previously and have been ascribed to steric crowding in the M_2C_2 core.[2b] The C5–C6–C7 angle 135.4 (4)° is consistent with a change in the hybridization of the alkyne carbons from sp toward sp^2 as a result of bonding to the metal atoms. It is interesting to note that this angle is close to the central C–C–C angle (139°) in cation **2**. The low-frequency IR band at 1820 cm^{-1} observed for **11** shows that the semibridging carbonyl (C3–O3) is maintained in solution.

^1H and ^{13}C NMR of **11** demonstrate that complex **11** is fluxional as are all the μ-alkyne adducts of **1** investigated to date.[2] At room temperature, all four Cp′ environments are identical, and the eight carbonyls give rise to only two ^{13}C NMR resonances. Similar behavior has been noted previously for $M_2(\mu\text{-}RC{\equiv}CR')$ adducts ($R \neq R'$).[2]

Further investigations of carbon-rich hydrocarbyl ligands are in progress.

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Supplementary Material Available: Tables of thermal parameters and complete bond distances and angles (8 pages); lists of F_o vs. F_c for $2{\cdot}BF_4$ and **11** (21 pages). Ordering information is given on any current masthead page.

Organometallic Compounds. 41.[1] [2]Metacyclo[2](1,1′)ferrocenophane

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[2]Metacyclo[2](1,1′)ferrocenophane (**1**), a standard organometallic system, was synthesized, and its crystal structure was determined by X-ray diffraction. Compound **1** crystallizes in the monoclinic system, space group $P2_1/a$, with unit-cell parameters a = 17.547 (9) Å, b = 5.914 (3) Å, c = 14.499 (7) Å, β = 92.3 (5)°, and Z = 4. The bond lengths and angles of the aromatic rings and methylene chains are normal. However, the two cyclopentadienyl (Cp) rings are tilted (dihedral angle 9.0°), and the bridge-carbon atoms linked directly to the Cp rings deviate considerably from the planes of the Cp rings (0.288 (9), 0.151 (9) Å) in the direction opposite to the iron atom. The benzene ring is situated to the side of the ferrocene nucleus, and the 9-hydrogen atom of the benzene ring is close to the iron atom of the ferrocene. The 9-proton signal in the ^1H NMR spectrum appears unusually downfield (δ 8.80) due to an anisotropic effect of the ferrocene nucleus. The electronic spectrum exhibits a large bathochromic shift of the d–d absorption band of the iron atom (λ_{max} = 470 nm). Attempted synthesis of [2]paracyclo[2](1,1′)ferrocenophane, which is more strained than **1**, was unsuccessful.

Introduction

A large number of monobridged (1,1′)ferrocenophanes[2,3] have been studied[4-6] since the discovery of ferrocene. Most of these are [*m*](1,1′)ferrocenophanes[4-6] which are intramolecularly linked with a carbon chain and [*m.n*](1,1′)-ferrocenohanes[4-10] which are intermolecularly bridged between two ferrocene nuclei. Recently, several (1,1′)-ferrocenophanes containing aromatic rings in the bridge were synthesized,[11,12] but there has been no report on [2]meta- and [2]paracyclo[2](1,1′)ferrocenophanes (**1** and **2**). By inspection of a Dreiding molecular model, the benzene ring of **1** is situated to the side of the ferrocene nucleus and the 9-hydrogen of the ring is unusually close to the iron atom of the ferrocene (ca. 2.4 Å). A space-filling (CPK) molecular model reveals that the 9-hydrogen and the ferrocene nucleus repel each other. This situation should cause a high strain and/or some distortion in the molecule. The ^1H NMR spectrum and the d–d absorption band in the electronic spectrum of **1** should reflect such an unusual molecular structure and show characteristic shifts. The magnetic anisotropy of ferrocene nucleus was

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[1] Part 40: Hisatome, M.; Watanabe, J.; Yamakawa, K.; Kozawa, K.; Uchida, T. *Nippon Kagaku Kaishi* **1985**, 572.

[2] The nomenclature of ferrocenophanes in this paper is according to that presented by Vögtle and Neumann.[3]

[3] Vögtle, F.; Neumann, P. *Tetrahedron* **1970**, *26*, 5847.

[4] Watts, W. E. *Organomet. Chem. Rev.* **1967**, *2*, 231.

[5] Kasahara, A. *Kagaku* **1983**, *38*, 859.

[6] Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702.

[7] Katz, T. J.; Slusarek, W. *J. Am. Chem. Soc.* **1980**, *102*, 1058.

[8] Barr, T. H.; Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1969**, *25*, 6001.

[9] (a) Rosenblum, M.; Brawn, N. M.; Clappenelli, D.; Tancrede, J. *J. Organomet. Chem.* **1970**, *24*, 469. (b) Kasahara, A.; Izumi, T. *Chem. Lett.* **1978**, 21. (c) Kasahara, A.; Izumi, T.; Shimizu, I. *Ibid.* **1979**, 1317.

[10] (a) Biernat, J. F.; Wilczewski, T. *Tetrahedron* **1980**, 36, 2521. (b) Sato, M.; Kubo, M.; Ebine, S.; Akabori, S. *Tetrahedron Lett.* **1982**, *23*, 185. (c) Czech, B.; Ratajczak, A.; Nagraba, K. *Monatsch. Chem.* **1982**, *113*, 965. (d) Izumi, T.; Tezuka, T.; Yusa, S.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2435.

[11] (a) Tanner, D.; Wennerstrom, O. *Acta Chem. Scand.* **1980**, *B34*, 529. (b) Kauffmann, K.; Ennen, J.; Lhotak, H.; Rensing, A.; Steinseifer, F.; Woltermann, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 328. (c) Shimizu, I.; Umezawa, H.; Kanno, T.; Izumi, T.; Kasahara, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2023.

[12] (a) Tanaka, S.; Sato, M.; Ebine, S.; Morinaga, K.; Akabori, S. 16th Symposium on Structural Organic Chemistry, Urawa, Japan, 1983; The Symposium Papers, p 289. (b) Sato, M.; Tanaka, T.; Ebine, S.; Morinaga, K.; Akabori, S. *J. Organomet. Chem.* **1985**, *289*, 91.

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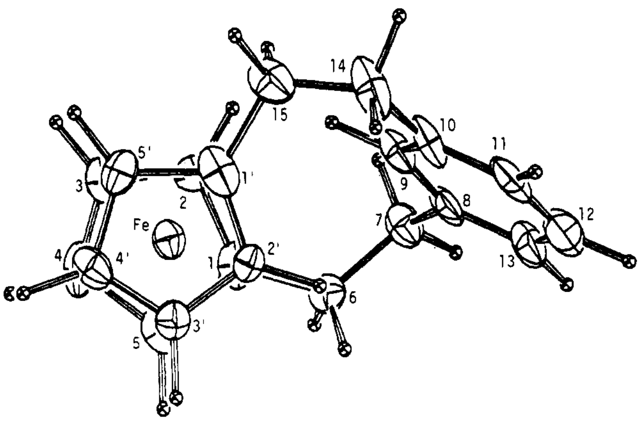
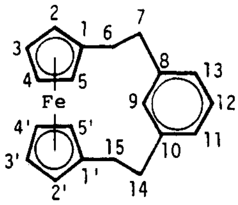


Figure 1. ORTEP drawing (30% probability thermal ellipsoids) of compound 1.

discussed by Turbit and Watts.[13] The actual sign and magnitude of the effect in the region close to the iron atom can be evaluated from the chemical shift of the 9-proton in the ^{1}H NMR spectrum of 1.

Paracyclophane 2 is even more highly strained than 1. The molecule cannot be constructed with molecular models. It should also have an unusual structure and spectroscopic behavior.



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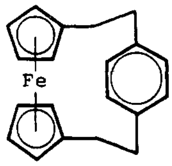


2

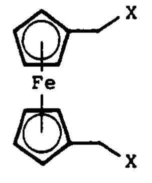
We attemted the synthesis of 1 and 2 via rearrangement of the corresponding precursor disulfides **7a** and **7b** and succeeded in obtaining 1 but not 2. This paper describes the synthesis, X-ray crystal structure, and spectral characterization of 1. The 6,15-dithia analogue of 1 was presented by Sato et al.[12] simultaneously with a preliminary report of this work[14] at the same symposium, but the X-ray crystal structure of the disulfide has not been investigated.

Results and Discussion

Synthesis. The method via cyclic sulfide, which is well-known as a convenient plane synthesis,[15-18] was applied to the present study. The sodium thiolate of dithiol **4**, prepared from diol **3**, was allowed to react with dibromide **5a** or **5b** in ethanol under high dilution conditions to give cyclic sulfide **7a** or **7b** in good yields (**7a**, 58%; **7b**, 75%) together with the intramolecularly bridged disulfide **8**. On the other hand, we found the coupling reaction of 1,3-bis(hydroxymethyl)ferrocene and dithiols **6** with trifluoroacetic acid (TFA) to give the corresponding cyclized disulfides.[19,20] Reaction of **3** with **6a** under the same conditions gave **7a** in a 40% yield, but coupling with **6b** afforded only macrocyclic sulfide **9**. The disadvantage in the acid-catalyzed reaction of **3** and **6b** to prepare **7b** is, possibly, due to the thermodynamical instability of **7b**.

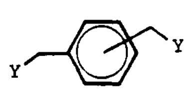
Table I. Bond Lengths (Å) of 1 with Estimated Standard Deviations in Parentheses

Fe-C(1)	2.131 (10)	C(2')-C(3')	1.399 (15)
Fe-C(2)	2.081 (11)	C(3')-C(4')	1.408 (18)
Fe-C(3)	2.015 (13)	C(4')-C(5')	1.475 (17)
Fe-C(4)	2.042 (12)	C(5')-C(1')	1.445 (17)
Fe-C(5)	2.083 (10)	C(1)-C(6)	1.484 (16)
Fe-C(1')	2.097 (10)	C(6)-C(7)	1.526 (16)
Fe-C(2')	2.058 (11)	C(7)-C(8)	1.524 (17)
Fe-C(3')	2.045 (11)	C(1')-C(15)	1.505 (16)
Fe-C(4')	2.038 (11)	C(15)-C(14)	1.468 (20)
Fe-C(5')	2.058 (11)	C(14)-C(10)	1.568 (20)
C(1)-C(2)	1.466 (17)	C(8)-C(9)	1.431 (18)
C(2)-C(3)	1.381 (16)	C(9)-C(10)	1.443 (18)
C(3)-C(4)	1.363 (18)	C(10)-C(11)	1.349 (21)
C(4)-C(5)	1.479 (18)	C(11)-C(12)	1.383 (21)
C(5)-C(1)	1.461 (15)	C(12)-C(13)	1.418 (20)
C(1')-C(2')	1.405 (18)	C(13)-C(8)	1.360 (19)



3: X=OH

4: X=SH

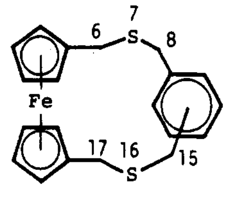


5: X=Br

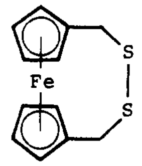
6: X=SH

a: meta

b: para



7a, b



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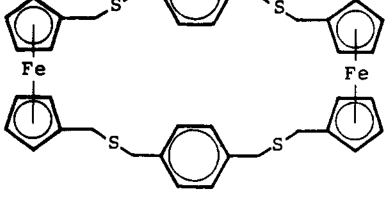

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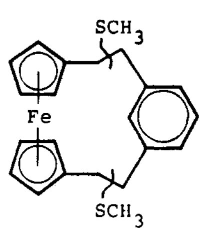

10

[2.2]Phanes can be generally prepared by Stevens rearrangement[15] via S-methylation of the corresponding sulfide with Boach reagent.[21] However, the methylation of **7a** and **7b** gave only complex mixtures but no sulfonium salt. Subsequently, Wittig rearrangement reported by Boekelheide et al.[16] for preparation of cyclophanes was

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(13) Turbitt, T. D.; Watts, W. E. *Tetrahedron* **1972**, *28*, 1227.

(14) Hisatome, M.; Yoshihashi, M.; Yamakawa, K.; Iitaka, Y. 16th Symposium on Structural organic Chemistry, Urawa, Japan, 1983; The Symposium Papers, p 293.

(15) (a) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1970**, *92*, 3510. (b) Boekelheide, V.; Hollins, R. A. *Ibid.* **1970**, *92*, 3512. (c) Umemoto, T.; Otsubo, T.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1973**, 593. (d) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547. (e) Mitchell, R. H.; Vinod, T. K.; Bushnell, G. W. *Ibid.* **1985**, *107*, 3340.

(16) (a) Mitchell, R. H.; Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 219. (b) Boekelheide, V.; Tsai, C.-H. *Tetrahedron* **1976**, *32*, 423.

(17) (a) Boekelheide, V.; Reingold, I. D.; Tuttle, M. *J. Chem. Soc., Chem. Commun.* **1973**, 406. (b) Bruhin, J.; Jenny, W. *Tetrahedron Lett.* **1973**, 1215. (c) Umemoto, T.; Otsubo, T.; Misumi, S. *Ibid.* **1974**, 1573. (d) Fukazawa, Y.; Aoyagi, M.; Ito, S. *Tetrahedron Lett.* **1978**, 1067.

(18) (a) Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 3881. (b) Otsubo, T.; Boekelheide, V. *J. Org. Chem.* **1977**, *42*, 1085. (c) Otsubo, T.; Kitasawa, M.; Misusmi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1515.

(19) Hisatome, M.; Yoshihashi, M.; Yamakawa, K.; Iitaka, Y. *Tetrahedron Lett.* **1983**, *24*, 5757.

(20) Czech, B.; Ratajczak, A. *Pol. J. Chem.* **1980**, *54*, 767.

(21) Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627.

Table II. Bond Angles (deg) of 1 with Estimated Standard Deviations in Parentheses

C(5)–C(1)–C(2)	106.4 (9)	C(7)–C(8)–C(9)	116.8 (10)
C(1)–C(2)–C(3)	108.4 (10)	C(7)–C(8)–C(13)	123.7 (10)
C(2)–C(3)–C(4)	110.8 (11)	C(5′)–C(1′)–C(15)	121.7 (11)
C(3)–C(4)–C(5)	109.3 (10)	C(2′)–C(1′)–C(15)	130.4 (11)
C(4)–C(5)–C(1)	105.0 (9)	C(1′)–C(15)–C(14)	117.4 (11)
C(5′)–C(1′)–C(2′)	107.7 (10)	C(15)–C(14)–C(10)	116.9 (12)
C(1′)–C(2′)–C(3′)	109.3 (10)	C(14)–C(10)–C(9)	115.0 (11)
C(2′)–C(3′)–C(4′)	109.9 (10)	C(14)–C(10)–C(11)	126.8 (12)
C(3′)–C(4′)–C(5′)	106.3 (10)	C(13)–C(8)–C(9)	119.5 (11)
C(4′)–C(5′)–C(1′)	106.7 (10)	C(8)–C(9)–C(10)	118.7 (11)
C(5)–C(1)–C(6)	123.1 (10)	C(8)–C(10)–C(11)	118.1 (12)
C(2)–C(1)–C(6)	129.3 (10)	C(10)–C(11)–C(12)	123.9 (13)
C(1)–C(6)–C(7)	120.0 (10)	C(11)–C(12)–C(13)	117.8 (13)
C(6)–C(7)–C(8)	112.9 (10)	C(12)–C(13)–C(8)	121.5 (12)

applied to the present system. Treatment of **7a** with lithium diisopropylamide (LDA) followed by addition of methyl iodide afforded a mixture of regioisomeric compounds **10** in an 18% yield. Desulfurization of **10** with Raney nickel gave the final compound 1 in a quantitative yield.

In the Wittig rearrangement of paracyclophanes, 1,6-elimination of the benzene moiety is apt to occur.[16,19] Accordingly, photochemical desulfurization[17,19,22] was attempted for **7b**. Sulfide **7b** was irradiated with a low- or high-pressure mercury lamp for 3–10 days. A slight amount of a low-polar compound that was presumed to be a desulfurization product of only one bridge was observed, but none of the desired compound **2** was observed. As predicted by inspection of molecular models, the structure of **2** may be too strained to be formed by means of the usual synthetic methods.

Crystal Structure. An ORTEP drawing of the molecular structure of 1 is shown in Figure 1. Bond lengths and bond angles are given in Tables I and II, respectively, and the other structural parameters are graphically illustrated in Figure 2.

The crystal analysis of 1 revealed some very interesting features that have not been found in other ferrocenophanes. The two side chains are on Cp ring carbons that are rotated ca. 70° about the Cp–Fe–Cp axis, and the ferrocene moiety is almost in the eclipse conformation. The benzene ring is asymmetrically placed at the side of the ferrocene nucleus, and the 9-hydrogen atom of the benzene ring is close to the 1-, 2-, and 1′-carbon and iron atoms of the ferrocene, 2.91 (9), 2.54 (9), 2.78 (9), and 3.01 (9) Å, respectively. The distances between the iron atom and the two Cp rings are not unusually (1.675 (6) and 1.663 (6) Å), but one of them is slightly extended in comparison with that of ferrocene.[23] The Cp rings are mutually tilted by 9° with the opening on the side of the bridge. The planality of each Cp ring is maintained, but the 6- and 15-carbons of the bridges deviate from the least-squares planes of the rings in the directions opposite to the iron atom (Figure 2a).

The benzene ring is in a chair conformation with the 9- and 12-carbons deviating from the least-squares plane through the 8-, 10-, 11-, and 13-carbons (Figure 2b). It is known that benzene skeletons of metacyclophanes[24] and the very crowded bis(2,4,6-tributylphenyl)phosphine chloride[25] are in boat forms. The behavior is supported by a theoretical calculation.[26] The chair conformation of the benzene ring in the present phane may be related to the proximity of the ring to the ferrocene nucleus, but the theoretical reasoning for the speculation has not yet been examined.

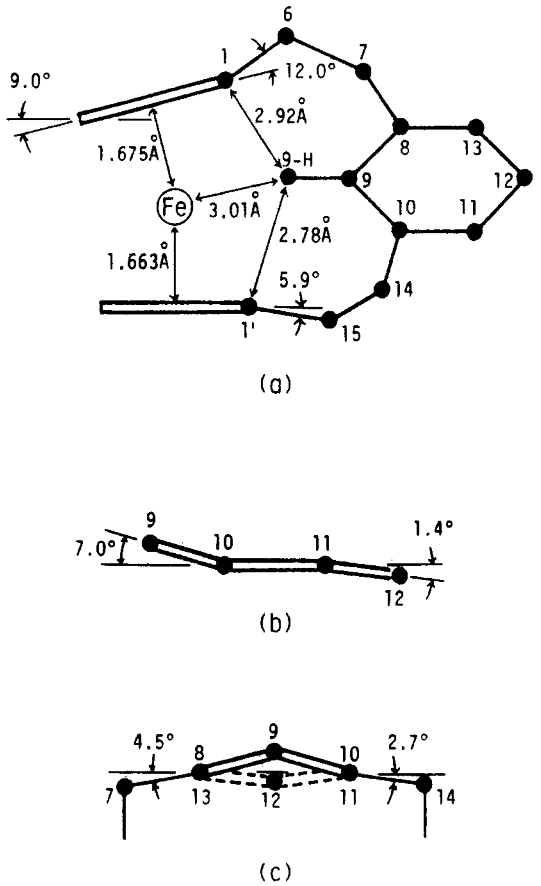

Figure 2. Selected structural parameters of compound 1.

Spectral Characterization. In the ^{1}H NMR spectrum of 1, a pronounced paramagnetic shift of the 9-proton on the benzene ring (δ 8.80) was observed, and the resonance signal is downfield by ca. 1.8 ppm than those of the 11-, 12-, and 13-positions. The 9-hydrogen is located on the side of the ferrocene nucleus near the iron atom, as mentioned above. Therefore, the unusual low-field shift should result from the magnetic effect of ferrocene nucleus through space. Turbit and Watts[13] gave a map of the shielding and deshielding zones according to the anisotropy around ferrocene molecule. The 9-proton is situated in the deshielding region of their map. The corresponding proton of the meta-substituted benzene ring in 6,15-dithia[2]-metacyclo[2](1,1′)ferrocenophane reported by Sato et al.[12] also has a resonance at an unusually low field (δ 8.92). Although there is no X-ray structural data of the sulfide, a Dreiding molecular model gives a conformation similar to that of 1. Recently, Musso et al.[27] reported on the ^{1}H NMR spectrum of 1,1′3,3′-tetramethyl-2,2′-bis(2,4,6-trimethylphenyl)ferrocene containing endo-methyl groups which are located on the side of the ferrocene nucleus. They found that the endo-2-methyl proton signal shifted

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(22) Corey, E. J.; Block, E. *J. Org. Chem.* **1969**, *34*, 1233.

(23) (a) Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta Crystallogr.* **1956**, *9*, 373. (b) Takusagawa, F.; Koetzle, T. F. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1074. (c) Seiler, P.; Dunitz, J. D. *Ibid.* **1979**, *B35*, 2020.

(24) (a) Kai, Y.; Yasuoka, N.; Kasai, N. *Acta Crystallogr., Sect. B.: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 754. (b) Hama, F.; Kai, Y.; Yasuoka, N.; Kasai, N. *Ibid.* **1977**, *B33*, 3905. (c) Jenneskens, L. W.; Klamer, J. C.; de Boer, H. J. R.; de Wolf, W. H.; Bickelhaupt, F.; Stam, C. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 238. (d) Shea, K. J.; Burke, L. D.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5305.

(25) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 399.

(26) (a) Iwamura, H.; Kihara, H.; Misumi, S.; Sakata, Y.; Umemoto, T. *Tetrahedron Lett.* **1976**, 615. (b) Yoshifuji, M.; Shima, I.; Inamoto, N.; Aoyama, T. *Ibid.* **1981**, *22*, 3057.

(27) Fuchs, B.; Fröhlich, R.; Musso, H. *Chem. Ber.* **1985**, *118*, 1968.

to lower field by 0.71 ppm than the 4-methyl protons. These results afford experimental evidence that the region close to the iron atom of ferrocene is strongly deshielding.[28]

The electronic spectrum of **1** exhibits a large bathochromic shift of the d–d absorption band in the visible region (470 nm), which is 32 nm higher than the same band in the spectrum of 1,1′-diethylferrocene. A bathochromic shift similar to that in **1** is observed in 6,15-dithia[2]metacyclo[2](1,1′)ferrocenophane (467 nm).[12] Barr and Watts[29] reported that the d–d band responded to a ring-tilt deformation of the ferrocene nucleus and shifted to a long wavelength with increasing dihedral angles between the two Cp rings. The pronounced shift of **1** cannot be explained only on the basis of tilting (dihedral angle 9°). The bands of [3]ferrocenophane derivatives having dihedral angles of abbout 10°[30] appear near 442 nm. Sato et al.[12] suggested that the large bathochromic shift of their dithia[2.2]phanes was caused by an interaction between the sulfur atom and the ferrocene nucleus. However, the present compound **1** contains no sulfur atom. One origin of the shift should be some change in the electronic configuration of the d orbital due to the proximity of the benzene ring to the ferrocene nucleus, but we do not yet have experimental or theoretical evidence for the assumption.

Experimental Section

NMR spectra were measured on a JEOL JNM-FX100 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) ionization at 70 eV unless otherwise stated. The molecular ions of sulfides **7a**, **7b**, and **9** were confirmed by means of field desorption (FD) ionizing technique because the EI-mass spectral pattern of dimer **9** could not be distinguished from that of **7b**. Empirical formulas 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.

Dichloromethane and ethanol used in the coupling reaction were distilled from CaH_2 and Na, respectively. Dioxygen in the solvents was removed as much as possible by ultrasonic vibration followed by bubbling dinitrogen or argon gas immediately before use.

1,1′-Bis(mercaptomethyl)ferrocene (4). A solution of PBr_3 (0.38 mL) in benzene (8 mL) was added dropwise to a solution of **3**[31] (600 mg) in benzene (60 mL) and THF (20 mL) containing pyridine (0.26 mL) at 0 °C under a dinitrogen atmosphere. The reaction mixture was stirred at room temperature for 1.5 h. Ethanol was added to the mixture, and the resulting yellow precipitate was removed by filtration. The filtrate was evaporated to dryness. Treatment of the residue with active carbon gave glossy brownish yellow crystals (1.1 g) which were sensitive to air: MS, *m/z* (relative intensity) 374, 372, and 370 (10, 22 and 12, respectively, M^+), 294 (20), 215 (27), 213 (30), 137 (22), 135 (25), 78 (100). The crude 1,1′-bis(bromomethyl)ferrocene was immediately used for the following reaction without further purification.

A solution of the dibromide (1.1 g) in THF (60 mL) was added dropwise to a boiling solution of thiourea (1.8 g) in THF (60 mL) under a dinitrogen atmosphere. The reaction mixture was refluxed for 1.5 h, and 10% aqueous NaOH (4 mL) was added. After the mixture was refluxed for 1.5 h, 10% hydrochloric acid was added followed by extraction with benzene. The extracts were washed with saturated aqueous Na_2CO_3 containing ascorbic acid, dried over Na_2SO_4, and evaporated. The residue was column chromatographed over silica gel with hexane–ether (9:1). The first yellow band yielded **4** (325 mg, 72% from **3**), a reddish orange oil: IR (liquid film) 2550 cm^{-1} (ν_{S-H}); ^1H NMR ($CDCl_3$) δ 1.75 (2 H, d, *J* = 7 Hz, –SH), 3.51 (4 H, d, *J* = 7 Hz, –CH_2–), 4.10 and 4.16 (each 4 H, an AA′BB′ system, Cp–H); MS, *m/z* 278 (36, M^+), 244 (100), 166 (97), 88 (25), 56 (18); mol wt calcd for $C_{12}H_{14}S_2Fe$ 278.9884, found M^+, 278.9882.

7,16-Dithia[3]metacyclo[3](1,1′)ferrocenophane (7a). (1) Coupling with Sodium Ethoxide. Two solutions of dibromide **5a** (48 mg) and sodium thiolate (**4**, 50 mg; sodium metal, 9 mg) in ethanol (each 12 mL) were prepared. Two milliliters each of the above solutions and 20 mL of ethanol were added at the same time to 120 mL of ethanol at intervals of 1 h. The procedures were carried out under argon atmosphere at room temperature. After all of both solutions were added, the reaction mixture was stirred for 1.5 h. Water was added, and the mixture was evaporated. The extracts of the residue with benzene–ether were washed with saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. The residue was column chromatographed over silica gel with hexane–dichloromethane (1:1). The first band yielded 7,8-dithia[4]ferrocenophane (**8**) (9 mg, 18%), which was recrystallized from hexane to give orrange–yellow plates: mp 99–100 °C; ^1H NMR ($CDCl_3$) δ 3.75 (4 H, s, –CH_2–), 4.16 and 4.24 (each 4 H, an AA′XX′ system, Cp–H); MS, *m/z* (relative intensity 276 (71, M^+), 244 (13), 212 (15), 198 (100), 134 (42). Anal. Calcd for $C_{12}H_{12}S_2Fe$: C, 52.19; H, 4.38; S, 23.22. Found: C, 52.23; H, 4.40; S, 23.04.

The second band yielded **7a** (39 mg, 58%), which was recrystallized from benzene–hexane to give orange-yellow flakes: mp 143–144 °C; ^1H NMR ($CDCl_3$) δ 3.29 (4 H, s, 6,17-H), 3.77 (4 H, s, 8,15-H), 3.83 and 4.00 (each 4H, an AA′XX′ system, Cp–H), 7.10–7.40 (3 H, m, 12,13,14-H), 7.63 (1 H, b s, 10-H); ^{13}C NMR ($CDCl_3$) δ 28.41 and 36.55 (methylene-C), 67.64, 69.88, and 86.25 (Cp–C), 128.26, 129.18, 130.84, and 138.34 (Ph–C); MS, *m/z* (relative intensity) 380 (100, M^+), 302 (36), 238 (20), 224 (21); FD-MS, *m/z* 380 (M^+). Anal. Calcd for $C_{20}H_{20}S_2Fe$: C, 63.16; H, 5.30; S, 16.86. Found: C, 63.39; H, 5.28; S, 16.83.

(2) Coupling with Trifluoroacetic Acid (TFA). Each solution of diol **3** (400 mg) and dithiol **6a** (276 mg) in dichloromethane (each 200 mL) was added dropwise from two dropping funnels to a solution of TFA (1.8 g) in dichloromethane (1200 mL) under a dinitrogen atmosphere at room temperature. The reaction mixture was stirred in the dark at room temperature for 18 h. Saturated aqueous $NaHCO_3$ was added, and the organic layer was phase-separated, washed with saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. Benzene was added to the residue, and the resulting insoluble material was removed by filtration. The filtrate was column chromatographed over silica gel with hexane–dichloromethane (1:1) to yield **7a** (256 mg, 41%).

7,16-Dithia[3]paracyclo[3](1,1′)ferrocenophane (7b). (1) Coupling with Sodium Ethoxide. The reaction was carried out according to the almost same procedure as that of **7a**. To 120 mL of ethanol were added 3 mL of a sodium thiolate solution (**4**, 120 mg; sodium metal, 120 mg; ethanol, 18 mL), 4 mL of a dibromide solution (**5b**, 114 mg; ethanol, 24 mL), and 40 mL of ethanol at invervals of 30 min. The reaction mixture was worked up, and the crude product was column chromatographed over silica gel with hexane–dichloromethane (1:1). The first eluted band yielded disulfide **8** (7 mg, 7%).

The second band yielded **7b** (102 mg, 75%), which was recrystallized from hexane–ethyl acetate to give yellow needles: mp 149–150 °C; ^1H NMR ($CDCl_3$) δ 3.19 (4 H, s, 6,17-H), 3.80 (4 H, s, 8,15-H), 3.75 and 3.95 (each 4 H, an AA′XX′ system, Cp–H), 7.80 (4 H, s, Ph–H); ^{13}C NMR ($CDCl_3$) δ 27.78 and 36.94 (methylene-C), 67.31, 71.25, and 85.92 (Cp–C), 130.52 and 137.88 (Ph–C); MS, *m/z* 380 (100, M^+), 302 (45), 244 (16), 224 (32), 198 (51), 166 (13), 134 (27), 104 (26), 88 (14); FD-MS, *m/z* 380 (M^+). Anal. Calcd for $C_{20}H_{20}S_2Fe$: C, 63.16; H, 5.30; S, 16.86. Found: C, 63.02; H, 5.57; S, 16.88.

(2) Coupling with TFA. The reaction was carried out according to the same procedure as that of **7a**. Each solution of **3** (600 mg) and **6b** (410 mg) in dichloromethane (each 300 mL) was added to a solution of TFA (2.8 g) in dichloromethane (1800 mL). The reaction mixture was stirred for 12 h and worked up. The crude product was column chromatographed over silica gel. The first band eluted with hexane–dichloromethane (1:1) yielded

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(28) In the case of bis(η^6-arene)metal complexes, the magnetic anisotropy of the sandwich unit was very recently established: Elschenbroich, C.; Schneider, J. *Organometallics* **1986**, *5*, 2091.

(29) Barr, T. H.; Watts, W. E. *J. Organomet. Chem.* **1968**, *15*, 177.

(30) Lecomte, P. C.; Dusausoy, Y.; Protas, J.; Moise, C.; Tirouflet, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 488.

(31) Rinehart, K. L., Jr.; Frerichs, A. K.; Kittle, P. A.; Westman, L. F.; Gustafson, D. H.; Pruett, R. L.; McMahon, J. E. *J. Am. Chem. Soc.* **1960**, *82*, 4111.

Table III. Crystal Data for 1

formula: $C_{20}H_{20}Fe$
mol wt: 316.2
cryst system: monoclinic
space group: $P2_1/a$
a = 17.547 (9) Å
b = 5.914 (3) Å
c = 14.499 (7) Å
β = 92.30 (5)°
Z = 4
V = 1503.4 Å^3
D_{calcd} = 1.402 g cm^{-1}
λ = 1.5418 Å (Cu Kα)
μ(Cu Kα) = 79.6 cm^{-1}

Table IV. Atomic Coordinates ($\times 10^5$ for Fe; $\times 10^4$ for C; $\times 10^3$ for H) and Isotropic Equivalent Thermal Parameters (Å^2) of 1 with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}
Fe	22038 (9)	27653 (30)	23621 (11)	3.46
C(1)	2599 (6)	3250 (22)	3757 (7)	4.43
C(2)	2757 (7)	963 (20)	3424 (7)	4.30
C(3)	2074 (7)	−24 (22)	3138 (8)	4.77
C(4)	1479 (7)	1398 (23)	3278 (7)	5.07
C(5)	1775 (6)	3577 (21)	3640 (7)	4.18
C(6)	3105 (6)	4820 (22)	4296 (7)	4.38
C(7)	3968 (7)	4492 (24)	4310 (8)	5.14
C(8)	4329 (6)	5426 (24)	3451 (8)	4.82
C(9)	4221 (6)	4143 (25)	2620 (8)	5.26
C(10)	4454 (6)	5120 (28)	1763 (9)	5.97
C(11)	4854 (6)	7067 (26)	1801 (9)	6.16
C(12)	4993 (7)	8297 (25)	2602 (11)	6.76
C(13)	4722 (6)	7406 (26)	3436 (9)	5.98
C(14)	4235 (7)	3706 (32)	877 (8)	7.23
C(15)	3614 (6)	2061 (26)	950 (7)	5.44
C(1′)	2839 (6)	2957 (26)	1170 (7)	5.13
C(2′)	2618 (6)	5116 (19)	1463 (7)	3.52
C(3′)	1821 (6)	5221 (20)	1465 (7)	4.09
C(4′)	1507 (6)	3110 (24)	1212 (8)	5.18
C(5′)	2156 (7)	1622 (21)	1020 (7)	4.73

atom	x	y	z
H(2)	322 (5)	12 (17)	342 (6)
H(3)	201 (6)	−179 (19)	285 (7)
H(4)	87 (5)	101 (16)	309 (6)
H(5)	143 (6)	511 (19)	381 (7)
H(6a)	291 (5)	472 (19)	500 (7)
H(6b)	297 (5)	645 (15)	399 (6)
H(7a)	423 (5)	537 (17)	492 (6)
H(7b)	411 (5)	268 (18)	436 (6)
H(9)	391 (5)	250 (19)	262 (6)
H(11)	503 (6)	776 (22)	112 (7)
H(12)	531 (5)	997 (19)	259 (6)
H(13)	482 (6)	837 (19)	410 (7)
H(14a)	479 (5)	284 (19)	68 (6)
H(14b)	410 (6)	499 (22)	35 (8)
H(15a)	355 (5)	103 (17)	33 (6)
H(15b)	376 (6)	86 (20)	155 (7)
H(2′)	300 (5)	653 (16)	165 (6)
H(3′)	149 (5)	671 (16)	166 (6)
H(4′)	89 (4)	268 (15)	114 (5)
H(5′)	211 (5)	−14 (17)	79 (6)

dimeric phane **9** (720 mg, 78%), which was recrystallized from benzene–ethyl acetate to give yellow needles: mp 166–167 °C; ^{1}H NMR ($CDCl_3$) δ 3.29 (8 H, s, $CpCH_2$–), 3.63 (8 H, s, $PhCH_2$–), 3.97 and 4.04 (each 8 H, an AA′BB′ system, Cp–H), 7.22 (8 H, s, Ph–H); ^{13}C NMR ($CDCl_3$) δ 30.46 ($CpCH_2$–), 36.06 ($PhCH_2$–), 68.37, 69.54, and 85.33 (Cp–C), 128.98 and 137.32 (Ph–C); MS, m/z (relative intensity) 760 (0, M$^+$), 380 (100), 302 (43), 224 (63), 224 (32), 198 (54), 166 (40), 134 (25), 104 (20), 88 (29); FD-MS, m/z 760 (M$^+$). Anal. Calcd for $C_{40}H_{40}S_4Fe_2$: C, 63.16; H, 5.30; S, 16.86. Found: C, 63.04; H, 5.29; S, 16.66.

[2]Metacyclo[2](1,1′)ferrocenophane (1). A solution (0.81 mL) of lithium diisopropylamide 0.65 mmol) in hexane–THF was added dropwise to a solution of **7a** (100 mg) in dry THF under an argon atmosphere at room temperature. To the resulting suspension was added dropwise methyl iodide (0.08 mL). The reaction mixture was stirred for 5 min, and water was added. The extract with dichloromethane was washed with saturated aqueous NaCl, dried over $CaCl_2$, and evaporated. The residue was column chromatographed over silica gel with hexane–dichloromethane (1:1). The first band yielded an unknown brown oil (7.6 mg). The second eluted component was rechromatographed over thin-layered silica gel with hexane–ether (40:1) to be separated into three bands. The lowest polar band yielded a mixture of the desired rearrangement products **10** (20 mg, 18%), a reddish brown oil: ^{1}H NMR ($CDCl_3$) δ 1.98, 2.03, 2.05, and 2.09 (6 H, each s, S–CH_3), 2.50–3.70 (6 H, m, methylene and methine-H), 3.80–4.20 (8 H, m, Cp–H), 7.00–7.50, 7.84, and 8.47 (4 H, m, Ph–H); mol wt calcd for $C_{22}H_{24}S_2Fe$ 408.0667, found M$^+$, 408.0661.

A suspension of **10** (30 mg) and active Raney nickel (W-7) in ethanol (10 mL) was refluxed for 30 min. The mixture was filtered, and evaporation of the filtrate afforded **1** (23 mg, 98%), which was recrystallized from methanol to give orange-yellow needles: mp 117–118 °C; ^{1}H NMR ($CDCl_3$) δ 2.84 and 2.93 (each 4 H, AA′BB′ system, methylene-H), 3.73 and 4.03 (each 4 H, AA′XX′ system, Cp-H), 6.90–7.25 (3 H, m, 11,12,13-H of Ph), 8.80 (1 H, b s, 9-H of Ph); ^{13}C NMR ($CDCl_3$) δ 27.39 (6,15-C), 32.02 (7,14-C), 65.59 and 69.83 (unsubstituted Cp-C), 90.15 (1,1′-C), 125.28 (11,13-C), 127.72 (9-C), 131.23 (12-C), 140.78 (8,10-C); MS, m/z (relative intensity) 316 (100, M$^+$), 238 (48), 180 (13). Anal. Calcd for $C_{20}H_{20}Fe$: C, 75.96; H, 6.37; Mol wt, 316.0912. Found: C, 75.67; H, 6.59; M$^+$, 316.0912.

Crystallographic Measurement. The yellow, platelike crystals of **1** were grown from a methanol solution. A crystal of dimensions 0.07 × 0.01 × 0.57 mm was used for data collection. The lattice parameters and intensity data were measured on a Phillips PW-1100 diffractometer by means of the θ–2θ scan method with a scan speed of 4° min^{-1} by using graphite-monochromated Cu Kα radiation. Crystal data are given in Table III. The intensities of 1454 independent reflections [$I_0 > 2\sigma(I_0)$] were obtained in the $6° \le 2\theta \le 120°$ range, corresponding to about 56% of the theoretically possible reflections within the same angular range. Lorentz and polarization corrections were made, but no absorption correction was applied.

The structure was solved by the heavy-atom method. Atomic coordinates of the Fe atom were deduced from the Patterson map, and all 20 carbon atoms were located in the Fourier map. The refinement was carried out by a block-diagonal-matrix least-squares procedure, and the final R value was reduced to 0.090. The final atomic parameters are shown in Table IV.

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Supplementary Material Available: Tables of temperature factors and deviations of atoms from least-squares planes through the Cp rings (2 pages); a listing of structure factors (6 pages). Ordering information is given on any current masthead page.