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Synthesis and Molecular Structure of $[4_5]$(1,2,3,4,5)Ferrocenophane ([4]Superferrocenophane)

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$[4_5]$(1,2,3,4,5)Ferrocenophane (**2**), which has been given the trivial name [4]superferrocenophane, was synthesized by the stepwise construction of a tetramethylene bridge via formation of a three-carbon bridge followed by bridge enlargement. The ^{1}H NMR spectrum of **2** showed two broad signals for the methylene resonances (δ 1.97 and 2.54). No other signal was present. In the ^{13}C NMR spectrum, only three signals were observed at δ 87.31, 28.66, and 25.12, which were assigned to the cyclopentadienyl rings and the α- and β-methylene carbons, respectively. The absorption band of d–d* transition in the visible region shifted to a considerably shorter wavelength (403 nm) as compared with that of ferrocene (443 nm). The crystal structure of **2** was determined by X-ray diffraction. Compound **2** crystallizes in the tetragonal system, space group $I\bar{4}2d$ with unit cell parameters $a = 15.453$ (8), $c = 18.968$ (10) Å, and $Z = 8$. The whole shape of **2** is nearly spherical. The thermal vibrations of the β-methylene carbons on the bridges are large and remarkably anisotropic. The distances between the β-carbon and the adjacent carbons are unusually short (1.286 (17)–1.420 (13) Å).

Introduction

A large number of interesting cage hydrocarbons have been synthesized in the two decades[3-7] since cubane was first prepared by Eaton.[8] The inner cavities of those molecules surrounded by the three-dimensional hydrocarbon framework are vacant. Some attempts have been made to entrap a metal ion or a small neutral atom into the cavity of such cage hydrocarbons,[9,10] but the desired "core compounds" have not yet been reported. Recently, a stable $C_{60}La$ cluster ion was observed in the photoionization mass spectrum of lanthanum-impregnated graphite substrates.[11,12] The cluster ion was expected to have a structure where a spheroidal carbon shell of C_{60} surrounds the metal atom, but there was no direct chemical characterization of the species. Cage metal complexes of cryptands[13] or Cram's carcerand[14] in which a small guest molecule is trapped in its interior may be classified in a different category (heterocyclic cage compounds) from the previously mentioned core hydrocarbons.

On the other hand, much effort has been made by several groups[15-21] to synthesize intramolecularly multibridged ferrocenophanes[22,23] wherein two cyclopentadienyl (Cp) rings of ferrocene are linked with polymethylene chains. Synthesis of ferrocenophane bridged with five polymethylene chains provides not only a ferrocene analogue of Boekelheide's "superphane"[5] but also an example of a cage hydrocarbon containing a metal in the center of the molecule. Several tribridged ferrocenophanes have been synthesized[15,16,19b] prior to 1978, but tetra- and pentabridged phanes have remained unknown. The descriptions[16,17,24] of the preparation of tetrabridged phanes with trimethylene chains have been revised after scrutiny[25,26] of the reaction or the X-ray crystal analysis of the product.[27]

Since a trimethylene chain proved too short to link two Cp rings of ferrocene without deformation, multilinking of ferrocene with trimethylene chains should produce too much strain. In $[3_2]$- and $[3_3]$ferrocenophanes, the deformations of the molecular structures such as tilting or shortening of the distance between the two Cp rings were found by X-ray crystal analysis.[27-30] By inspection of a

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[3] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

[4] (a) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520. (b) Irngartinger, H.; Goldmann, A.; Jahn, R.; Nixdorf, M.; Rodewald, H.; Maier, G.; Malsch, K.-D.; Emrich, R. *Ibid.* **1984**, *23*, 993.

[5] (a) Sekine, Y.; Brown, M.; Boekelheide, V. *J. Am. Chem. Soc.* **1979**, *101*, 3126. (b) Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65.

[6] (a) Eaton, P. E.; Or, Y. S.; Branca, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 2134. (b) Eaton, P. E.; Or, Y. S.; Branca, S. J.; Shankar, B. K. R. *Tetrahedron* **1986**, *42*, 1621.

[7] (a) Paquette, L. A.; Balogh, D. W.; Usha, R.; Kountz, D.; Christoph, G. G. *Science* **1981**, *211*, 575. (b) Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503. (c) Gallucci, J. C.; Doecke, C. W.; Paquette, L. A. *Ibid.* **1986**, *108*, 1343.

[8] Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157.

[9] Stinson, S. C. *Chem. Eng. News* **1982**, *60*(33), 25.

[10] Gladysz, J. A.; Fulcher, J. G.; Lee, S. J.; Bocarsley, A. B. *Tetrahedron Lett.* **1977**, 3421.

[11] Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smaller, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779.

[12] Cox, D. M.; Trevor, D. J.; Reichmann, K. C.; Kaldor, A. *J. Am. Chem.* **1986**, *108*, 2457.

[13] (a) Creaser, I. I.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181. (b) Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *Ibid* **1982**, *104*, 6016.

[14] Cram, D. J.; Karbach, S.; Kim, Y. H.; Baczynskj, L.; Kalleymeyn, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 2575.

[15] Rinehart, K. L., Jr.; Bublitz, D. E.; Gustafson, D. H. *J. Am. Chem. Soc.* **1963**, *85*, 970.

[16] Schlögl, K.; Peterlik, M. *Tetrahedron Lett.* **1962**, 573; *Monatsh, Chem.* **1962**, *93*, 1328.

[17] Vigo, F. M. Ph.D. Thesis, University of Illinois, Urbana, IL, 1969; *Diss. Abstr.* **1970–1971**, *31*, 598-B.

[18] Brown, A. D., Jr.; Winstead, J. A. *J. Org. Chem.* **1971**, *36*, 2832.

[19] (a) Hisatome, M.; Sakamoto, T.; Yamakawa, K. *J. Organomet. Chem.* **1976**, *107*, 87. (b) Hisatome, M.; Watanabe, N.; Sakamoto, T.; Yamakawa, K. *Ibid.* **1977**, *125*, 79.

[20] Hillman, M.; Gordon, B.; Weiss, A. J.; Guzikowski, A. P. *J. Organomet. Chem.* **1978**, *155*, 77.

[21] Hisatome, M.; Hillman, M. *J. Organomet. Chem.* **1981**, *212*, 217.

[22] The nomenclature of ferrocenophanes in the present paper is a modification of that presented by Vögtle and Neumann.[23]

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

[24] Hisatome, M.; Watanabe, N.; Yamakawa, K. *Chem. Lett.* **1977**, 743.

[25] Bublitz, D. E.; Rinehart, K. L., Jr. *Tetrahedron Lett.* **1964**, 827.

[26] Hisatome, M.; Watanabe, J.; Yamakawa, K. *J. Organomet. Chem.* **1984**, *266*, 159.

[27] Hillman, M.; Fujita, E. *J. Organomet. Chem.* **1978**, *155*, 99.

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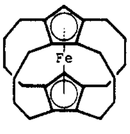
molecular model, tetramethylene chain appears long enough to bridge between the two Cp rings of ferrocene. Accordingly, preparation of fully bridged ferrocenophanes with tetramethylene chains was started. In this paper, synthesis of $[4_4]$(1,2,3,4)- and $[4_5]$(1,2,3,4,5)ferrocenophanes (1 and 2) is described in detail,[31] and the molecular structure of 2 as determined by X-ray diffraction are reported.



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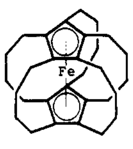


2

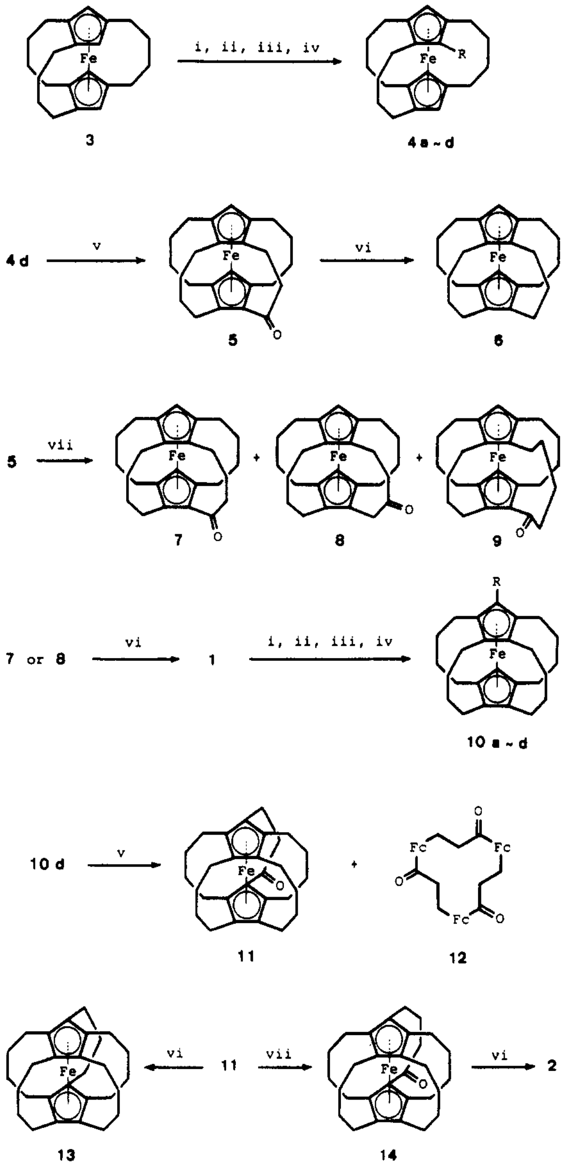
We proposed the trivial name "superferrocenophane"[31c] for a fully bridged ferrocenophane with five polymethylenes of the same length as the ferrocene analogue of Boekelheide's "superphane".[5] The compound 2 fully bridged with tetramethylene chains is then called [4]-superferrocenophane. The trivial name was already cited in the review by Mueller-Westerhoff[32] and in the book by Nickon and Silversmith.[33]

Results and Discussion

Synthesis. One-step formation of tetramethylene bridge by cyclization of ferrocenylbutyric acid is impossible because of the occurrence of selective homoannular cyclization.[34-36] Rosenblum et al.[37] prepared [4](1,1')-ferrocenophane by bridge enlargement of α-oxo[3](1,1')-ferrocenophane with diazomethane and methanol. The authors[19] synthesized several di- and tribridged ferrocenophanes containing tetramethylene chains by application of the bridge-enlargement method. Sterically hindered α-oxotrimethylene bridges adjacent to the other bridges could not be enlarged by the use of methanol as a catalyst, but we found that the treatment with diazomethane in the presence of BF_3 etherate in benzene as a solvent resulted in enlargement of such α-oxo bridges.[38] The starting material (3) of the present work was prepared by this modified method using BF_3 etherate.[38]

Another key step in the synthesis of $[4_5]$ferrocenophane was the bridging reaction of the propionic acid side chain. Use of trifluoroacetic anhydride (TFAA) as a condensation agent provided the most convenient method for bridging of a trimethylene chain until the third bridge.[19] The reagent did not work at all in forming the fourth bridge. Consequently, bridging reactions with various reagents were examined by using model compounds, and it was found that $ClCOOEt/Et_3N/AlCl_3$, polyphosphoric acid (PPA), and polyphosphoric acid ethyl ester (PPE) were suitable for multibridge formation.[39] Among these the reaction with PPE afforded the most favorable result for bridging of the sterically hindered side chain.

Scheme I. Synthesis of $[4_5]$Ferrocenophane (2) and Related Compounds[a]



[a] Fc = 5,5'-$[4_4]$(1,2,3,4)ferrocenophane. a, R = CHO; b, R = CH═CHCOOEt; c, R = CH_2CH_2COOEt; d, R = CH_2CH_2COOH. i, DMF/$POCl_3$ in chloroform; ii, $BrCH_2COOEt$/Zn in benzene; iii, H_2/PtO_2 in ethanol; iv, aqueous NaOH in ethanol; v, PPE in dichloromethane or 1,2-dichloroethane; vi, $LiAlH_4/AlCl_3$ in ether; vii, CH_2N_2/BF_3 etherate in benzene.

Thus, a synthetic route by stepwise construction of tetramethylene bridge via formation of three-carbon bridge followed by bridge enlargement was designed in order to synthesize 2 starting from the tribridged $[4_3]$(1,2,4)-ferrocenophane (3).[38,40]

The results are summarized in Scheme I. Formylation of 3 with dimethylformamide (DMF) and phosphorus oxychloride in chloroform afforded aldehyde **4a** (96%).

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(28) Paul, I. C. *J. Chem. Soc., Chem. Commun.* **1966**, 377.

(29) Hillman, M.; Fujita, E. *J. Organomet. Chem.* **1978**, *155*, 87.

(30) Spaulding, L. D.; Hillman, M.; Williams, G. J. B. *J. Organomet. Chem.* **1978**, *155*, 109.

(31) Portions of this work have been published as preliminary reports: (a) Hisatome, M.; Kawajiri, Y.; Yamakawa, K.; Iitaka, Y. *Tetrahedron Lett.* **1979**, 1777. (b) Hisatome, M.; Kawajiri, Y.; Yamakawa, K.; Harada, Y.; Iitaka, Y. *Ibid.* **1982**, *23*, 1713. (c) Histatome, M.; Watanabe, J., Yamakawa, K.; Iitaka, Y. *J. Am. Chem. Soc.* **1986**, 108, 1333.

(32) Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702.

(33) Nickon, A.; Silversmith, E. F. *Organic Chemistry: The Name Game*; Pergamon Press: New York, 1987; p 211.

(34) Rinehart, K. J., Jr.; Curby, R. J., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 3290.

(35) Rinehart, K. L., Jr.; Curby, R. J. Jr.; Gustafson, D. H.; Harrison, K. G.; Bozak, R. E.; Bublitz, D. E. *J. Am. Chem. Soc.* **1962**, *84*, 3263.

(36) Schlögl, K.; Fried, M. *Tetrahedron Lett.* **1963**, 1473.

(37) Rosenblum, M.; Banerjee, A. K.; Danieli, N.; Fish, R. W.; Schlatter, V. *J. Am. Chem. Soc.* **1963**, *85*, 316.

(38) Hisatome, M.; Kawajiri, Y.; Yamakawa, K. *J. Organomet. Chem.* **1982**, *226*, 71.

(39) Hisatome, M.; Watanabe, J.; Yamakawa, K.; Kozawa, K.; Uchida, T. *J. Organomet. Chem.* **1984**, *262*, 365.

(40) Hillman, M.; Fujita, E.; Dauplaise, H. *Organometallics* **1984**, *3*, 1170.

Condensation of **4a** with malonic acid and piperidine in pyridine, a conventional method for the preparation of acrylic acid from formyl derivative of ferrocenophane, afforded the corresponding acrylic acid only in extremely low yield (ca. 1%). The Reformatsky reaction of **4a** with ethyl bromoacetate and zinc produced acrylate **4b** in a good yield (89%). The acrylate **4b** was converted to propionic acid **4d** by catalytic hydrogenation followed by hydrolysis. Bridged ferrocenophane ketone **5** was obtained in a 54% yield by treatment of **4d** with PPE in dichloromethane, whereas the reaction with PPA or ClCOOEt/$Et_3N/AlCl_3$ (a mixed anhydride method)[31a] gave **5** in only 10 or 17% yield, respectively. The Cp ring protons in the ^1H NMR spectrum of **5** appeared at δ 3.75 and 4.09 as two singlets. The bridged structure of **5** was confirmed by NMR spectral characterization and X-ray crystal analysis[31a] of its reduction product **6**.

Treatment of **5** with diazomethane in benzene in the presence of BF_3 etherate afforded the three products **7**–**9** in 24, 37, and 3% yields, respectively. The mass spectra of **7** and **8** showed the molecular ion peak of the desired bridge-enlarged compound at m/z 416. Reduction of **7** and **8** with $LiAlH_4/AlCl_3$ afforded the same product **1**. The ^1H and ^{13}C NMR spectra of **1** showed only one singlet of the Cp ring protons (δ 3.88) and four methylene and three Cp ring carbon signals, respectively. These spectral patterns indicate a C_{2v} symmetric structure of **1**, which was determined by X-ray crystal analysis.[41]

Synthesis of propionic acid **10d** from **1** was carried out by the same procedure as that of **4d**. Cyclization of **10d** with PPE in dichloromethane afforded pentabridged product **11** and trimerized product **12** in 7 and 8% yields, respectively. The structure of the trimer **12** that was produced by intermolecular electrophilic substitution among three molecules of **10d** was determined by X-ray diffraction.[42] The yield of the pentabridged ferrocenophane ketone **11** was improved to the extent of 35%, when 1,2-dichloroethane was used as a solvent in place of dichloromethane and the reaction was carried out under high-dilution conditions. The trimer **12** was not produced under these conditions. In the ^1H NMR spectrum of **11**, no signal for the Cp ring proton was observed. Compound **13**, obtained by reduction of **11**, showed a ^{13}C NMR spectrum that indicated the presence of C_{2v} symmetry in the molecule; there appeared five and three signals that could be assigned to the methylene carbons and the Cp ring carbons, respectively. Attempted X-ray crystal analyses of **11** and **13** did not give well-defined structural evidence due to a rotational disorder about the Cp–Fe–Cp axis and additional disorder about the axis of 2-fold symmetry through the iron atom.[31b]

Insertion of a one-carbon unit into the oxotrimethylene bridge of **11** was unsuccessful by application of the reaction conditions we had developed for the bridge enlargement of the other multibridged ferrocenophanes.[38] This difficulty was finally overcome by using an excess of reagents and running the reaction under strict control. The dark violet solution, prepared by addition of 10 equiv of BF_3 etherate to ketone **11** in benzene, was stirred for 30 min. A large excess of diazomethane in ether, free from alcohol and moisture, was added to the solution of the aged complex. Chromatographic separation of the product yielded bridge-enlarged compound **14** though in low yield (18%). The mass spectrum of **14** showed the molecular ion of the desired α-oxo$[4_5]$ferrocenophane as the base peak at *m/z* 470. Reduction of **14** with $LiAlH_4/AlCl_3$ gave the ultimate target compound **2**. The ^1H NMR spectrum of **2** at 400 MHz showed two broad signals for the methylene resonances at δ 1.97 and 2.54. No other signal was present. The ^{13}C NMR spectrum, obtained under complete decoupling conditions, was dramatically simple as expected. Only three signals were observed at δ 87.31, 28.66, and 25.12. The crystal structure of **2** was determined by X-ray diffraction, as described below. Thus, we succeeded in the synthesis of $[4_5]$(1,2,3,4,5)ferrocenophane.

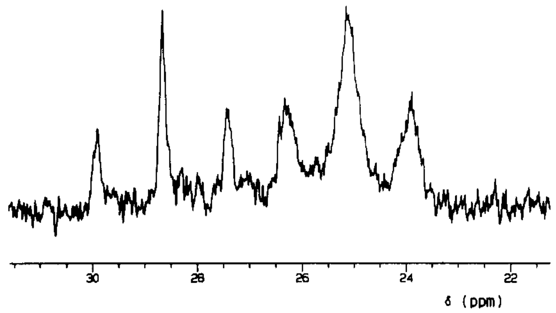

Figure 1. Methylene region of the proton-coupled ^{13}C NMR spectrum of **2** measured under conditions with NOE by a gated ^1H noise irradiation technique at 100.4 MHz.

Spectroscopic Characterization. Both the methylene protons and carbons on the bridge of $[4_5]$ferrocenophane (**2**) are separated into two signals in the NMR spectra. The separation should be based on the difference between the α- and β-positions on the bridge methylene. The methylene region of the proton-coupled ^{13}C NMR spectrum is shown in Figure 1. The triplet signal of the β-methylene carbons should further split into a quintet by long-range coupling with the four protons of the α-methylene and β′-methylene groups, whereas the α-methylene carbons should appear as a triple–triplet because of one adjacent methylene group. Therefore, the broader triplet at the high field in Figure 1 was assigned to the β-methylene carbons. Next, the ^{13}C NMR spectra was measured by a selective $^{13}C\{^1H\}$ decoupling technique. Irradiations of the proton signals at δ 1.97 and 2.54 sharpened the carbon signal at δ 25.12 and 28.66, respectively. These spectral studies revealed that the lower and higher field signals in both ^1H and ^{13}C NMR spectra were assigned to the α-methylene and β-methylene groups, respectively.

The methylene protons of **2** appeared as broad signals in the ^1H NMR spectrum at both 100 and 400 MHz. Below 10 °C both methylene signals broadened further, and the signal at the low field resolved to two peaks at −20 °C. When the spectrum was measured at 120 °C, the signals sharpened with the appearance of fine structure. Accordingly, the broadening of the signals at room temperature indicated that the conformational thermal motions of the methylene bridges are slow on the ^1H NMR time scale. This suggested that the five tetramethylene bridges are crowded together and the steric interaction between the bridges is considerable.

In the visible absorption spectrum of **2**, the band assigned to the d–d* transition of the iron shows a fairly large hypsochromic shift (403 nm) as compared with that of ferrocene (443 nm). We have found a linear relationship between the wavelength of the d–d* absorption and the number of the tetramethylene bridges in $[4_n]$-ferrocenophanes (n = 0–4).[43] This correlation holds for **2**, as shown in Figure 2. Such a pronounced hyposo-

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[41] Kawajiri, Y. Ph.D. Thesis, Science University of Tokyo, Tokyo, 1983.

[42] Hisatome, M.; Kawajiri, Y.; Yamakawa, K.; Mamiya, K.; Harada, Y.; Iitaka, Y. *Inorg. Chem.* **1982**, *21*, 1345.

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

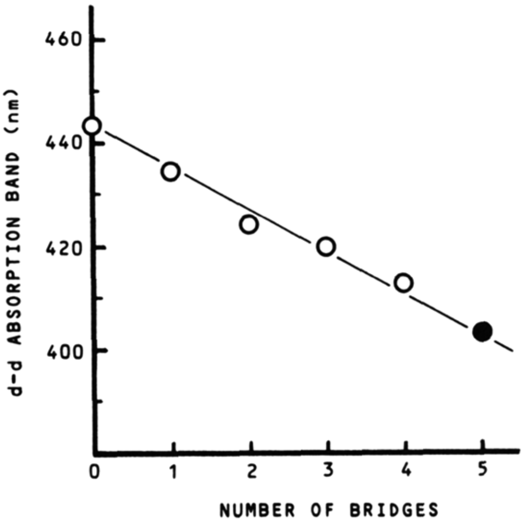

Figure 2. Correlation of d–d* absorption band shifts with the number of bridges in [4_n]ferrocenophanes. The black circle is for [4_5]ferrocenophane **2**.

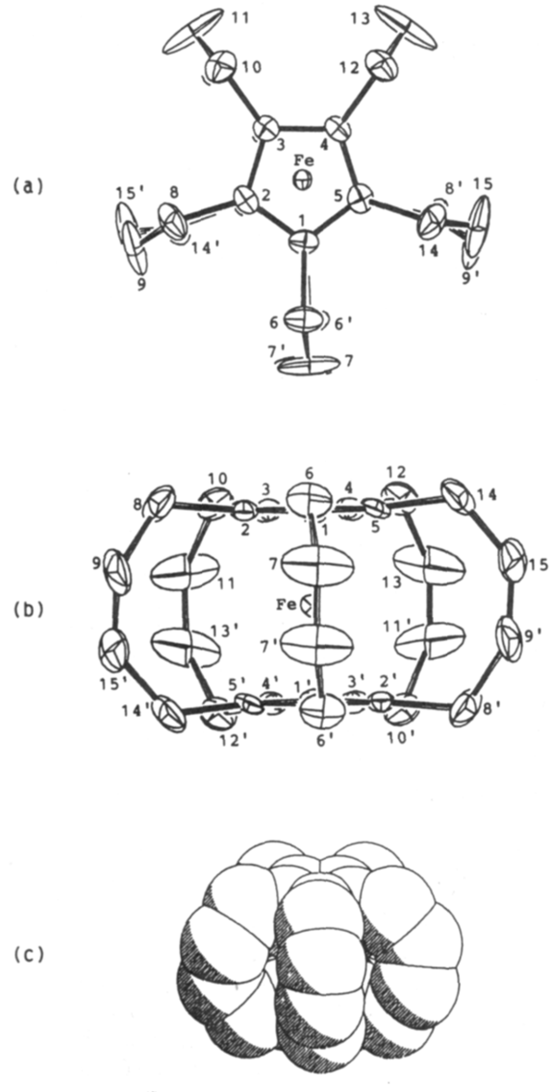

Figure 3. ORTEP[45] drawings of **2** projected on the Cp ring (a) and on the side of the molecule (b) and space-filling representation by PLUTO[46] drawing (c).

Table I. Atomic Coordinates (×10⁵ for Fe, ×10⁴ for C) and Equivalent Isotopic Thermal Parameters (Å²) of 2 with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq}
Fe	5642 (6)	0	0	2.03
C(1)	1351 (4)	−739 (4)	601 (3)	3.5
C(2)	809 (4)	−1268 (4)	187 (3)	3.0
C(3)	−89 (4)	−1062 (3)	347 (3)	3.0
C(4)	−66 (4)	−402 (3)	878 (3)	3.0
C(5)	820 (4)	−210 (4)	1034 (2)	3.3
C(6)	2323 (5)	−834 (6)	642 (4)	5.6
C(7)	2899 (4)	−292 (9)	260 (6)	10.2
C(8)	1069 (6)	−2006 (4)	−307 (4)	5.7
C(9)	1392 (9)	−1850 (6)	−1020 (4)	9.0
C(10)	−873 (5)	−1523 (4)	75 (5)	5.0
C(11)	−1327 (7)	−1260 (8)	−550 (7)	11.9
C(12)	−847 (4)	−58 (7)	1272 (3)	5.0
C(13)	−1321 (7)	689 (9)	1039 (6)	12.5
C(14)	1132 (6)	375 (6)	1617 (3)	5.5
C(15)	1201 (10)	1295 (7)	1552 (5)	10.3

Equivalent Positions (Origin at 212_1) (0,0,0; $^1/_2$,$^1/_2$,$^1/_2$)⁺

X	Y	Z
Y	$^1/_2 + X$	$^1/_4 + Z$
$-X$	$-Y$	$^1/_2 + Z$
$-Y$	$^1/_2 - X$	$^3/_4 + Z$
X	$-Y$	$-Z$
Y	$^1/_2 - X$	$^3/_4 - Z$
$-X$	Y	$^1/_2 - Z$
$-Y$	$^1/_2 + X$	$^1/_4 - Z$

Table II. Bond Lengths (angstroms) of 2 with Estimated Standard Deviations in Parentheses

bond	length	bond	length
Fe–C(1)	2.021 (6)	C(2)–C(8)	1.530 (9)
Fe–C(2)	2.027 (6)	C(8)–C(9)	1.461 (12)
Fe–C(3)	2.037 (6)	C(9)–C(15′)	1.356 (13)
Fe–C(4)	2.027 (5)	C(3)–C(10)	1.496 (10)
Fe–C(5)	2.026 (5)	C(10)–C(11)	1.437 (15)
C(1)–C(2)	1.409 (8)	C(11)–C(13′)	1.286 (17)
C(2)–C(3)	1.456 (9)	C(4)–C(12)	1.515 (10)
C(3)–C(4)	1.433 (7)	C(12)–C(13)	1.431 (16)
C(4)–C(5)	1.432 (9)	C(13)–C(11′)	1.286 (17)
C(5)–C(1)	1.419 (8)	C(5)–C(14)	1.507 (9)
C(1)–C(6)	1.512 (9)	C(14)–C(15)	1.432 (14)
C(6)–C(7)	1.420 (13)	C(15)–C(9′)	1.356 (13)
C(7)–C(7′)	1.336 (17)		

Table III. Bond Angles (degrees) of 2 with Estimated Standard Deviations in Parentheses

bonds	angle	bonds	angle
C(5)–C(1)–C(2)	108.2 (5)	C(4)–C(5)–C(14)	125.6 (5)
C(1)–C(2)–C(3)	108.9 (5)	C(1)–C(5)–C(14)	125.8 (6)
C(2)–C(3)–C(4)	106.1 (5)	C(1)–C(6)–C(7)	122.7 (7)
C(3)–C(4)–C(5)	108.5 (5)	C(6)–C(7)–C(7′)	140.7 (10)
C(4)–C(5)–C(1)	108.3 (5)	C(2)–C(8)–C(9)	122.3 (7)
C(5)–C(1)–C(6)	126.9 (6)	C(8)–C(9)–C(15′)	135.9 (10)
C(2)–C(1)–C(6)	124.2 (6)	C(3)–C(10)–C(11)	123.0 (8)
C(1)–C(2)–C(8)	128.1 (5)	C(10)–C(11)–C(13′)	142.0 (11)
C(3)–C(2)–C(8)	122.8 (5)	C(4)–C(12)–C(13)	122.5 (8)
C(2)–C(3)–C(10)	126.6 (5)	C(12)–C(13)–C(11′)	141.4 (12)
C(4)–C(3)–C(10)	126.9 (6)	C(5)–C(14)–C(15)	123.8 (8)
C(3)–C(4)–C(12)	125.2 (5)	C(14)–C(15)–C(9′)	135.1 (11)
C(5)–C(4)–C(12)	125.9 (5)		

chromic shift of the d–d* band was not observed in 1,1′-diethylferrocene (440 nm) and homoannularly cyclized [4](1,2)[4](1′,2′)ferrocenophane (440 nm). Consequently, the successive shift to the short wavelength with the increase in *n* of [4_n]ferrocenophanes cannot be caused by the alkyl substituent effect alone, but also delicate deformations of the ferrocene nucleus caused by the bridging must be responsible, although the differences in the molecular structures of [4_n]ferrocenophanes may not be great.[44] We have not yet found a definitive explanation for the cause of the regular shift of the band.

X-ray Crystal Structure. The crystal structure of **2** was determined by X-ray diffraction analysis. The structural parameters are given in Tables I–III. The molecular structure, in which each atom is drawn by a thermal ellipsoid of 30% probability, is shown in Figure 3a,b. The phane **2** in the crystal has a c_2 axis through the iron atom and the middle point of the β- and β'-carbon bond of one bridge. Accordingly, the numbering system of the atoms shown in Figure 3 is used in this section.

The thermal vibrations of the atoms of the ferrocene nucleus are small and almost isotropic, but those of the bridge atoms, especially the β-carbon atoms (e.g., C(7), C(7')), are large and remarkably anisotropic, the major axes being directed almost perpendicularly to the C_β–$C_{\beta'}$ bonds. Whereas the distances of the C_{Cp}–C_{Cp} or C_{Cp}–C_α bonds are in the normal range, those between the β-carbon and α- or β'-carbons are unusually short (Table II). The bond angles around the β-carbons are too large for that of the sp^3 carbon (Table III). The anomalous behavior of the structural parameters concerning the β-carbons is a result of the anisotropic thermal motions and/or static disorders of the bridging carbons in the crystal. In fact, if one calculates the C_β–$C_{\beta'}$ distances by taking the positions of the C_β and $C_{\beta'}$ atoms, not at the center of the ellipsoid but shifted in the direction opposite to each other within their thermal ellipsoids, one can find the positions that give a normal C–C bond length.[47]

The Cp rings are stacked almost parallel to each other and are in an eclipsed conformation about the Cp–Fe–Cp axis. The distance between the Cp ring and iron atom is 1.622 (3) Å, which is slightly smaller than that found in [4$_4$]ferrocenophane (**1**, 1.630 (2) Å).[41] The Cp rings show a good planarity, and the derivations of the Cp carbon atoms from its own least-squares plane are less than 0.006 Å.[48] On the other hand, all the α-carbons linked to the Cp ring deviate by 0.127 (6)–0.160 (5) Å from this plane in the direction opposite to the iron atom. The magnitude of the exo deviation of the α-carbon depends on the length and conformation of the bridge.[31,39,41–43,49] The large exo deviation of the α-carbons is characteristic of the tetramethylene bridges having a zigzag conformation, while the α-carbons of tetramethylene bridges having a boat form deviate only slightly from the Cp ring plane.[39,49] Therefore, all the bridges of **2** probably take a zigzag conformation, although it is not visible in the ORTEP drawings of Figure 3. The suggested conformation was supported by the results of molecular dynamic calculations, which were published elsewhere.[47]

The entire shape of [4$_5$]ferrocenophane (**2**) is nearly spherical as shown in Figure 3c. The compound has been reviewed in *Chem. Eng. News*[50] as "the molecule resembles a beachball squashed in at both ends".

Experimental Section

All melting points were uncorrected. IR spectra were measured by using a Hitachi Model 215 grating infrared spectrometer. NMR spectra were measured on a JEOL JNM-FX100 spectrometer relative to tetramethylsilane as an internal standard, unless otherwise stated. ^{1}H and ^{13}C NMR spectra at 400 and 100.4 MHz, respectively, were measured by using a JEOL JNM-GX400 spectrometer. 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. Empirical formulas of oily or unstable compounds were determined by high-resolution mass spectra, which were analyzed on a Hitachi M-003 data processing system.

3-Formyl[4$_3$](1,2,4)ferrocenophane (4a). A solution of [4$_3$](1,2,4)ferrocenophane (**3**,[38] 314 mg) and dimethylformamide (329 mg) in freshly distilled chloroform (9 mL) was stirred for 10 min at 0 °C under a nitrogen atmosphere. To the cooled mixture phosphorus oxychloride (690 mg) was added dropwise. The reaction mixture was stirred for 5 h at 50–55 °C under a nitrogen atmosphere and then evaporated to dryness. Water was added to the residue, and the aqueous mixture was neutralized with aqueous 10% NaOH. The mixture was extracted with ether several times, and the extracts were washed with saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. The residue was column chromatographed over alumina by using hexane/acetone (20:1) as an eluent. The first band yielded the starting material **3** (7 mg, 2%). The second band yielded formylated product **4a** (327 mg, 96%), which was recrystallized from hexane to give deep red granules: mp 103–105 °C; IR (KBr) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50–3.00 (24 H, m, CH_2), 3.92 and 4.09 (each 1 H, an AX system, J = 1.6 Hz, 3'- and 5'-H), 4.41 (1 H, s, 5-H), 10.45 (1 H, s, CHO); mass spectrum, m/z (rel intensity) 376 (100, M^+), 347 (10). Anal. Calcd for $C_{23}H_{28}OFe$: C, 73.41; H, 7.50. Found: C, 73.22; H, 7.51.

Ethyl [4$_3$](1,2,4)Ferrocenophane-3-acrylate (4b). To a solution of aldehyde **4a** (290 mg) in dry benzene (10 mL) and dry ether (2 mL) was added activated zinc powder (1.0 g) and a small amount of iodine (10 mg), and the mixture was stirred at room temperature under a nitrogen atmosphere. Ethyl bromoacetate (257 mg) was added dropwise, and the resulting mixture was refluxed for 10 min. The reaction mixture was quenched with water, and the hydrolyzate was phase separated. The organic layer was washed with 6 N HCl and then saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. The residue was column chromatographed over alumina by using hexane/acetone (30:1) as an eluent. A red band yielded acrylate **4b** (307 mg, 89%) as a red oil: IR (neat) 1710, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (3 H, t, J = 7.2 Hz, CH_3), 1.50–2.80 (24 H, m, CH_2), 3.80 and 3.89 (each 1 H, an AX system, J = 1.6 Hz, 3'- and 5'-H), 4.24 (1 H, s, 5-H), 4.25 (2 H, q, J = 7.2 Hz, OCH_2), 6.09 and 7.90 (each 1 H, an AX system, J = 16 Hz, olefin H); mass spectrum, m/z (rel intensity) 446 (100, M^+), 418 (8), 373 (5); high-resolution mass calcd for $C_{27}H_{34}O_2Fe$ 446.1905, found 446.1890.

Ethyl [4$_3$](1,2,4)Ferrocenophane-3-propionate (4c). Acrylate **4b** (307 mg) was reduced with H_2 gas (3.5 atm) and 10% Pd–C (40 mg) in ethanol (50 mL) for 10 h at room temperature. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in benzene, and the solution was washed with saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. The residual crude product was subjected to column chromatographic purification over alumina with hexane/acetone (30:1) to give propionate **4c** (299 mg, 97%) as a yellow oil: IR (neat) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (3 H, t, J = 7.2 Hz, CH_3), 1.50–3.15 (28 H, m, CH_2), 3.57 and 3.87 (each 1 H, an AX system, J = 1.5 Hz, 3'- and 5'-H), 3.92 (1 H, s, 5-H), 4.13 (2 H, q, J = 7.2 Hz, OCH_2); mass spectrum, m/z (rel intensity) 448 (100, M^+), 420 (3), 347 (9); high-resolution mass calcd for $C_{27}H_{36}O_2Fe$ 448.2063, found 448.2064.

[4$_2$]-α-Oxo[3][4](1,2,3,4)ferrocenophane (5). Propionate **4c** (286 mg) was dissolved in ethanol (50 mL), and 20% aqueous NaOH (20 mL) was added to the solution. The resulting solution was stirred for 10 min at 80 °C. After the reaction mixture was neutralized with 6 N HCl, the hydrolyzate was extracted with dichloromethane. The extracts were washed with saturated aqueous NaCl, dried over $CaCl_2$, and evaporated. The residue was a yellow crystalline solid (255 mg, mp 51–68 °C) which was sensitive to air in solvent; IR (KBr) 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40–3.00 (28 H, m, CH_2), 3.62 (1 H, br s, Cp H), 3.95 (2 H, br s, Cp H). The crude [4$_3$](1,2,4)ferrocenophane-3-propionic acid (**4d**) was immediately used for the following reaction without further purification.

To a solution of acid **4d** (500 mg) in dichloromethane was added ethyl polyphosphate ester (PPE, 10 mL), which was prepared in

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(44) The Cp–Fe–Cp distances and dihedral angles of the two Cp rings: **1**, 3.26 Å and 1.5°,[41] **2**, 3.24 Å and 0° (this work); **3**, 3.25 and 3.26 Å, and 4.5° and 5.0°.[40]

(45) Johnson, C. K. ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1970.

(46) Motherwell, W. D. S. PLUTO, A Program for Drawing Crystal and Molecular Structures, Cambridge Crystallographic Data Centre, Cambridge CB21EW, England, 1983.

(47) Rudzinski, J. M.; Osawa, E.; Hisatome, M.; Watanabe, J.; Yamakawa, K. *J. Phys. Org. Chem.* **1989**, *2*, 602.

(48) Supplementary material.

(49) Hisatome, M.; Kawajiri, Y.; Yamakawa, K.; Kozawa, K.; Uchida, T. *J. Organomet. Chem.* **1982**, *236*, 359.

(50) *Chem. Eng. News* **1986**, *64*(14), 16.

the usual way.[51] The reaction mixture was stirred for 5 min at 100 °C under a nitrogen atmosphere. The reaction mixture was quenched with water, and the aqueous mixture was neutralized with 10% aqueous NaOH containing ascorbic acid and extracted with benzene. The extracts were washed with saturated aqueous NaCl, dried over Na_2SO_4 and evaporated. To a solution of the residual oil in dichloromethane was added a solution of diazomethane in ether to esterify the starting acid. The mixture was evaporated and the residue was chromatographed over thin-layered silica gel in a preparative scale with benzene. The first band yielded a mixture of methyl and ethyl esters of the starting material (66 mg) as a yellow oil. The second, third, and fourth bands yielded unidentifiable orange–yellow oils. The fifth band yielded the desired product **5** (257 mg, 54%), which was recrystallized from hexane to give yellow needles: mp 175 °C (dec); IR (KBr) 1659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30–3.75 (28 H, m, CH_2), 3.95 (1 H, s, 5-H), 4.09 (1 H, s, 5′-H); ^{13}C NMR ($CDCl_3$) δ 21.90, 22.25, 22.54, 23.01, 26.13, 26.36, 26.54, 27.30, 27.95, 28.06, 28.36, 28.94 and 48.79 (methylene-C), 69.98 and 72.10 (unsubstituted Cp C), 72.98, 82.49, 84.19, 85.37, 85.83, 86.66, 87.60 and 88.89 (substituted Cp C), 213.06 (carbonyl C); mass spectrum, *m/z* (rel intensity) 402 (100, M$^+$), 372 (3). Anal. Calcd for $C_{25}H_{30}OFe$: C, 74.63; H, 7.52. Found: C, 74.38; H, 7.73.

[4$_2$][3][4](1,2,3,4)Ferrocenophane (6). To a suspension of $AlCl_3$ (51 mg) and $LiAlH_4$ (15 mg) in dry ether (7 mL) was added dropwise a solution of ketone **5** (31 mg) in benzene/ether (5:3, 8 mL) under a nitrogen atmosphere. The reaction mixture was stirred for 20 min at room temperature. The reaction was quenched with a mixture of ether and water, and the organic layer was washed with saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. The residue was column chromatographed over alumina with hexane/acetone (30:1). The first band yielded ferrocenophane **6** (19 mg, 65%), which was recrystallized from hexane to give yellow needles: mp 234–236 °C; ^{1}H NMR ($CDCl_3$) δ 1.50–2.60 (30 H, m, CH_2), 3.91 (2 H, s, Cp H); ^{13}C NMR ($CDCl_3$) δ 18.91, 21.49, 22.46, 27.00, 27.68, 28.60, 29.38 and 35.77 (methylene C), 69.05 (unsubstituted Cp C), 81.23, 83.47, 85.42 and 86.35 (substituted Cp C); mass spectrum, *m/z* (rel intensity) 388 (100, M$^+$), 360 (5). Anal. Calcd for $C_{25}H_{32}Fe$: C, 77.32; H, 8.30. Found: C, 77.40; H, 8.41.

Bridge Enlargement of Ketone 5. To a solution of ketone **5** (77 mg) in dry benzene (5 mL) was added 47% BF_3 etherate (0.037 mL) under a nitrogen atmosphere, and the mixture was stirred for 1 h at room temperature. A large excess of an ether solution of diazomethane (50 mL), free from alcohol and moisture, was rapidly added to the solution of the complex. The reaction mixture was stirred for 5 min at room temperature. The reaction was quenched with water containing ascorbic acid, and the organic layer was washed with saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. The residue was chromatographed over thin-layered silica gel with benzene. The first band yielded [4$_2$]-β-oxo[4][4](1,2,3,4)ferrocenophane **8** (29 mg, 37%), which was recrystallized from hexane/ethyl acetate to give sublimable yellow needles: mp 259–261 °C (dec, in a sealed tube); IR (KBr) 1696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50–3.25 (28 H, m, CH_2), 3.31 (2 H, s, isolated CH_2), 3.90 and 3.94 (each 1 H, s, Cp H); ^{13}C NMR ($CDCl_3$) δ 25.60, 25.89, 26.01, 26.60, 26.77, 26.95, 27.07, 27.48, 27.59, 41.27 and 45.97 (methylene C), 68.40 (substituted Cp C), 77.15, 83.37, 83.84, 84.01 and 84.60 (substituted Cp C), 212.06 (carbonyl C); mass spectrum, *m/z* (rel intensity) 416 (100, M$^+$), 388 (7). Anal. Calcd for $C_{26}H_{32}OFe$: C, 75.00; H, 7.75. Found: C, 75.37; H, 7.91.

The second band yielded the starting material **5** (19 mg, 24%). The third band yielded [4$_2$]-α-oxo[5][4](1,2,3,4)ferrocenophane **9** (2.3 mg, 3%), which was recrystallized from ethyl acetate to give sublimable orange prisms: mp 262–264 °C (dec, in a sealed tube); IR (KBr) 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30–3.20 (32 H, m, CH_2), 3.88 and 4.21 (each 1 H, s, Cp H); ^{13}C NMR ($CDCl_3$) δ 22.96, 24.13, 24.42, 24.78, 24.89, 25.66, 26.13, 26.48, 27.24, 27.83, 28.71, 29.36 and 39.45 (methylene C), 69.04 and 73.56 (unsubstituted Cp C), 77.03, 82.08, 82.37, 84.36, 84.48, 87.48, 87.89 and 89.59 (substituted Cp C), 209.54 (carbonyl C); MS, *m/z* (rel intensity) 430 (M$^+$, 100), 402 (8). Anal. Calcd for $C_{27}H_{34}OFe$: C, 75.35; H, 7.96. Found: C, 75.42; H, 7.91.

The fourth band yielded [4$_2$]-α-oxo[4][4](1,2,3,4)ferrocenophane **7** (19 mg, 24%), which was recrystallized from hexane/ethyl acetate to give sublimable yellow needles: mp 259–261 °C (in a sealed tube); IR (KBr) 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50–3.10 (30 H, m, CH_2), 3.95 and 4.19 (each 1 H, s, Cp H); ^{13}C NMR ($CDCl_3$) δ 24.07, 26.07, 26.30, 27.24, 27.41, 27.71, 27.89, 31.88 and 43.50 (methylene C), 70.04 and 72.62 (unsubstituted Cp C), 81.14, 83.66, 84.31, 84.83, 85.13, 86.60 and 87.53 (substituted Cp C), 208.65 (carbonyl C); mass spectrum *m/z* (rel intensity) 416 (100, M$^+$), 388 (5). Anal. Calcd for $C_{26}H_{32}OFe$: C, 75.00; H, 7.75. Found: C, 75.01; H, 7.77.

[4$_4$](1,2,3,4)Ferrocenophane (1). (1) Reduction of α-ketone **7** (26 mg) with $LiAlH_4$ (7 mg) and $AlCl_3$ (21 mg) in bezene/ether (1:4, 10 mL) was carried out according to the same procedure as in the preparation of **6**. Column chromatographic purification of the crude product over alumina with hexane/ethyl acetate (40:1) afforded ferrocenophane **1** (24 mg, 95%), which was recrystallized from hexane to give sublimable yellow plates: mp 258–259 °C (dec, in a sealed tube); ^{1}H NMR ($CDCl_3$) δ 1.70–2.65 (32 H, m, CH_2), 3.88 (2 H, s, Cp H); ^{13}C NMR ($CDCl_3$) δ 26.27, 27.05, 27.39 and 27.83 (methylene C), 68.42 (unsubstituted Cp C), 82.79 and 83.77 (substituted Cp C); λ_{max} (THF) 413 nm (ϵ = 107); mass spectrum, *m/z* (rel intensity) 402 (100, M$^+$), 374 (5). Anal. Calcd for $C_{26}H_{34}Fe$: C, 77.61; H, 8.52. Found: C, 77.34; H, 8.18.

(2) Reduction of β-ketone **8** (247 mg) with $LiAlH_4$ (68 mg) and $AlCl_3$ (160 mg) in benzene/ether (2:3, 25 mL) was carried out according to the same procedure as in the reduction of **7**. The crude product was column chromatographed over alumina to be separated into two bands. The first band eluted with hexane/ethyl acetate (40:1) yielded ferrocenophane **1** (181 mg, 75%). The second band eluted with ethyl acetate yielded [4$_2$]-β-hydroxy-[4][4](1,2,3,4)ferrocenophane (54 mg, 22%), which was recrystallized from hexane/ethyl acetate to give yellow powder: mp 226–229 °C; IR (KBr) 3330 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20–2.80 (30 H, m, CH_2), 3.90 (2 H, br s, Cp H), 4.54 (1 H, m, methine H); mass spectrum, *m/z* (rel intensity) 418 (100, M$^+$), 400 (3).

5-Formyl[4$_4$](1,2,3,4)ferrocenophane (10a). Formylation of **1** (196 mg) with dimethylformamide (178 mg) and phosphorus oxychloride (374 mg) in chloroform (8 mL) was carried out according to the same procedure as in the reaction of **3** except for the reaction time (4 h). The crude product was column chromatographed over alumina. The first band eluted with hexane/ethyl acetate (40:1) yielded the starting material **1** (53 mg, 27%). The second band eluted with hexane/ethyl acetate (2:1) yielded formylated product **10a** (152 mg, 72%), which was recrystallized from hexane/acetone to give an orange–red powder: mp 236–238 °C; IR (KBr) 1665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60–3.10 (32 H, m, CH_2), 4.01 (1 H, s, Cp H), 10.57 (1 H, s, CHO); mass spectrum, *m/z* (rel intensity) 430 (100, M$^+$), 401 (6). Anal. Calcd for $C_{27}H_{34}OFe$: C, 75.35; H, 7.96. Found: C, 75.08; H, 7.79.

Ethyl [4$_4$](1,2,3,4)Ferrocenophane-5-acrylate (10b). The Reformatsky reaction of **10a** (151 mg) with ethyl bromoacetate (177 mg), active zinc powder (400 mg), and iodine (10 mg) in dry benzenes/ether (10:1, 11 mL) was carried out according to the same procedure as in the reaction of **4a**, except for the reaction time (20 min). Column chromatography of the crude product over alumina with hexane/ethyl acetate (2:1) gave acrylate **10b** (154 mg, 87%), which was recrystallized from hexane to give red needles: mp 159–161 °C; IR (KBr) 1700, 1615 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.34 (3 H, t, *J* = 7.0 Hz, CH_3), 1.70–2.80 (32 H, m, CH_2), 3.71 (1 H, s, Cp H), 4.23 (2 H, q, *J* = 7.0 Hz, OCH_2), 6.08 and 7.95 (each 1 H, an AX system, *J* = 16 Hz, olefin H); mass spectrum, *m/z* (rel intensity) 500 (100, M$^+$), 486 (5), 472 (9). Anal. Calcd for $C_{31}H_{40}O_2Fe$: C, 74.39; H, 8.06. Found: C, 74.75; H, 8.07.

Ethyl [4$_4$](1,2,3,4)Ferrocenophane-5-propionate (10c). Hydrogenation of acrylate **10b** (154 mg) with hydrogen gas (3.5 atm) and 10% Pd–C (20 mg) in ethanol (10 mL) was carried out according to the same procedure as in the reaction of **4b** except for the reaction time (7 h). Column chromatographic purification of the crude product over alumina with hexane/ethyl acetate (30:1) gave propionate **10c** (159 mg, a quantitative yield), which was recrystallized from hexane/ethyl acetate to give yellow prisms: mp 122–124 °C; IR (KBr) 1730, 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (3 H, t, *J* = 6.8 Hz, CH_3), 1.40–3.10 (36 H, m, CH_2), 3.57 (1

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[51] Hayes, F. N.; Hansbury, E. *J. Am. Chem. Soc.* **1964**, *86*, 4172.

H, s, Cp H), 4.13 (2 H, q, J = 6.8 Hz, OCH_2); mass spectrum, m/z (rel intensity) 502 (100, M^+), 488 (2), 474 (2), 429 (2). Anal. Calcd for $C_{31}H_{42}O_2Fe$: C, 74.09; H, 8.42. Found: C, 73.97; H, 8.51.

$[4_4]$-α-Oxo[3](1,2,3,4,5)ferrocenophane (11). (1) Hydrolysis of propionate **10c** (109 mg) with 20% aqueous NaOH (10 mL) and ethanol (20 mL) was carried out according to the same procedure as in the reaction of **4c**. The reaction mixture was worked up, and the extracts with dichloromethane were washed with saturated aqueous NaCl and dried over $CaCl_2$. The resulting dry solution of $[4_4]$(1,2,3,4)ferrocenophene-5-propionic acid (**10d**) was added dropwise to 200 mL of PPE, which was prepared in the usual way.[51] The mixture was heated for 30 min on an oil bath at 80 °C with stirring. The reaction mixture was quenched with 6 N HCl, and the aqueous mixture was extracted with dichloromethane. The extracts were washed with saturated aqueous NaCl, dried over $CaCl_2$, and evaporated. The thin-layer chromatograph of the residue over silica gel with benzene separated into several bands. Orange–yellow solid from the second band was again chromatographed over thin-layered silica gel with benzene to separate into two bands. The first band yielded trimerized compound **12** (6.4 mg, 7%) as an orange–yellow powder (mp > 300 °C). The compound was crystallized from a deuteriochloroform solution prepared for measurement of the NMR spectrum to give red prisms: mp 451 °C (dec); IR (KBr) 1656 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75–2.95 (m, CH_2); ^{13}C NMR ($CDCl_3$) δ 26.36, 26.83, 27.59, 28.18, 29.65 and 42.74 (methylene C), 81.55, 83.31, 83.72, 85.72 and 86.07 (Cp C), 205.02 (carbonyl C); mass spectrum (field desorption ionization), m/z (rel intensity) 1369 (100, $[M + 1]^+$), 456 (14).

The second band in the second chromatograph yielded pentabridged ferrocenophane **11** (8.7 mg, 9%), which was crystallized from a benzene solution by a vapor diffusion method using hexane/ether as a diffusion solvent to give sublimable orange–yellow prisms: mp > 300 °C (in a sealed tube); IR (KBr) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80–3.05 (34 H, m, CH_2), 3.44 (2 H, m, $COCH_2$); ^{13}C NMR ($CDCl_3$) δ 25.54, 26.18, 26.54, 26.71, 27.07, 27.36, 27.77, and 51.43 (methylene C), 72.51, 81.19, 82.60, 84.31, 84.60 and 84.90 (Cp C), 213.64 (carbonyl C); mass spectrum, m/z (rel intensity) 456 (M^+, 100), 442 (9), 428 (8). Anal. Calcd for $C_{29}H_{36}OFe$: C, 76.31; H, 7.95. Found: C, 76.13; H, 7.99.

(2) Propionate **10c** (100 mg) was dissolved to warm ethanol and 20% aqueous NaOH was added dropwise to the solution. The mixture was refluxed for 10 min and cooled to 0 °C. After dichloromethane was added, the reaction mixture was neutralized with 6 N HCl. The organic layer was washed with water and then saturated aqueous NaCl and dried over $MgSO_4$. The resulting dry dichloromethane solution of propionic acid **10d** was degassed under reduced pressure at −196 °C and then used for the following cyclization reaction without evaporation. PPE prepared from phosphorus pentoxide (15 g), ether, and 1,2-dichloroethane was placed in a three-necked flask. The viscous solution of PPE was diluted with 300 mL of 1,2-dichloroethane and refluxed in a stream of argon for 30 min to remove oxygen in the solution. The previously mentioned solution of **10d** in dichloromethane was added dropwise to the solution of PPE under an argon atmosphere. The reaction mixture was refluxed for 2 min and cooled to 0 °C. After successive, water, 20% aqueous NaOH, and ascorbic acid were added with care, the alkaline mixture was stirred for 30 min. The resulting quenched mixture was extracted with benzene, and the extracts were washed with 20% aqueous NaOH and saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. The same chromatographic separation of the residue as in method 1 gave pentabridged ferrocenophane **11** (34 mg, 35%) but no trimer **12**.

$[4_4]$[3](1,2,3,4,5)Ferrocenophane (13). Reduction of ketone **11** (2.3 mg) with $LiAlH_4$ (5 mg) and $AlCl_3$ (10 mg) in dry benzene/ether (1 mL) was carried out according to the same procedure as in the preparation of **1**. The crude product was column chromatographed over alumina with hexane/ethyl acetate (30:1) to yield reduced product **13** (2.0 mg, 80%). Recrystallization of **13** from a benzene solution by a vapor diffusion method with hexane gave yellow needles: mp > 300 °C; ^1H NMR (at 400 MHz, $CDCl_3$) δ 1.89, 1.99, 2.07, 2.47, and 2.54 (4 H, 8 H, 8 H, 10 H, and 8 H, respectively, each m, CH_2); ^{13}C NMR ($CDCl_3$) δ 18.42, 26.07, 26.85, 27.29, 29.73 and 37.86 (methylene C), 80.70, 82.11 and 83.86 (Cp C); mass spectrum, m/z (rel intensity) 442 (100, M^+), 428 (6), 414 (2); high-resolution mass calcd for $C_{29}H_{38}Fe$ 442.2322, found 442.2313.

$[4_4]$-α-Oxo[4](1,2,3,4,5)ferrocenophane (14). To a solution of ketone **11** (35 mg, 0.077 mmol) in dry benzene (20 mL) was added BF_3 etherate (0.10 mL, 10 equiv of **11**) under a nitrogen atmosphere. The mixture was stirred at room temperature for 30 min. A large excess amount of diazomethane in ether, free from alcohol and moisture, was rapidly added to the violet solution of the aged BF_3 complex with vigorously stirring. Saturated aqueous Na_2CO_3 and ascorbic acid were added, and the resulting aqueous mixture was extracted with benzene. The extracts was washed with saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. The residue was column chromatographed over thin-layered silica gel with benzene. The first band yielded a mixture of bridge-enlarged products (4.7 mg) containing $[4_4]$-β-oxo[4](1,2,3,4,5)ferrocenophane (4.7 mg). Attempted chromatographic separations of the β-ketone were unsuccessful. The second band afforded the starting material (17 mg, 48%). The third band yielded α-ketone **14** (6.3 mg, 18%), which was recrystallized from dichloromethane/ethyl acetate to give orange–yellow prisms; mp > 300 °C; IR (KBr) 1655 cm^{-1}; ^1H NMR (at 400 MHz, $CDCl_3$) δ 1.68, 1.98, 2.09, 2.21, 2.31, 2.39, 2.45, 2.49, 2.67, and 3.00 (2 H, 4 H, 8 H, 2 H, 2 H, 2 H, 8 H, 6 H, 2 H, and 2 H, respectively, each m, CH_2); ^{13}C NMR at 100.4 MHz, $CDCl_3$) δ 24.18, 26.19, 26.42, 26.57, 26.80, 27.52, 27.55, 27.58, 27.68, 32.20 and 44.31 (methylene C), 80.46, 82.10, 82.74, 83.20, 84.56 and 85.69 (Cp C), 209.32 (carbonyl C); mass spectrum, m/z (rel intensity) 470 (100, M^+); high-resolution mass calcd for $C_{30}H_{38}OFe$ 470.2270, found 470.2293.

$[4_5]$(1,2,3,4,5)Ferrocenophane (2). A solution of α-ketone **14** (11 mg) in dry benzene was added to a suspension of $LiAlH_4$ (50 mg) and $AlCl_3$ (100 mg) in dry ether (10 mL). The reaction mixture was stirred for 2.5 h at room temperature. Ice water was added, and the resulting aqueous mixture was extracted with benzene. The extracts were washed with saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. Column chromatographic purification of the residue with benzene afforded reduced product **2** (10 mg, quantitative), which was recrystallized from 1,2-dichloroethane to give yellow prisms: mp > 300 °C; ^1H NMR (at 400 MHz, $CDCl_3$) δ 1.97 (20 H, br s, $W_{h/2}$ = 24.8 Hz, β-CH_2), 2.54 (20 H, br s, $W_{h/2}$ = 15.2 Hz, α-CH_2); ^{13}C NMR ($CDCl_3$) δ 23.54 (β-methylene C), 26.90 (α-methylene C), 84.46 (Cp C); λ_{max} (THF) 403 nm (ϵ = 88); mass spectrum, m/z (rel intensity) 456 (100, M^+); high-resolution mass calcd for $C_{30}H_{40}Fe$ 456.2477, found 456.2470.

X-ray Crystallographic Analysis of 2. Crystals grown from a 1,2-dichloroethane solution were transparent yellow thick plates. A small specimen with approximate dimensions 0.2 × 0.3 × 0.5 mm was cut from the crystal and used for the X-ray diffraction study. The lattice constants and intensity data were measured on a Philips PW-1100 diffractometer using graphite monochromated Mo Kα radiation.

Crystal data: $C_{30}H_{40}Fe$, MW = 456.5, tetragonal, space group $I\bar{4}2d$, a = 15.453 (8), c = 18.968 (10) Å, V = 4529 $Å^3$, Z = 8, D_{calcd} = 1.334 g cm^{-3}, μ for Mo Kα = 6.79 cm^{-1}.

Intensities of 2603 reflections were measured as above the $2\sigma(I)$ level out of 3193 within the 2θ range of 6–60° (involved in an octant of the reciprocal space). These data were processed to yield 1279 independent structure factors by averaging symmetry-equivalent reflections (khl vs hkl) and by correcting for Lorentz and polarization factors. No correction for absorption was applied. The crystal structure was determined by the heavy-atom method and refined to an R factor of 0.065 by the block-diagonal matrix least-squares calculations. In the final stage of the refinement, the anomalous dispersion corrections were applied for iron atoms. (The space group $I\bar{4}2d$ has a glide plane and is nonenantiomorphic but has no center of symmetry.) Hydrogen atoms were not included. If the hydrogen atoms were placed at the calculated positions and refined with isotropic temperature factors, the R factor decreases to 0.053, but in view of the fact that the bridging carbon atoms have pronounced temperature factors, all the hydrogen atoms are not shown in Figure 3.

Supplementary Material Available: Tables of anisotropic thermal parameters and deviations of atoms from the least-squares plane through the Cp ring for **2** (1 page); a listing of observed and calculated structure factors for **2** (4 pages). Ordering information is given on any current masthead page.