,3)ferrocenophanes (each 442 nm), which were synthesized as reference compounds in this work.

Benzenoid metal π-complexes of cyclophanes have been investigated by many groups in recent years.[2)] On the other hand, there are few reports[3,4)] on intermolecularly bridged (1,3)ferrocenophanes which are ferrocene analogues of the cyclophane π-complexes, although a great number of intramolecular ferrocenophanes and intermolecular (1,1′)ferrocenophanes have been synthesized[5)] since the discovery of ferrocene. One of the reasons why (1,3)ferrocenophanes could not be synthesized until recently would be the difficulty of preparing 1,3-disubstituted ferrocenes, a precursor of the phanes. Since the method obtaining 1,3-disubstituted ferrocene derivatives on a preparative scale was established,[3,4)] it became feasible to synthesize various (1,3)ferrocenophanes by means of conventional methods well-known in preparation of cyclophanes. Incorporation of η^5-C_5H_5 (cyclopentadienyl: Cp) π-complex into [2.2]phane structure is interesting in that it would lead to a more strained system than benzenoid π-complexes. Furthermore, such phanes would enable NMR spectral observation of diamagnetic anisotropy in the upper zone of Cp ring. In this paper we report on the synthesis and characterization of [2]metacyclo- and [2]paracyclo[2](1,3)ferrocenophanes (**1** and **2**),[6,7)] which are the first examples of [2.2](1,3)ferrocenophanes. [3]Metacyclo- and [3]paracyclo[3](1,3)ferrocenophanes (**11a** and **11b**) prepared as reference compounds in spectroscopic study are also described.



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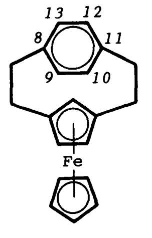
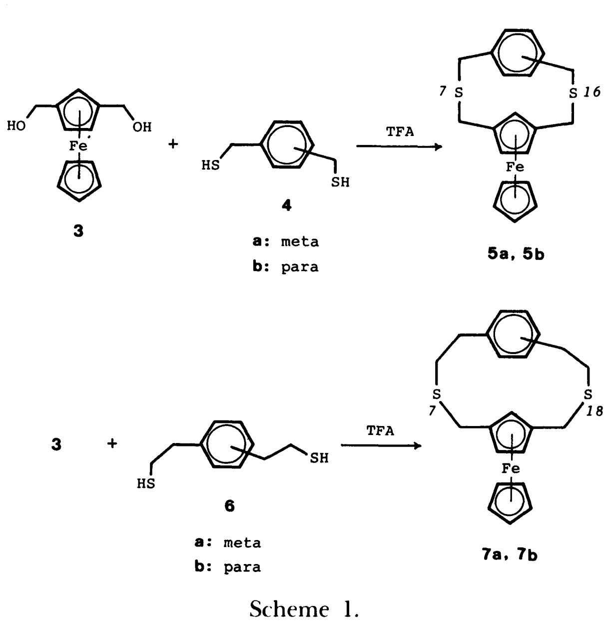


2

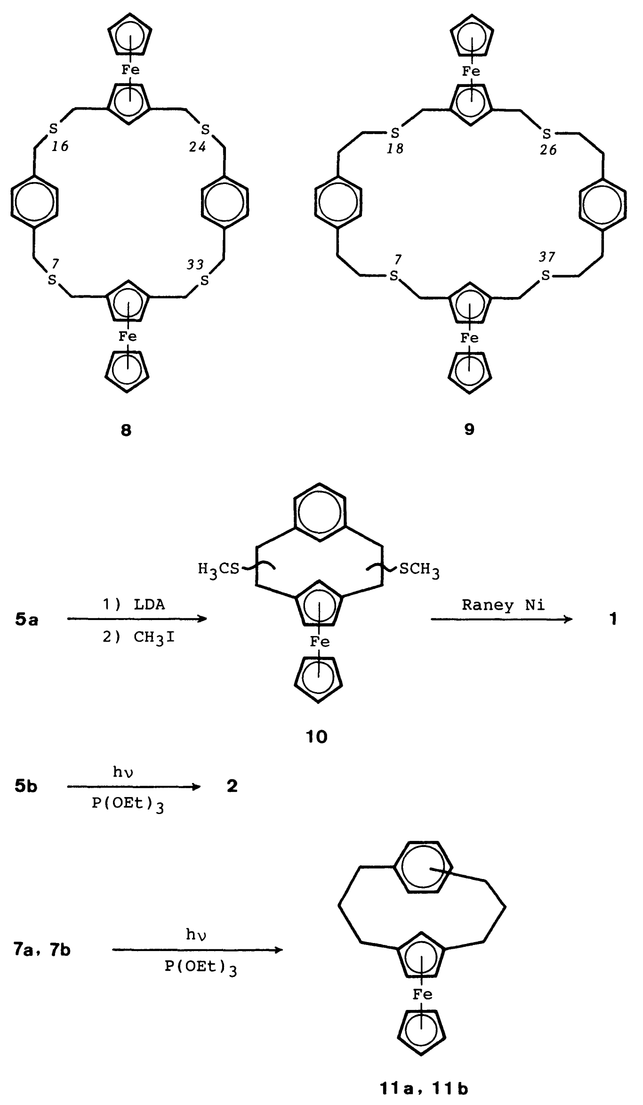
Results and Discussion

Synthesis. The route via bridge-rearrangement of dithia[3.3]phanes, which is the most convenient method[8–10)] for synthesis of [2.2]phanes, was applied to this work. Dithia[3.3]phanes are generally prepared by coupling of the corresponding mercaptomethyl and bromomethyl derivatives in the presence of base. However, reaction between 1,3-bis(mercaptomethyl)ferrocene and bis(bromomethyl)benzenes with NaOH or alkali metal/18-crown-6 gave a complex mixture or only a small amount of product. Czeck and Ratajczak[11)] described a coupling reaction between 1,1′-bis(hydroxymethyl)ferrocene and dimercaptoalkanes with trifluoroacetic acid (TFA) to afford (1,1′)ferrocenophanes. Consequently, the acid catalyzed reaction was applied to the present system. Diol **3** and dithiol **4a** or **4b** were treated with TFA in dichloromethane under



Scheme 1.

high dilution conditions for 15—20 h to give the desired dithia[3.3]ferrocenophanes (**5a**, 55%; **5b**, 21%). In the reaction of **4b** a cyclic dimer **8** containing two benzene rings and two ferrocene moieties was formed in a high yield (67%) besides dithia[3.3]phane **5b**. Macrocyclic dimer **9** was also produced predominantly in the reaction of diol **3** and para-substituted dithiol **6b** (**7b**, 8%, **9**, 62%). The preferential formation of the dimers in the reaction of the para systems is probably due to its thermodynamic stability in comarison with **5b** or **7b**. In fact, treatment of **5b** with TFA gave an equilibrium mixture of **5b** and **8**. The mass spectra of the dimers **8** and **9** by means of the electron impact (EI) ionization showed almost the same spectral patterns as **5b** and **7b**, respectively. The molecular ions of **8** and **9** could be observed only by the field desorption (FD) ionizing technique. The macrocyclic structure of **8** was determined by X-ray crystal analysis.[12]



Scheme 2.

Methylation of sulfides **5a** and **5b** with Borch reagent[13] to convert these into precursors for Stevens rearrangement[8] afforded only a mixture of unidentifiable products. Wittig rearrangement with lithium diisopropylamide (LDA)/CH_3I was reported by Boekelheide et al.[9] for a convenient synthesis of metacyclophane. An application of the reaction to **5a** gave methylthio[2.2]phane **10** in a good yield (79%). The compound **10** was desulfurized with Raney nickel to give the desired metacyclophane **1**. On the other hand, the Wittig rearrangement of paracycloferrocenophane **5b** afforded only bridge-cleaved compounds in a similar manner as the reaction of paracyclophanes.[9a] Consequently, photochemical extrusion of sulfur bridge[10,14] was attempted. Irradiation of **5b** in triethyl phosphite and benzene with high- or low-pressure

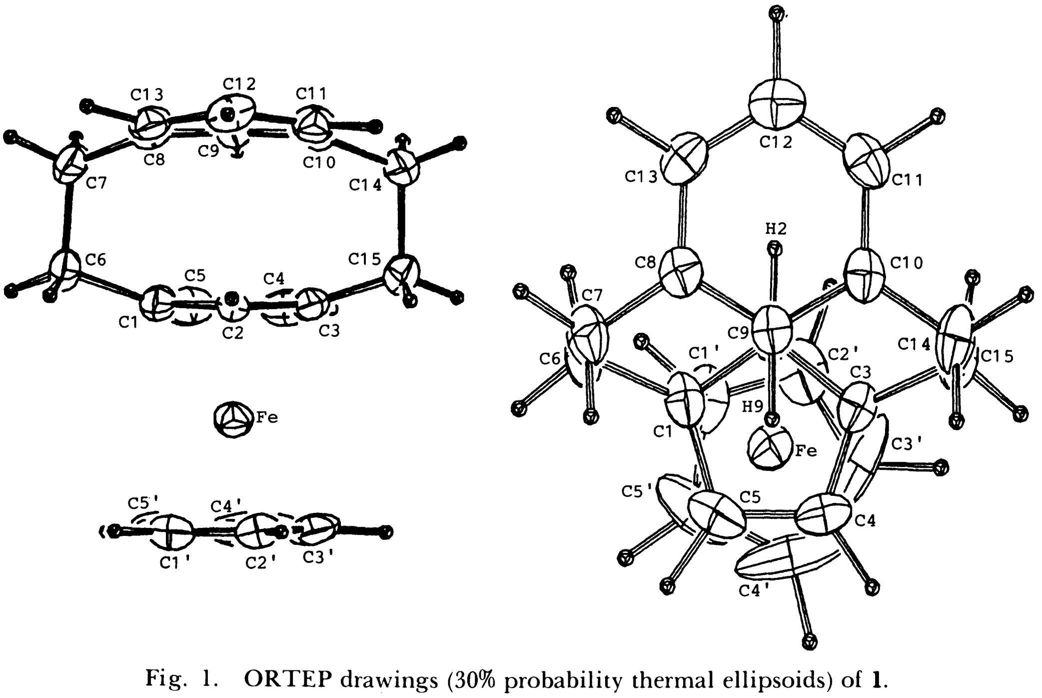


Fig. 1. ORTEP drawings (30% probability thermal ellipsoids) of **1**.

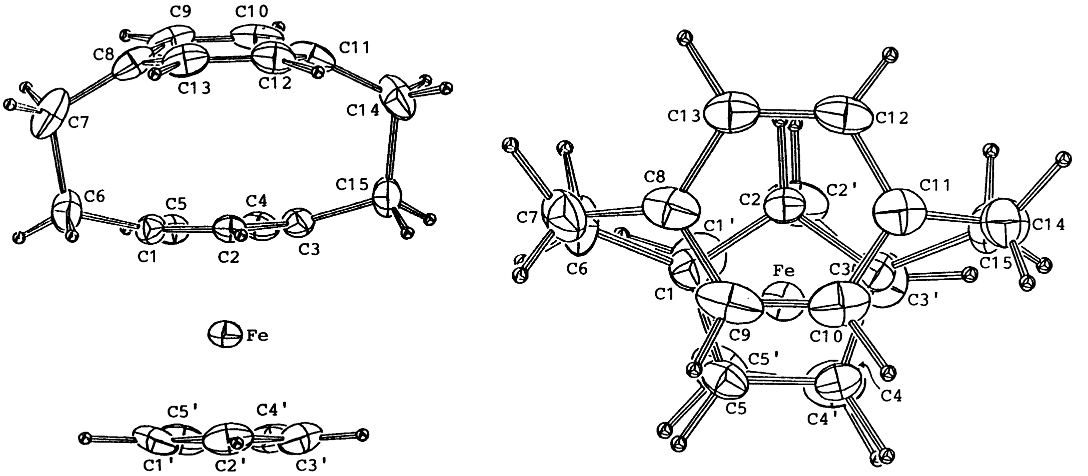


Fig. 2. ORTEP drawings (30% probability thermal ellipsoids) of **2**.

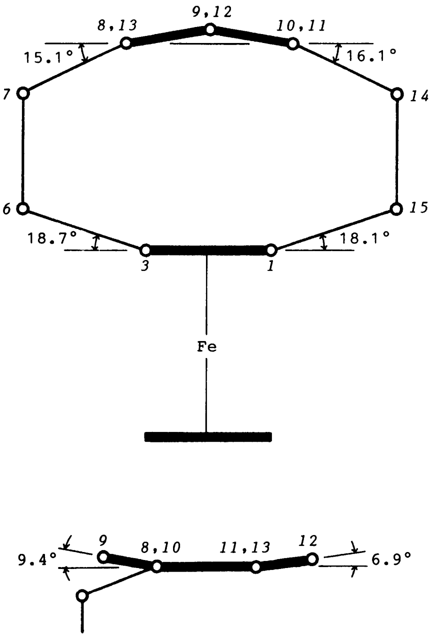


Fig. 3. Selected structural parameters of **1**.

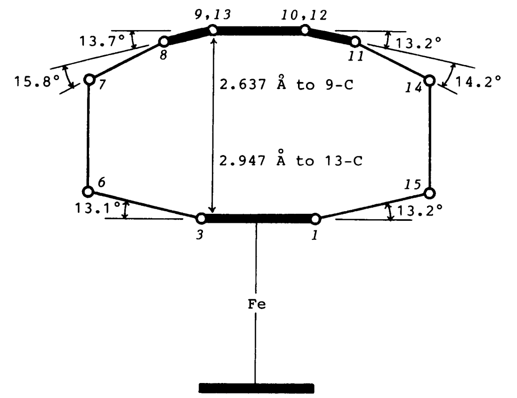


Fig. 4. Selected structural parameters of **2**.

mercury lamp gave [2.2]ferrocenophane **2** in reasonable yields (ca. 50%).

Desulfurization of dithia[4.4]phanes (**7**) was carried out by photochemical method and the corresponding [3.3]phanes **11** were obtained though in low yields.

X-Ray Crystal Structures. The molecular structures and structural parameters of both phanes **1** and **2**

Table 1. Bond Lengths (in Å) of **1** and **2** with Estimated Standard Deviations in Parentheses

Bond	Length		Bond	Length	
	1	**2**		**1**	**2**
Fe-C(1)	2.077(8)	2.086(5)	C(3′)-C(4′)	1.364(17)	1.408(9)
Fe-C(2)	2.032(7)	2.030(5)	C(4′)-C(5′)	1.401(23)	1.422(10)
Fe-C(3)	2.091(8)	2.076(5)	C(5′)-C(1′)	1.424(18)	1.413(9)
Fe-C(4)	2.060(8)	2.042(5)	C(3)-C(6)	1.518(14)	1.513(8)
Fe-C(5)	2.060(8)	2.028(5)	C(6)-C(7)	1.564(12)	1.565(10)
Fe-C(1′)	2.018(9)	2.059(6)	C(7)-C(8)	1.509(12)	1.504(10)
Fe-C(2′)	2.030(8)	2.037(7)	C(1)-C(15)	1.522(12)	1.498(8)
Fe-C(3′)	2.046(10)	2.035(6)	C(14)-C(15)	1.572(12)	1.566(9)
Fe-C(4′)	2.000(10)	2.034(6)	C(10)-C(14)	1.518(14)	—
Fe-C(5′)	2.024(17)	2.039(7)	C(11)-C(14)	—	1.497(10)
C(1)-C(2)	1.418(13)	1.416(7)	C(8)-C(9)	1.411(13)	1.400(9)
C(2)-C(3)	1.392(10)	1.423(7)	C(9)-C(10)	1.395(10)	1.390(9)
C(3)-C(4)	1.463(15)	1.427(8)	C(10)-C(11)	1.390(13)	1.409(8)
C(4)-C(5)	1.416(13)	1.409(8)	C(11)-C(12)	1.385(15)	1.413(10)
C(5)-C(1)	1.379(12)	1.426(8)	C(12)-C(13)	1.397(13)	1.361(9)
C(1′)-C(2′)	1.370(18)	1.396(9)	C(13)-C(8)	1.387(13)	1.388(9)
C(2′)-C(3′)	1.335(13)	1.408(10)			

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

Bond	Angle		Bond	Angle	
	1	**2**		**1**	**2**
C(5)-C(1)-C(2)	108.2(7)	105.5(5)	C(2)-C(1)-C(15)	120.3(7)	123.2(5)
C(1)-C(2)-C(3)	109.8(7)	110.2(4)	C(5)-C(1)-C(15)	128.5(8)	129.8(5)
C(2)-C(3)-C(4)	105.7(7)	106.4(4)	C(1)-C(15)-C(14)	108.0(7)	112.0(5)
C(3)-C(4)-C(5)	107.5(8)	108.0(5)	C(15)-C(14)-C(10)	112.2(8)	—
C(4)-C(5)-C(1)	108.7(8)	109.7(5)	C(9)-C(10)-C(14)	118.8(7)	—
C(5′)-C(1′)-C(2′)	107.9(11)	107.7(6)	C(11)-C(10)-C(14)	121.0(8)	—
C(1′)-C(2′)-C(3′)	108.8(9)	108.6(6)	C(15)-C(14)-C(11)	—	110.5(5)
C(2′)-C(3′)-C(4′)	109.9(10)	108.3(6)	C(10)-C(11)-(C14)	—	121.4(6)
C(3′)-C(4′)-C(5′)	108.2(11)	107.1(6)	C(12)-C(11)-C(14)	—	121.3(6)
C(4′)-C(5′)-C(1′)	105.1(12)	108.2(6)	C(13)-C(8)-C(9)	118.7(7)	116.4(6)
C(2)-C(3)-C(6)	124.2(8)	122.1(5)	C(8)-C(9)-C(10)	120.8(8)	121.5(6)
C(4)-C(3)-C(6)	126.6(8)	130.0(5)	C(9)-C(10)-C(11)	118.9(8)	120.1(6)
C(3)-C(6)-C(7)	108.1(8)	111.6(5)	C(10)-C(11)C(12)	119.8(8)	115.1(6)
C(6)-C(7)-C(8)	111.6(7)	110.8(6)	C(11)-C(12)-C(13)	121.0(9)	122.4(6)
C(7)-C(8)-C(9)	117.7(7)	121.6(6)	C(12)-C(13)-C(8)	119.4(8)	120.7(6)
C(7)-C(8)-C(13)	122.3(7)	119.4(6)			

Table 3. Deviations of Atoms from Least-Squares Planes[a] through the Cp Rings of **1** and **2** with Estimated Standard Deviations in Parentheses

Atom	Deviation/Å	
	1	**2**
	Bridged ring[b]	Bridged ring[d]
C(1)	−0.020(6)	−0.022(4)
C(2)	0.025(6)	0.025(4)
C(3)	−0.019(6)	−0.018(4)
C(4)	0.007(6)	0.004(4)
C(5)	0.008(7)	0.011(4)
C(6)	−0.507(6)	−0.360(5)
C(15)	−0.494(7)	−0.365(5)
Fe	1.678(4)	1.659(3)
	Unsubstituted ring[c]	Unsubstituted ring[e]
C(1′)	0.000(9)	0.006(5)
C(2′)	−0.011(8)	−0.007(5)
C(3′)	0.018(8)	0.006(5)
C(4′)	−0.017(9)	−0.002(5)
C(5′)	0.010(11)	−0.003(5)
Fe	−1.649(6)	−1.652(4)

a) The least-squares planes are shown in *b*—*e*. b) $0.6411X+0.7012Y+0.3119Z=3.3642$. c) $0.6475X+0.7070Y+0.2844Z=6.6805$. d) $-0.7237X+0.4495Y+0.5237Z=-0.3052$. e) $-0.7402X+0.4272Y+0.5193Z=2.9045$.

are shown in Figs. 1—4 and Tables 1—3. The two aromatic moieties of meta-ferrocenophane **1** are in an anti conformation in analogy with [2.2]metacyclophane.[15] The 2-hydrogen of the Cp ring and the 9-hydrogen of the benzene ring are situated right above each other's rings. The distances between the 9-hydrogen and the Cp ring carbons are 2.60(6)—2.65(6) Å and those between the 2-hydrogen and the benzene carbons are 2.80(6)—3.16(7) Å. The benzene and the bridged Cp ring in para-ferrocenophane **2** are more stacked over each other than those of **1**.

The benzene rings of both phanes **1** and **2** are distorted in a similar manner to [2.2]cyclophanes[15–17] and tricarbonylchromium complex of [2.2]paracyclophane.[18] The deformation of the benzene moiety in **2** is somewhat larger than those of [2.2]paracyclophane.[16] and its metal complex.[18] On the other hand, the Cp carbon atoms of both **1** and **2** deviate only slightly from their least-squares planes (Table 3) and the planarities of the bridged Cp rings are almost maintained in spite of their highly strained structures. However, the deviations of the methylene carbons at 6- and 15-positions from the Cp planes are extremely large. The bond of the Cp ring and 6-carbon (or 15-carbon) in **1** is more bent than that of **2** (Fig. 3). This great bending in **1** indicates that its methylene bridges are more strained than that of **2** due to the rigid meta-substituted benzene ring in comparison with the para-substituted ring.

The distance between the iron atom and the bridged Cp ring plane of **1** is considerably extended (1.678(4) Å) as compared to ferrocene (1.66 Å),[19] whereas that of **2** (1.659(3) Å) is almost similar to ferrocene. The distance of **1** is the largest of ferrocene derivatives previously described. These results in X-ray crystal analysis indicate that **1** is an extremely strained compound in comparison with **2** or other [2.2]cyclophanes.

NMR Spectra. In the ^{1}H NMR spectrum of dithia-[3.3]meta-ferrocenophane **5a**, the signals of the 2- and 4,5-protons on the Cp ring appear at δ 3.97 and 3.65, respectively (ferrocene, δ 4.04). The corresponding Cp ring protons of [3.3]meta-ferrocenophane **11a** resonate at δ 3.85 and 3.27. The upfield shifts of the 4,5-protons in comparison with the 2-protons in **5a** and **11a** indicate that these phanes are in syn conformations. The conformational features of the [3.3]meta-ferrocenophanes are similar to those of [3.3]metacyclophane[20] and [3.3](1,3)ferrocenophane.[4]

In contrast to the [3.3]phanes, the signal of the 2-proton of [2.2]meta-ferrocenophane **1** dramatically shifted to a high field (δ 1.18), whereas the 4,5-proton signal appeared at δ 3.75. The chemical shift difference ($\Delta\delta$) between the 2-protons of **1** and a reference compound (1,3-diethylferrocene) is 2.82 ppm. The value is larger than those of the corresponding aromatic protons in [2.2]metacyclophanes ($\Delta\delta$=2.62 ppm),[21] [2]metacyclo[2](1,3)azulenophane ($\Delta\delta$=2.34 ppm),[22] and [2]metacyclo[2](5,7)azulenophane ($\Delta\delta$= 2.46 ppm).[23] This extremly high field shift of the 2-proton signal in **1** reflects its molecular structural feature revealed by X-ray crystal analysis; the 2-hydrogen is situated right above the benzene ring plane.

On the other hand, the benzenoid 9-proton of **1** resonates at δ 5.34 and the upfield shift difference ($\Delta\delta$) from the coresponding signal of a reference compound (1,3-diethylbenzene) is 1.58 ppm. Despite unusually close proximity of the 9-proton to the Cp ring plane, the upfield shift value is smaller than that of the 2-proton. This shift behavior of the 9-proton indicates that the shielding effect of the above zone of the Cp ring is smaller than that of benzene ring. Muray and Fox[24] determined the magnetic susceptibilities of ferrocene and found the magnetic anisotropy of the molecule. Turbit and Watts[25] presented a map of the shielding and deshielding zone around ferrocene molecule based on the result of the susceptibilities and discussed on the proton chemical shifts of ferrocene derivatives. However, the shielding shift value of the proton situated right above the Cp ring plane has not been detected until recently. Musso et al.[26] reported on the ^{1}H NMR spectra of 1,1′,3,3′-tetramethyl-2,2′-bis(2,4,6-trialkylphenyl)ferrocenes having *"exo"* alkyl groups which are located on the shielding zone of ferrocene nucleus. The upfield shift difference of the alkyl protons from the reference proton shifts are 0.49—0.74 ppm. The shift difference of the 9-proton (1.58 ppm) of **1** is the largest value in the upfield shifts due to the diamagnetic anisotropy of ferrocene nucleus.

The ^{13}C NMR spectra of **1** and **2** show unusual paramagnetic shifts of the inner aromatic carbon signals at 2- and 9-positions (2- and 9-carbons of **1**, δ 72.90 and 139.07; 2-carbon of **2**, δ 72.32). Such downfield shifts of the inner aromatic carbon resonance are generally observed in [2.2]metacyclophanes,[27] but the chemical shift difference of the benzenoid 9-carbon in **1** ($\Delta\delta$=9.0 ppm) from the corresponding signal of *m*-xylene is larger than that of [2.2]metacyclophane ($\Delta\delta$=6.2 ppm). The shift difference of the 2-carbons in **1** and **2** from that of 1,3-diethylferrocene is 5.7 and 5.1 ppm, respectively. The downfield shifts of those carbons of **1** and **2** seem to reflect the proximity of the carbons to the other aromatic rings. The major origin of the shift is attributable to rehybridization due to excessive strain and direct *p*-orbital compression.[27]

Electronic Spectra. The most remarkable difference in the electronic absorption spectra in ethanol between [2.2]phanes (**1**, **2**) and [3.3]phanes (**11a**, **11b**) is seen in the d-d absorption band near 440 nm. The bands of **1** and **2** appear at 451 and 447 nm (ε=150 and 140), respectively, whereas both **11a** and **11b** exhibit the band at wavelength of 442 nm (ε=130 and 110, respectively) similar to that of 1,3-diethylferrocene (439 nm, ε=110). Pronounced difference in absorption coeficient between [2.2]phanes and [3.3]phanes was not seen in these band. The origin of the bathochromic shifts in **1** and **2** would be mainly attributed to the following factors: (i) Some transannular π-electronic interactions between the two aromatic rings, and (ii) a change of the electronic state in the d-orbital of the iron due to excessive strain.

In the study on intramolecularly bridged ferrocenophanes we found that there was a linear relationship between the wavelengths of the d-d absorption and the Cp-Fe-Cp distances in the X-ray crystal structure.[28] This correlation almost holds for **1** although the wavelength of **2** slightly deviates from the straight line.[28] The elongation of the Cp-Fe distance in **1** should result in a change of the d-electronic configuration of the iron and a shift of the d-d absorption. On the other hand, the large bathochromic shift of the band was observed in [3.3](1,3)ferrocenophane (488 nm)[4] having a strainless molecular structure based on the inspection of a molecular model. Kasahara et al.[4] described that the shift was probably due to a transannular π-electronic interaction between the two ferrocene moieties. Transannular intraction between the Cp and benzene rings should be present in [2.2]ferrocenophanes (**1** and **2**), because the two ring planes approach each other. Therefore, it is likely that the bathochromic shifts of the d-d absoption band in **1** and **2** are caused by the two factors mentioned above, although the degree of their contribution cannot be estimated.

The absorption shoulders in the region near 300 nm in [2.2]phanes **1**, **2** and [3.3]phanes **11a**, **11b** are somewhat swollen in comparison with 1,3-diethylferrocene. The swellings possibly arise from some change of electronic configuration in benzene moieties due to charge-transfer intraction with the Cp ring, because the absorption bands based on the interaction between two benzene rings in cyclophanes are observed in this region.

Experimental

All melting points were uncorrected. NMR spectra were measured on a JEOL JNM-FX100 spectrometer relative to tetramethylsilane as an internal standard. The assignments of the signals were made by homo- (^{1}H{^{1}H}) and selective hetero-nuclear (^{13}C{^{1}H}) decoupling technique. Mass spectra were obtained with a Hitachi RMU-7M or a Hitachi M-80 double focusing mass spectrometer by electron impact (EI) ionizing technique at 70 eV unless otherwise stated. Field desorption (FD) ionization was carried out using a carbon or silicon emitter and the FD mass spectra were measured on the M-80 spectrometer. Empirical formulae of oily or unstable compounds were determined by means of high-resolution mass spectra, which were analyzed on a Hitachi M-003 data processing system. Electronic absorption spectra were recorded on a Hitachi 323 spectrophotometer in ethanol. 1,3-Bis(hydroxymethyl)ferrocene (**3**) (mp 115—117 °C),[3] 1,3-bis(mercaptoethyl)benzene (**6a**) (oil),[29] and 1,4-bis(mercaptoethyl)benzene (**6b**) (oil)[29] were prepared according to the usual procedures.

General Procedures. Coupling reaction between diol **3** and bis(mercaptoalkyl)benzenes **4**, **6** with trifluoroacetic acid (TFA): Dichloromethane freshly distilled from CaH_2 was used as solvent and oxygen in the solvent was removed as much as possible by ultrasonic vibration followed by bubbling dry nitrogen gas immediately before use. Each solution of 1,3-bis(hydroxymethyl)ferrocene (**3**) and the corresponding bis(mercaptoalkyl)benzene (**1** mol equiv to **3**) in dichloromethane was added dropwise to a stirring solution of TFA in dichloromethane under a nitrogen atmosphere. The solvent was used in enough volume to keep a high dilution condition (concn of **3**: ca. 10^{-3} mol dm^{-3}) of the reaction system. The reaction mixture was stirred in the dark at room temperature. Saturated aq $NaHCO_3$ was added and the organic layer was phase-separated, washed with saturated aq NaCl, dried over Na_2SO_4 and evaporated. The residue was column-chromatographed to isolate the coupling products.

Photochemical extrusion of sulfur: A solution of sulfide in benzene and triethyl phosphite was placed in a qaltz tube. A stream of argon gas was bubbled through the solution for 30 min. External irradiation was carried out using a 100 W high pressure mercury lamp (Ushio electric Inc. UM-102 type) or eight of 30 W low pressure mercury lamps (The Southern N.E. Ultraviolet Co., Royal type RS Preparative Photochemical Reactor). The temperature of the reaction mixture was maintained below 30 °C with the aid of a water bath throughout irradiation. After evaporating benzene and triethyl phosphite in vacuo, the residue was column-chromatographed over silica gel.

7,16-Dithia[3]metacyclo[3](1,3)ferrocenophane (5a). Each solution of diol **3** (400 mg, 1.6 mmol) and 1,3-bis-(mercaptomethyl)benzene (**4a**) (276 mg, 1.6 mmol) in dichloromethane (each 200 ml) was added to a solution of TFA (1.8 g, 16 mmol) in dichloromethane (1200 ml), and the mixture was stirred for 20 h. The product was column-chromatographed over silica gel, and the first band eluted with hexane-dichloromethane (1 : 1) yielded sulfide **5a** (339 mg, 55%), which was recrystallized from hexane-benzene to give yellow needles; mp 136—137 °C. ^{1}H NMR ($CDCl_3$) δ=3.51 and 3.71 (each 2H, an AB system, J=14.5 Hz, 6, 17-H), 3.53 and 3.69 (each 2H, an AB system, J=11.5 Hz, 8, 15-H), 3.65 (2H, d, J=1.4 Hz, 4, 5-H), 3.93 (5H, s, unsubstd. Cp-H), 3.97 (1H, t, J=1.4 Hz, 2-H), 6.79 (1H, bs, 10-H), 6.90—7.00 (3H, m, 12, 13, 14-H); ^{13}C NMR ($CDCl_3$) δ=33.04 (6, 17-C), 37.13 (8, 15-C), 68.37 (4, 5-C), 68.81 (unsubstd. Cp-C), 72.51 (2-C), 84.60 (1, 3-C), 126.31 (12, 14-C), 127.96 (13-C), 131.57 (10-C), 137.95 (9, 11-C); MS m/z (rel intensity) 380 (100, M^+), 315 (50), 222 (21), 193 (23), 135 (33), 121 (56), 91 (93); FD-MS m/z 380 (M^+).

Found: C, 64.06; H, 5.39; S, 15.99%; M^+, m/z 380.0349. Calcd for $C_{20}H_{20}S_2Fe\cdot1/6C_6H_6$: C, 64.12; H, 5.38; S, 16.30%; M for $C_{20}H_{20}S_2Fe$, 380.0353.

The second band eluted with hexane-dichloromethane (1 : 2) yielded a yellow powder (218 mg), which was possibly a mixture of oligomer and polymers.

7,16-Dithia[3]paracyclo[3](1,3)ferrocenophane (5b). Each solution of diol **3** (200 mg, 0.81 mmol) and 1,4-bis-(mercaptomethyl)benzene **4b** (138 mg, 0.81 mmol) in dichloromethane (each 100 ml) was added to a solution of TFA (0.92 g, 8.1 mmol) in dichloromethane (600 ml), and the mixture was stirred for 15 h. The product was column-chlomatograghed over silica gel, and the first band eluted with hexane-dichloromethane (1 : 1) yielded sulfide **5b** (66 mg, 21%), which was recrystallized from benzene-ethyl acetate to give yellow needles; mp 172—173 °C (decomp). ^{1}H NMR ($CDCl_3$) δ=2.89 (1H, t, J=1.4 Hz, 2-H), 3.20 and 3.46 (each 2H, an AB system, J=14.5 Hz, 6, 17-H), 3.79 (4H, s, 8, 15-H), 3.84 (5H, s, unsubstd. Cp-H), 3.91 (2H, d, J=1.4 Hz, 4, 5-H), 6.95 and 7.01 (each 2H, an AA'BB' system, Ph-H); ^{13}C NMR ($CDCl_3$) δ=32.02 (6, 17-C), 38.11 (8, 15-C), 67.59 (4, 5-C), 68.71 (unsubstd. Cp-C), 69.49 (2-C), 86.49 (1, 3-C), 128.11 (10, 11-C), 130.45 (13, 14-C), 137.56 (9, 12-C); MS m/z (rel intensity) 380 (100, M^+), 315 (12), 244 (10), 212 (8), 185 (9), 121 (12), 91 (20); FD-MS m/z 380 (M^+).

Found: C, 62.96; H, 5.29; S, 16.68%; M^+, m/z 380.0364. Calcd for $C_{20}H_{20}S_2Fe$: C, 63.16; H, 5.30; S, 16.86%; M, 380.0353.

The second band eluted with hexane-dichloromethane (1 : 2) yielded 7,16,24,33-tetrathia[3]paracyclo[3](1,3)ferroceno-[3]paracyclo[3](1,3)ferrocenophane (**8**) (206 mg, 67%), which was recrystallized from benzene-ethyl acetate to give orange-yellow needles; mp 172—174 °C (decomp). ^{1}H NMR ($CDCl_3$) δ=3.34 and 3.39 (each 2H, an AB system, J=14.5 Hz, $CpCH_2$-), 3.62 (4H, s, $PhCH_2$-), 3.96 (1H, t, J=1.4 Hz, 2-H), 4.02 (5H, s, unsubstd. Cp-H), 4.13 (2H, d, J=1.4 Hz, 4, 5-H), 7.19 (4H, s, Ph-H); ^{13}C NMR ($CDCl_3$) δ=30.82 ($CpCH_2$-), 35.23 ($PhCH_2$-), 68.69 (4, 5-C), 69.45 (unsubstd. Cp-C), 70.28 (2-C), 84.90 (1, 3-C), 129.05 (unsubstd. C of Ph), 136.91 (substd. C of Ph); MS m/z (rel intensity) 760 (0, M^+), 380 (100), 315 (13), 244 (12), 212 (5), 185 (8), 121 (16), 91 (23); FD-MS m/z 760 (M^+).

Found: C, 63.10; H, 5.28; S, 16.61%. Calcd for $C_{40}H_{40}S_4Fe_2$: C, 63.16; H, 5.30; S, 16.86%.

7,18-Dithia[4]metacyclo[4](1,3)ferrocenophane (7a). Each solution of diol **3** (400 mg, 1.6 mmol) and 1,3-bis(2-mercaptoethyl)benzene **6a** (320 mg, 1.6 mmol) in dichloromethane (each 200 ml) was added to a solution of TFA (1.9 g, 17 mmol) in the same solvent (1200 ml), and the mixture was stirred for 18 h. The product was column-chromatographed over silica gel, and the first band eluted with hexane-dichloromethane (1 : 1) yielded sulfide **7a** (530 mg, 80%), which was recrystallized from hexane-benzene to give yellow plates; mp 148—149 °C. ^{1}H NMR ($CDCl_3$) δ=2.74 (8H, s, 8, 9, 16, 17-H), 3.49 (4H, s, 6, 19-H), 4.06 (5H, s, unsubstd. Cp-H), 4.11 (1H, t, J=1.4 Hz, 2-H), 4.15 (2H, d, J=1.4 Hz, 4, 5-H), 6.65—7.15 (4H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=30.46, 31.43 and 34.45 (methylene-C), 68.90 (4,5-C), 69.49 (unsubstd Cp-C), 70.80 (2-C), 85.23 (1, 3-C), 126.60 (13, 15-C), 127.14 and 127.67 (11, 14-C), 140.04 (10, 12-C); MS m/z (rel intensity) 408 (100, M^+), 343 (29), 252 (23), 251 (35), 218 (14), 206 (20), 121 (33), 91 (56); FD-MS m/z 408 (M^+).

Found: C, 65.87; H, 6.47; S, 15.05%; M^+, m/z 408.0649. Calcd for $C_{22}H_{24}S_2Fe\cdot1/6C_6H_6$: C, 65.55; H, 5.98; S, 15.22%; M for $C_{22}H_{24}S_2Fe$, 408.0666.

7,18-Dithia[4]paracyclo[4](1,3)ferrocenophane (7b). Each solution of diol **3** (284 mg, 1.2 mmol) and 1,4-bis(2-mercaptoethyl)benzene **6b** (228 mg, 1.2 mmol) in dichloromethane (each 200 ml) was added to a solution of TFA (13.1 g, 1.2 mmol) in dichloromethane (750 ml), and the mixture was stirred for 2 h. The product was column-chromatographed over silica gel. The first band eluted with hexane-dichloromethane (1 : 1) yielded sulfide **7b** (38 mg, 8%), which was recrystallized from hexane-benzene to give yellow needles; mp 163—164 °C (decomp). ^{1}H NMR (CDCl$_3$) δ=2.40—3.00 (8H, m, 8, 9, 16, 17-H), 3.23 (4H, s, 6, 19-H), 3.60 (1H, t, J=1.4 Hz, 2-H,), 3.78 (2H, d, J=1.4 Hz, 4, 5-H), 3.92 (5H, s, unsubstd. Cp-H), 6.88 and 6.94 (4H, an AA'XX' system, Ph-H); ^{13}C NMR (CDCl$_3$) δ=33.72, 35.23 and 35.43 (methylene-C), 68.71 (4, 5-C), 69.49 (unsubstd. Cp-C), 69.70 (2-C), 85.86 (1, 3-C), 128.50 (unsubstd. C of Ph), 137.37 (substd. C of Ph); MS m/z (rel intensity) 408 (100, M^{+}), 343 (33), 252 (27), 206 (19), 181 (8), 121 (27), 91 (34); FD-MS m/z 408 (M^{+}).

Found: C, 65.48; H, 6.43; S, 15.27%; M^{+}, m/z 408.0676. Calcd for $C_{22}H_{24}S_2Fe\cdot 1/6C_6H_6$: C, 65.55; H, 5.98; S, 15.22%; M for $C_{22}H_{24}S_2Fe$, 408.0666.

The second band eluted with hexane-dichloromethane (1 : 2) yielded 7,18,26,37-tetrathia[4]paracyclo[4](1,3)ferroceno[4]paracyclo[4](1,3)ferrocenophane (**9**) (292 mg, 62%). Recrystallization of **9** from hexane-benzene gave yellow needles; mp 196—197 °C (decomp). ^{1}H NMR (CDCl$_3$) δ=2.40—2.80 (8H, m, PhCH$_2$CH$_2$-), 3.49 (4H, s, CpCH$_2$-), 4.08 (5H, s, unsubstd. Cp-H), 3.14 (2H, d, J=1.4 Hz, 4, 5-H), 4.22 (1H, t, J=1.4 Hz, 2-H), 6.86 (4H, s, Ph-H); ^{13}C NMR (CDCl$_3$) δ=31.87, 32.80 and 36.01 (methylene-C), 68.71 (4, 5-C), 69.54 (unsubstd. Cp-C), 69.83 (2-C), 85.71 (1, 3-C), 128.35 (unsubstd. C of Ph), 138.49 (substd. C of Ph); FD-MS m/z 816 (M^{+}).

Found: C, 64.90; H, 6.24; S, 15.65%. Calcd for $C_{44}H_{48}S_4Fe_2$: C, 64.70; H, 5.92; S, 15.70%.

[2]Metacyclo[2](1,3)ferrocenophane (1). A solution of lithium diisopropyl amide (LDA) in hexane-THF (0.81 ml, 0.65 mmol) was added dropwise to a solution of dithia[3]metacyclo[3]ferrocenophane (**5a**) (100 mg, 0.26 mmol) in THF (2 ml) under an argon atmosphere at room temperature. After stirring for 3 min, iodomethane (0.08 ml, 1.3 mmol) was added to the brownish yellow solution. The resulting pink solution was stirred for 5 min at room temperature and water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with saturated aq NaCl, dried over CaCl$_2$ and evaporated. The residue was column-chromatograghed over silica gel with hexane-dichloromethane (1 : 1) to yield a mixture of rearrangement products **10** (84 mg, 79%) from the first eluted band. Recrystallization of **10** from hexane-benzene gave orange-yellow crystals; mp 178—181 °C (decomp). ^{1}H NMR (CDCl$_3$, only assignable peaks) δ=1.25 (t, 2-H), 1.95 and 2.09 (each s, SCH$_3$), 3.98 (s, unsubstd. Cp-H), 5.40 and 5.87 (each bt, 9-H), 6.80—7.50 (m, Ph-H).

Found: M^{+}, m/z 408.0671. Calcd for $C_{22}H_{24}Fe$: M, 408.0666.

A suspension of methyl sulfide **10** (32 mg, 0.08 mmol) and active Raney nickel(W-7) in ethanol (10 ml) was refluxed for 30 min. The mixture was filtered and evaporation of the filtrate left [2]metacyclo[2](1,3)ferrocenophane (**1**) (24 mg, 98%), which was recrystallized from methanol to give orange-yellow needles; mp 131—132 °C. ^{1}H NMR (CDCl$_3$) δ=1.18 (1H, t, J=1.4 Hz, 2-H), 1.82, 2.22, 2.55, and 2.90 (each 2H, m, methylene-H), 3.75 (2H, d, J=1.4 Hz, 4, 5-H), 3.97 (5H, s, unsubstd. Cp-H), 5.34 (1H, m, 9-H), 6.80—7.15 (3H, m, 11, 12, 13-H). ^{13}C NMR (CDCl$_3$) δ=32.21 (6, 15-C), 39.52 (7, 14-C), 64.71 (4, 5-C), 67.35 (unsubstd. Cp-C), 72.90 (2-C), 89.22 (1, 3-C), 125.38 (11, 12, 13-C), 127.87 (12-C), 139.07 (9-C), 140.15 (8, 10-C); MS m/z (rel intensity) 316 (100, M^{+}), 246 (13), 222 (9), 191 (6), 190 (6), 189 (6), 165 (6), 121 (17).

Found: C, 75.67; H, 6.59%, M^{+}, m/z 316.0904. Calcd for $C_{20}H_{20}Fe$: C, 75.96; H, 6.37%, M, 316.0912.

[2]Paracyclo[2](1,3)ferrocenophane (2). A solution of dithia[3]paracyclo[3]ferrocenophane **5b** (30 mg, 0.08 mmol) in benzene (24 ml) and triethyl phosphite (48 ml) was irradiated with a high-pressure mercury lamp for 18 h. On column chromatography of the product over silica gel with hexane-ether (1 : 1), the first band yielded [2]paracyclo[2](1,3)ferrocenophane (**2**) (13 mg, 53%), which was recrystallized from methanol to give orange-yellow needles; mp 106—107 °C. ^{1}H NMR (CDCl$_3$) δ=2.00—3.15 (8H, m, methylene-H), 2.37 (1H, t, J=1.4 Hz, 2-H), 3.37 (2H, d, J=1.4 Hz, 4, 5-H), 3.87 (5H, s, unsubstd. Cp-H), 6.23 and 6.93 (each 2H, an AA'XX' system, Ph-H); ^{13}C NMR (CDCl$_3$) δ=28.26 (6, 15-C), 35.62 (7, 14-C), 64.76 (4, 5-C), 67.20 (unsubstd. Cp-C), 72.32 (2-C), 90.00 (1, 3-C), 129.82 and 131.77 (unsubstd. C of Ph), 139.95 (substd. C of Ph); MS m/z (rel intensity) 316 (97,

Table 4. Crystal Data and Some Conditions for Data Collections

	1	2
Formula	$C_{20}H_{20}Fe$	$C_{20}H_{20}Fe$
Molecular weight	316.23	316.23
Crystal dimensions/mm	0.015×0.060×0.30	0.17×0.10×0.60
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$Pbca$
a/Å	8.851(4)	15.308(8)
b/Å	15.742(8)	24.716(12)
c/Å	5.963(3)	8.034(4)
β/°	109.76(5)	—
Z	2	8
V/Å^3	781.9	3039.7
D_x/g cm^{-1}	1.343	1.382
λ/Å	1.5418(Cu $K\alpha$)	0.7107(Mo $K\alpha$)
μ/cm^{-1}	76.5(Cu $K\alpha$)	9.81(Mo $K\alpha$)
Scan speed (2θ min^{-1})	4	6
Independent reflections used [$I_0>2\sigma(I_0)$]	1326	1552
2θ range	6°—156°	6°—50°
Final R value	0.053	0.046

Table 5. Atomic Coodinates (×10^5 for Fe; ×10^4 for C; ×10^3 for H) and Isotropic Equivalent Thermal Parameters (in Å^2 Unit) of **1** with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Fe	82867(13)	0(0)	74706(20)	4.26	H(2)	693(8)	−137(5)	934(12)	
C(1)	8034(9)	−1273(5)	6495(15)	4.22	H(4)	572(8)	21(6)	297(12)	
C(2)	7010(8)	−1040(4)	7778(13)	3.64	H(5)	829(8)	−79(5)	317(12)	
C(3)	5917(9)	−429(5)	6509(17)	4.81	H(6a)	439(9)	−28(4)	873(13)	
C(4)	6366(11)	−232(5)	4419(16)	5.98	H(6b)	377(7)	35(4)	605(11)	
C(5)	7671(11)	−766(6)	4496(14)	5.18	H(7a)	287(9)	−95(5)	353(14)	
C(6)	4298(10)	−271(5)	6786(20)	6.32	H(7b)	199(8)	−99(5)	584(12)	
C(7)	3138(9)	−1003(6)	5484(17)	5.68	H(9)	521(8)	−178(5)	378(12)	
C(8)	3881(8)	−1865(5)	6234(14)	4.32	H(11)	690(9)	−367(5)	922(13)	
C(9)	4981(10)	−2164(5)	5168(15)	4.08	H(12)	477(9)	−323(5)	1085(12)	
C(10)	6125(9)	−2776(5)	6296(15)	4.52	H(13)	273(10)	−217(6)	875(15)	
C(11)	5997(10)	−3195(5)	8275(16)	5.29	H(14a)	736(9)	−277(5)	371(13)	
C(12)	4773(11)	−2983(7)	9130(15)	5.95	H(14b)	820(8)	−348(5)	616(12)	
C(13)	3777(9)	−2286(6)	8220(15)	5.05	H(15a)	936(8)	−227(5)	893(12)	
C(14)	7649(10)	−2832(6)	5674(18)	5.93	H(15b)	994(9)	−213(5)	634(13)	
C(15)	8898(9)	−2125(6)	6956(18)	5.76	H(1′)	1167(8)	−10(6)	896(12)	
C(1′)	10633(10)	301(9)	8931(23)	11.15	H(2′)	1029(8)	−8(6)	1231(12)	
C(2′)	9938(10)	310(6)	10665(16)	6.30	H(3′)	800(10)	103(6)	1116(15)	
C(3′)	8778(11)	895(7)	10107(18)	6.46	H(4′)	783(10)	177(6)	706(14)	
C(4′)	8629(15)	1252(6)	7958(21)	9.59	H(5′)	999(12)	103(6)	545(17)	
C(5′)	9822(19)	910(10)	7169(19)	13.30					

Table 6. Atomic Coodinates (×10^5 for Fe; ×10^4 for C; ×10^3 for H) and Isotropic Equivalent Thermal Parameters (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	6695(5)	14541(3)	11417(9)	3.09	H(2)	97(3)	164(2)	−218(7)	
C(1)	1859(3)	1583(2)	−64(6)	3.23	H(4)	131(3)	38(2)	162(6)	
C(2)	1205(3)	1389(2)	−1161(6)	2.89	H(5)	232(3)	120(2)	216(6)	
C(3)	916(3)	868(2)	−648(6)	3.07	H(6a)	3(4)	26(2)	−125(7)	
C(4)	1358(4)	752(2)	874(7)	3.45	H(6b)	3(4)	74(2)	−254(8)	
C(5)	1922(3)	1188(2)	1225(7)	3.50	H(7a)	127(4)	−15(2)	−254(8)	
C(6)	414(4)	496(2)	−1799(8)	4.90	H(7b)	68(4)	7(2)	−407(7)	
C(7)	1042(5)	163(3)	−2946(9)	6.15	H(9)	148(4)	91(2)	−507(7)	
C(8)	1887(4)	460(2)	−3213(7)	4.64	H(10)	244(3)	175(2)	−455(6)	
C(9)	1941(4)	908(3)	−4278(7)	4.59	H(12)	350(4)	77(2)	−84(7)	
C(10)	2491(4)	1341(3)	−3933(7)	4.43	H(13)	252(4)	3(3)	−142(8)	
C(11)	3017(4)	1335(3)	−2494(8)	4.65	H(14a)	372(4)	182(2)	−85(7)	
C(12)	3102(4)	824(3)	−1720(7)	5.10	H(14b)	340(4)	220(2)	−240(8)	
C(13)	2557(5)	403(2)	−2062(3)	5.04	H(15a)	266(3)	224(2)	41(7)	
C(14)	3247(4)	1845(3)	−1594(8)	5.53	H(15b)	209(4)	239(3)	−105(9)	
C(15)	2462(5)	2039(3)	−493(8)	5.21	H(1′)	54(3)	253(2)	195(7)	
C(1′)	207(4)	2184(3)	2012(9)	5.31	H(2′)	−61(4)	216(2)	−2(7)	
C(2′)	−399(4)	1941(3)	948(8)	5.41	H(3′)	−106(4)	109(2)	122(8)	
C(3′)	−636(4)	1435(3)	1615(9)	5.50	H(4′)	−18(3)	100(2)	386(7)	
C(4′)	−161(4)	1354(3)	3094(8)	5.29	H(5′)	73(3)	191(2)	433(6)	
C(5′)	365(4)	1822(3)	3339(8)	5.41					

M$^+$), 212 (100), 121 (52), 91 (25).

Found. C, 75.85; H, 6.40%; M$^+$, m/z 316.0887. Calcd for $C_{20}H_{20}Fe$: C, 75.96; H, 6.37%; M, 316.0912.

The second band eluted with hexane-ether (10 : 1) yielded yellow solid (10 mg) whose ^{1}H NMR and mass spectra showed extrusion of one sulfur bridge. The compound was so unstable that cannot be further purified. The third band yielded the starting material (2 mg, 7%).

Irradiation of **5b** with a low pressure mercury lamp also afforded **2** in a comparable yield (54%).

[3]Metacyclo[3](1,3)ferrocenophane (11a). A solution of dithia[4]metacyclo[4]ferrocenophane **11a** (376 mg, 0.92 mmol) in benzene (10 ml) and triethyl phosphite (75 ml) was irradiated with a low-pressure mercury lamp for 85 h. The resulting residue was column-chromatographed over silica gel with hexane-ether (20 : 1). The solid yielded from the first band was further chromatographed over thin-layered alumina in a preparative scale with hexane-ether (100 : 1) to separate into three bands. The first band yielded unknown yellow oil (6 mg), and the yellow crystals (3 mg) yielded from the third band was possibly a partially desulfurized compound. The second band in the thin-layered chromatography afforded [3]metacyclo[3](1,3)ferrocenophane (**11a**) (8 mg, 3%), which was recrystallized from methanol to give yellow needles mp 88—89 °C. ^{1}H NMR ($CDCl_3$) δ=1.60—3.00 (12H, m, methylene-H), 3.27 (2H, d, J=1.4 Hz, 4, 5-H), 3.83 (5H, s, unsubstd. Cp-H), 3.85 (1H, t, J=1.4 Hz, 2-H), 6.50—6.90 (4H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=29.87, 31.92, and 35.91 (methylene-C), 66.71 (4, 5-C), 68.22 (unsubstd. Cp-C), 69.10 (2-C), 87.08 (1,3-C), 124.41 (12, 14-C), 126.89 (13-C), 134.59 (10-C), 140.78 (9, 11-C); MS m/z (rel intensity) 344 (100, M$^+$), 279 (20), 277 (9), 172 (4), 121 (13), 91 (5).

Found: M$^+$, m/z 344.1212. Calcd for $C_{22}H_{24}Fe$: M$^+$, 344.1225.

The second band in the first column chromatography yielded the starting material **7a** (40 mg, 11%).

[3]Paracyclo[3](1,3)ferrocenophane (11b). A solution of dithia[4]paracyclo[4]ferrocenophane **7b** (17 mg, 0.042 mmol) in benzene (3 ml) and triethyl phosphite (30 ml) was irradiated with a low pressure mercury lamp for 85 h. The resulting product was column-chromatographed over silica gel with hexane-ether (20:1). The first band yielded [3]paracyclo[3](1,3)ferrocenophane (**11b**) (2 mg, 14%), which was recrystallized from methanol to give yellow needles; mp 115—117 °C. ^{1}H NMR (CDCl$_3$) δ=1.65—3.10 (12H, m, methylene-H), 2.77 (1H, t, J=1.4 Hz, 2-H), 3.59 (2H, d, J=1.4 Hz, 4, 5-H), 3.77 (5H, s, unsubstd. Cp-H), 6.54 and 6.88 (each 2H, an AA'XX' system, Ph-H); ^{13}C NMR (CDCl$_3$) δ=28.90, 32.60, and 35.91 (methylene-C), 65.49 (4, 5-C), 68.32 (unsubstd. Cp-C), 70.46 (2-C), 89.32 (1, 3-H), 128.79 and 128.89 (unsubstd. C of Ph), 139.12 (substd. C of Ph); MS m/z (rel intensity) 344 (100, M$^+$), 279 (19), 277 (13), 213 (4), 172 (6), 121 (23), 117 (15), 91 (10).

Found: M$^+$, m/z 344.1204. Calcd for $C_{22}H_{24}Fe$: M, 344.1225.

Crystallographic Measurements. Both crystals of **1** and **2** (yellow plates) used in the X-ray diffraction were grown from methanol solutions. The lattice parameters and intensity data were measured on a Phillips PW-1100 diffractometer by means of the θ—2θ scan method by using graphite-monochromated radiation. For the crystal of **1**, Cu$K\alpha$ radiation was used due to the small size of the crystal but for **2**, Mo$K\alpha$ radiation was used. Crystal data and some conditions for data collection are given in Table 4. Lorentz and polarization corrections were made but no absorption correction was applied.

The structures were solved by the heavy atom method. Both atomic coordinates of Fe atoms in the two compounds were reduced from the Patterson maps, and all carbon atoms were located in the Fourier maps. The refinements were carried out by block-diagonal-matrix least-squares procedure. The final atomic parameters are given in Tables 5 and 6.[††]

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