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ORGANOMETALLIC COMPOUNDS

XXI*. SYNTHESES OF [4](1,1′)[4](3,3′)FERROCENOPHANE AND RELATED COMPOUNDS

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Summary

Synthesis of [4](1,1′)[4](3,3′)- and [4](1,1′)[3](3,3′)ferrocenophanes were attempted via two routes. Bridge enlargement of [3][3]ferrocenophane-6,11-dione with CH_2N_2 afforded [4][4]ferrocenophane-7,12-dione (IX), [4][3]-ferrocenophane-6,11-dione, and [4][4]ferrocenophane-6,7,12-trione. [4][3]-Ferrocenophane-6-one (XXII) was prepared from [4]ferrocenophane. Reaction of the ketone XXII with CH_2N_2 gave [4][4]ferrocenophane-7-one (XXIII). The reduction product of the ketone XXIII was identical with that of the diketone IX. Bridge enlargement reactions of other ferrocenophanes are also described.

Introduction

The chemical and physical properties of multibridged ferrocenophanes [2] are of interest because of their shape as a cage compound containing a metal ion at the center. Of the ferrocenophanes that have already been synthesized, the tribridged [3][3][3]ferrocenophanes reported by Schlögl and Peterlik [3] and Rinehart et al. [4] are the most multiple bridged ferrocenophanes. Synthesis of a tetrabridged [3][3][3][3]ferrocenophane has been described [3], but convincing evidence in conflict with this report has been provided by Bublitz and Rinehart [5].

Since there is a strain in [3](1,1′)ferrocenophane-6-one [6], a monobridged ferrocenophane with a three-carbon chain, di- or more multi-linking of ferrocene with three-carbon chains should produce an additional strain. Thus, it is anticipated that multi-linking with four-carbon chains would be more favorable than

* For part XX see ref. 1.

with three-carbon chains. However, there has been no report on the preparation of di- and more multibridged ferrocenophanes with four-carbon chains. This paper describes syntheses of [4](1,1′)[4](3,3′)-ferrocenophane* and related compounds, which can be used as intermediate compounds for the syntheses of tri- and more multibridged ferrocenophanes with four-carbon chains.

Intramolecular electrophilic substitution of (3-carboxypropyl)ferrocene or 1,1′-bis(3-carboxypropyl)ferrocene greatly favors the formation of the homoannular cyclization product in preference to the bridged ferrocenophane with four-carbon chains [8–10]. Rosenblum et al. [11] prepared [4](1,1′)-ferrocenophanes by bridge enlargement of [3](1,1′)ferrocenophane-6-one with CH_2N_2. In the present study, dibridged [4][4]- and [4][3]ferrocenophane were synthesized via two routes by the application of bridge enlargement with CH_2N_2.

Results and discussion

One-step cyclization and bridge enlargement of two bridges (Scheme 1)

The dicarboxylic acid III [4] was treated with PCl_3 and then $AlCl_3$ in dichloromethane according to the procedure of Schlögl and Peterlik [3]. The reaction products were separated by column chromatography over silica gel into three isomeric ketones (V) (33%), (VI) (0.9%), and (VII and/or VIII) (2.1%). The two isomers (VI, VII and/or VIII), hetero-homo- and bis-homoannular cyclization products, respectively, were not found by Schlögl and Peterlik [3].

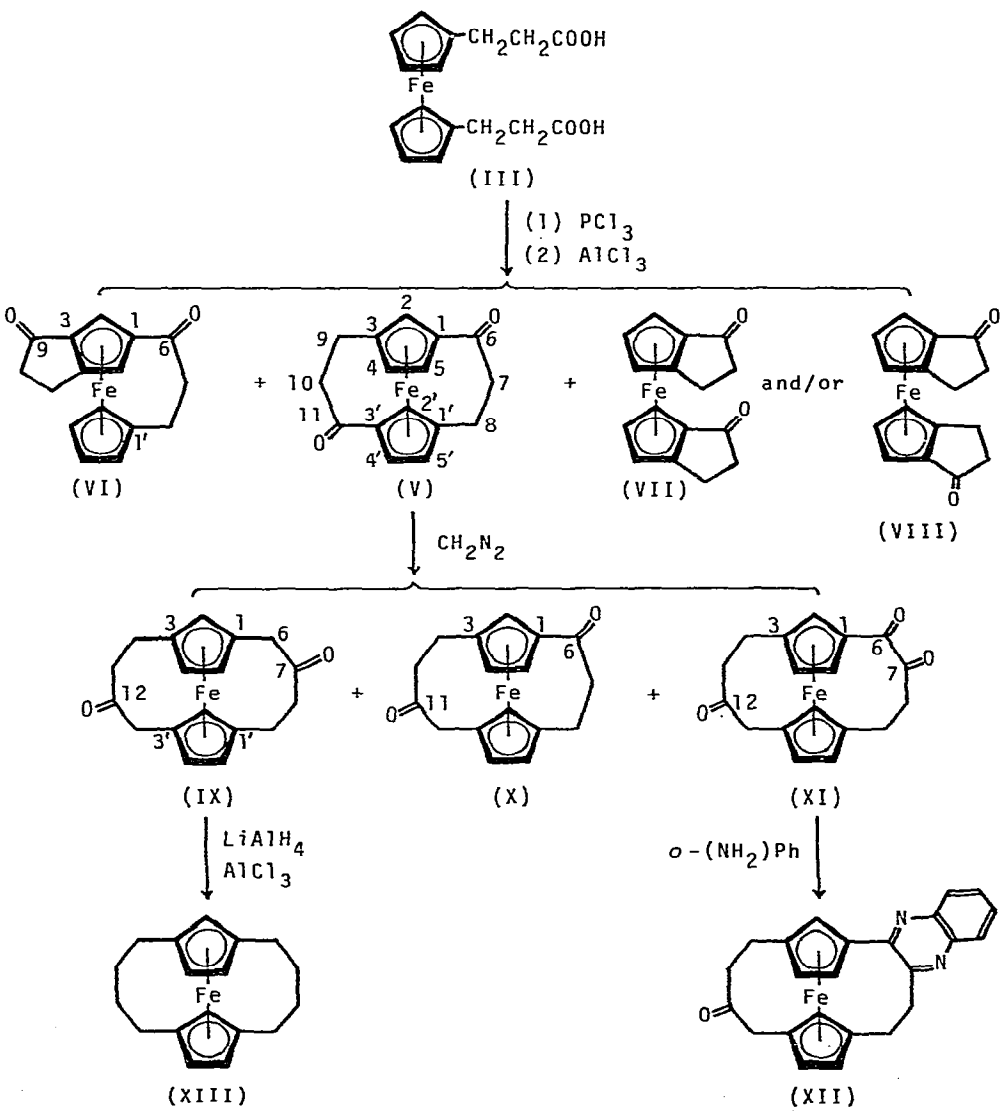
The IR spectrum of [3](1,2)[3](1′,2′)ferrocenophane-6,9-dione (VII and/or VIII) exhibited a ν(C=O) band at 1685 cm^{-1}, which is characteristic of α-carbonyl groups of homoannular cyclized ferrocene derivatives with a five-membered ring [5,12]. The patterns of the PMR and mass spectra also supported the structure of a bis-homoannular cyclized diketone. The corresponding diketone with six-membered rings, [4](1,2)[4](1′,2′)ferrocenophane-6,10-dione, has been separated into *meso* and racemic isomers by Falk et al. [13]. The present diketone with five-membered rings, however, could not be separated into two diastereoisomers even by rechromatography several times. The IR spectrum of [3](1,1′)[3](3,4)ferrocenophane-6,9-dione (VI) showed two ν(C=O) bands at 1690 and 1688 cm^{-1}, which were assigned to the α-carbonyl groups on the five-membered ring and three-carbon bridge, respectively [4,5]. In the PMR spectrum of VI, H_5 and H_2 proton signals on the diketo-substituted cyclopentadienyl (Cp) ring appeared at δ 4.78 and 4.92 as doublets, respectively.

The procedure described by Rosenblum et al. [11] for bridge enlargement of monobridged [3]ferrocenophane was applied to the one-step enlargement of the two bridge chains in [3][3]ferrocenophane-6,11-dione (V) obtained as main product in the cyclization. The products of the reaction of V with CH_2N_2 were column-chromatographed over silica gel and separated into three compounds, IX (43%), X (2.2%) and XI (4.5%). The spectra of the ferrocenophane IX indi-

* The nomenclature and numbering system of the ferrocenophanes, as illustrated in the schemes, is a modification of that proposed by Vogle and Neumann [7]. Most of the compounds described in this paper were obtained as racemic mixtures, only one enantiomorph is shown in the schemes.

cated a ν(C=O) band at 1678 cm^{-1}, a proton signal of two isolated methylene groups at δ 3.24 (4H) as a singlet, and a molecular ion peak at *m/e* 322. Thus, the diketone IX was the expected compound formed by one-step bridge enlargement of V. In the spectra of X, assigned to partially bridge-enlarged [4][3]-ferrocenophane, ν(C=O) absorptions and a molecular ion appeared at 1696 and 1658 cm^{-1}, and at *m/e* 308, respectively. The isolated methylene protons of X appeared at δ 3.08 and 3.17 as an *AB* system due, possibly, to a strain caused by linking with a three-carbon chain.

SCHEME 1. SYNTHESIS OF [4](1,1')[4](3,3')FERROCENOPHANE (XIII) VIA ONE-STEP HETERO-ANNULAR CYCLIZATION AND BRIDGE ENLARGEMENT



The PMR spectrum of compound XI showed a singlet signal (2H) of an isolated methylene group at δ 3.21 and multiplets of eight methylene protons

at δ 2.55—2.95. The elemental composition of XI was $C_{18}H_{16}FeO_3$. Compound XI was treated with *o*-phenylenediamine to give a quinoxaline derivative (XII) ($C_{24}H_{20}FeN_2O$) in 85% yield. Thus, the structure of XI was assigned as [4](1,1′)-[4](3,3′)ferrocenophane-6,7,12-trione. In the bridge enlargement of V with CH_2N_2 at —50°C to —80°C, the triketone XI became the main product (35%). It has been found that the corresponding monobriged α-diketone, 9-methyl[4]-(1,1′)ferrocenophane-6,7-dione, was also formed in the bridge enlargement of 8-methyl[3](1,1′)ferrocenophane-6-one with CH_2N_2 [14]. Isolation of the diol XXXII in the bridge enlargement of [3][3]ferrocenophane-6-one (XXIX) with CH_2N_2 (see Scheme 3) would suggest that the triketone was formed via a hydrolysis product of an intermediate epoxide [15] followed by rearrangement and oxidation.

[4](1,1′)[4](3,3′)Ferrocenophane-7,12-dione (IX) was converted into [4]-(1,1′)[4](3,3′) ferrocenophane (XIII) by reduction with the $LiAlH_4$—$AlCl_3$ system. The overall yield based on ferrocene in the synthesis of XIII by this route was rather low because of the low yield in the preparation of the dicarboxylic acid III.

Stepwise cyclization and bridge enlargement (Scheme 2)

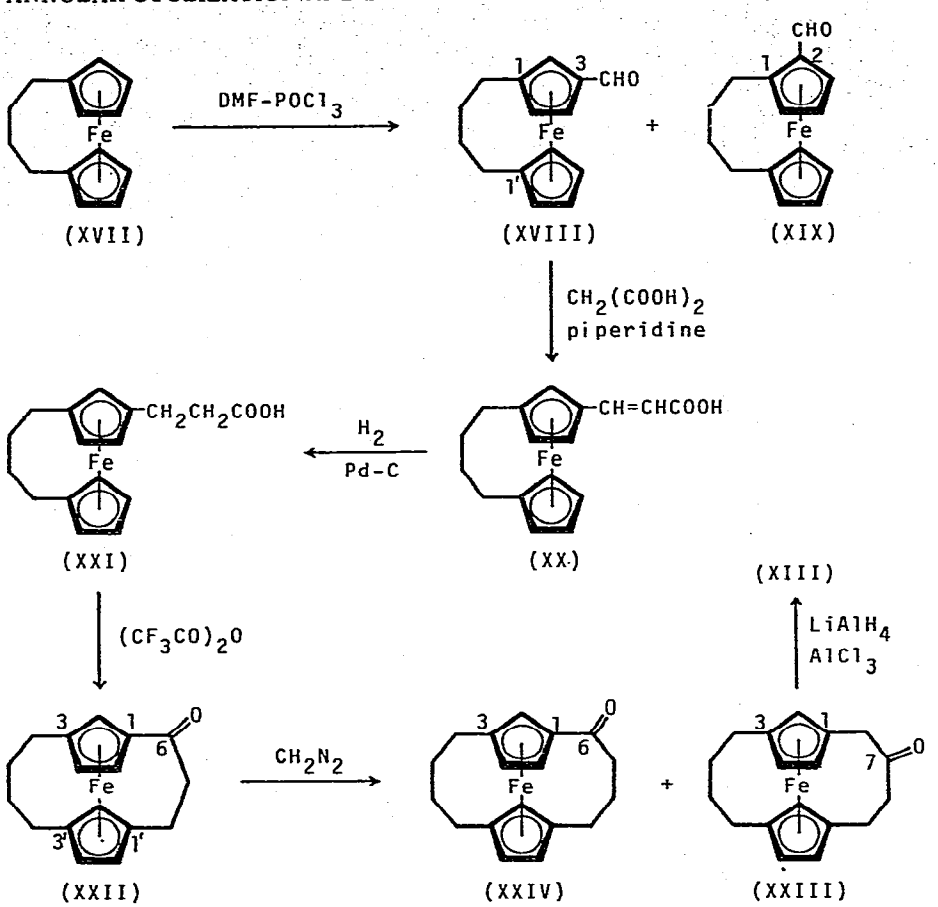
The preparation of [3](1,1′)ferrocenophane-6-one (XV) by the Knoevenagel condensation of formylferrocene (XIV), followed by reduction and heteroannular cyclization has been reported by Rinehart and Curby [8]. Rosemblum et al. [11] converted [3]ferrocenophane-6-one (XV) into [4](1,1′)ferrocenophane-7-one (XVI) by bridge enlargement with CH_2N_2. The present synthesis of [4][4]-ferrocenophane (XIII) was carried out by application of the modified procedures of Rinehart and Curby [8], and Rosenblum et al. [11].

[4](1,1′)Ferrocenophane (XVII) was formylated with DMF—$POCl_3$ according to Hata's procedure [16] for the preparation of formylferrocene (XIV). The reaction products were separated into two isomers, XVIII (69%) and XIX (14%), by column chromatography. The proton signals of the formylated Cp ring in the main product (XVIII) appeared as a triplet (δ 4.73) with J = 1.4 Hz and two double doublets (δ 4.50 and 4.65) with J = 1.4 and 2.6 Hz, while in the minor product (XIX) the signals appeared as a triplet (δ 4.46) with J = 2.7 Hz and two double doublets (δ 4.57 and 4.66) with J = 1.5 and 2.7 Hz. In general, the *ortho* and *meta* coupling constants in acylated Cp rings of ferrocenes are 2.3—3.1 Hz and 1.0—1.6 Hz, respectively [17—19]. Thus, the products XVIII and XIX of the formylation are 3- and 2-formylated ferrocenophanes, respectively.

The major product (XVIII) was condensed with malonic acid to give an α,β-unsaturated carboxylic acid (XX) (88%). Reduction of the acid XX with H_2/Pd—C at 4 atm gave quantitatively saturated carboxylic acid (XXI). Treatment of the acid XXI with $(CF_3CO)_2O$ afforded only the dibridged ferrocenophane (XXII) in 96% yield. The spectra of XXII exhibited a ν(C=O) band at 1662 cm^{-1} and a triplet signal with J = 1.4 Hz at a low field (δ 4.86). The chemical shift and splitting of the Cp ring proton indicate linking between the 3- and 3′-positions.

Bridge enlargement of XXII with CH_2N_2 afforded two isomeric homologous ketones, XXIII (90%) and XXIV (3.7%). The major product (XXIII) had a

SCHEME 2. SYNTHESIS OF [4](1,1')[4](3,3')FERROCENOPHANE (XIII) VIA STEPWISE HETERO-ANNULAR CYCLIZATION AND BRIDGE ENLARGEMENT



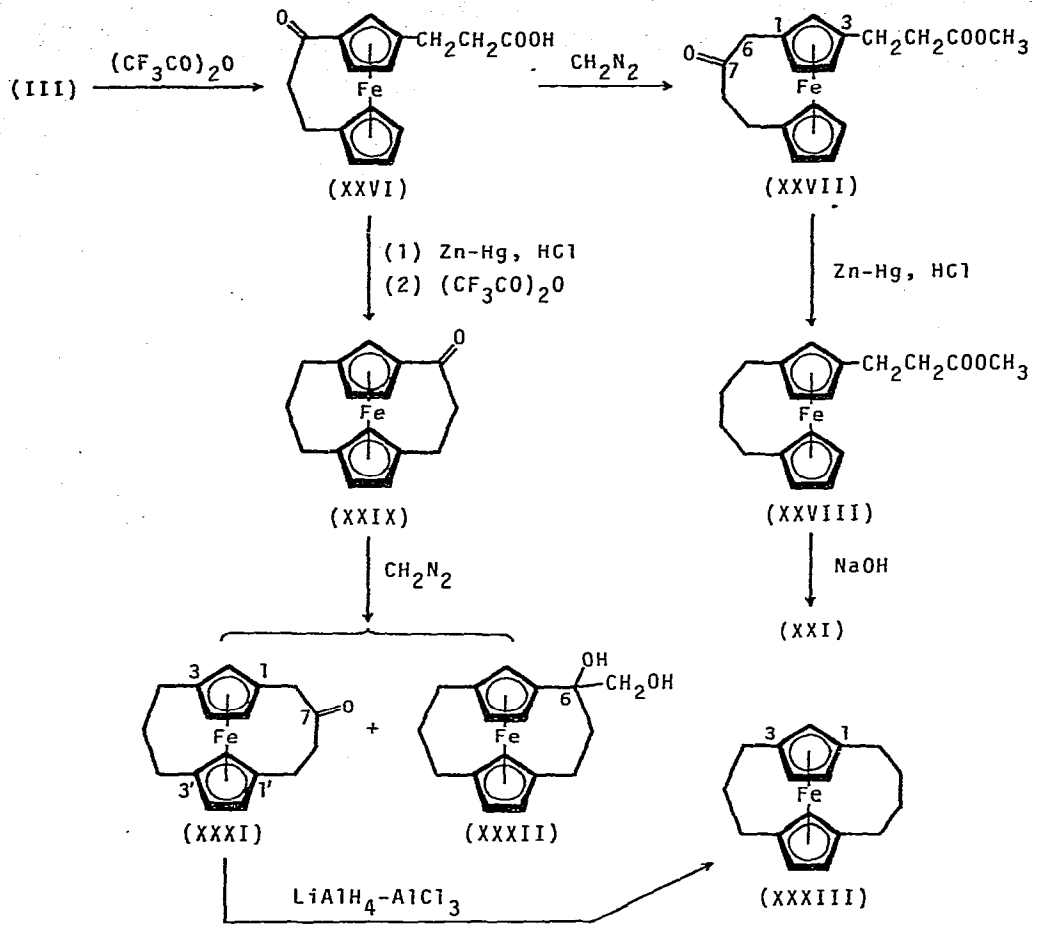
singlet signal (2H) of the isolated methylene protons at δ 3.20 and an absorption due to an unconjugated carbonyl group at 1696 cm^{-1}. The other ketone (XXIV) showed a conjugated carbonyl band at 1646 cm^{-1}.

[4][4]Ferrocenophane-7-one (XXIII) was reduced with $LiAlH_4$—$AlCl_3$ to give [4][4]ferrocenophane (XIII) in 93% yield, which proved to be indetical to the reduction product of the diketone IX described above. The overall yield, based on ferrocene, in the synthesis of XIII by the present process was much better than that by one-step bridge enlargement.

Rinehart et al. [4] have synthesized [3](1,1')[3](3,3')ferrocenophane (XXX) via linking of 3-(2-carboxyethyl)[3](1,1')ferrocenophane, and have given evidence for the prismatic configuration of XXIX or XXX. On the other hand, the reduction product of [3][3]ferrocenophane-6,11-dione (V) was identified with XXX by Schlögl and Peterlik [3]. These facts confirm that [4][4]ferrocenophane (XIII) and related ferrocenophanes synthesized in this study also have the prismatic configuration.

In addition, some bridge enlargement reactions of other [3]ferrocenophanes with CH_2N_2 were examined (Scheme 3). 3-(2-Carboxyethyl)[3]ferrocenophane-6-one (XXVI) [4], prepared by cyclization of the dicarboxylic acid III with

SCHEME 3. BRIDGE ENLARGEMENT REACTIONS OF [3]FERROCENOPHANE-6-ONES



$(CF_3CO)_2O$, was converted to the methyl ester of 3-(2-carboxyethyl)[4]ferrocenophane-7-one (XXVII) in 58% yield by treatment with CH_2N_2. Clemmensen reduction of the ester XXVII followed by hydrolysis with alkali led to 3-(2-carboxyethyl)[4]ferrocenophane (XXI). Treatment of [3][3]ferrocenophane-6-one (XXIX) with CH_2N_2 afforded a bridge enlargement product (XXXI) (89%) and a diol (XXXII) (7%), which was possibly formed by hydrolysis of the intermediate epoxide [15] in the reaction. However, bridge enlargement of 2-substituted [3](1,1′)ferrocenophane-6-ones ([3](1,1′)[3](2,2′)ferrocenophane-6-one, 2-(2-carboxyethyl)[3](1,1′)ferrocenophane-6-one, etc.) was unsuccessful, possibly because of steric hindrance.

For the preparation of [4][4]ferrocenophanes and [4][3]ferrocenophanes, which can be used as starting materials in the synthesis of tri- and more multibridged ferrocenophanes, the process via stepwise cyclization and bridge enlargement is more advantageous in yield than the process via one-step cyclization and bridge enlargement.

Synthesis of other multibridged ferrocenophanes will be reported in forthcoming papers.

Experimental

All melting points are uncorrected. Column-chromatographic separations were carried out with Wako activated alumina (300 mesh), Kanto-kagaku silica gel (100 mesh), Wakogel C-200 (200 mesh), and Mallinckrodt silicic acid (100 mesh). The concentration of the solution of CH_2N_2 in ether which was used in the bridge enlargement reactions was ca. 0.02 mol l^{-1}. IR spectra were measured using a Hitachi—Perkin—Elmer model 225 grating infrared spectrophotometer. PMR spectra were measured on a JEOL JNM-4H-100 spectrometer at 100 MHz at room temperature with TMS (tetramethylsilane) as internal standard. Double resonance experiments for the assignment of Cp ring proton signals were run on a JEOL JNM-SD-30 spin decoupler instrument. Mass spectra were obtained with a Hitachi RMU-7M double focussing mass spectrometer with a direct insertion probe at 70 eV ionizing energy. Numbers in parentheses of mass spectral data indicate the relative intensities of the peaks versus the intensity of the base peak. High-resolution mass spectra were treated on a Hitachi datalyser system 002.

1,1′-Bis(2-carboxyethyl)ferrocene (III)

Since re-examination of the procedure described by Rinehart et al. [4] resulted in a low yield of the diacid III, the preparation of III was carried out by a modified procedure. The crude product obtained by condensation of 1,1′-diacetylferrocene with diethyl carbonate and NaH was column-chromatographed over silica gel with benzene—ethyl acetate (10:1) as eluent, whereby 1,1′-bis-(ethoxycarbonylacetyl)ferrocene (I) was obtained in 64% yield. A mixture of the keto-ester I (6.8 g), benzene (100 ml), ethanol (30 ml), zinc amalgam (40 g) and conc. HCl (80 ml) was stirred at 50°C for 20 h. After filtration to remove zinc amalgam, the reduction mixture was extracted with benzene. The organic layer was washed with aq. $NaHCO_3$ and aq. NaCl, dried over Na_2SO_4, and evaporated. The crude residue was column-chromatographed over silica gel to afford an oily product (4.2 g). Since the reduction product was contaminated with small amounts of partially reduced compounds containing C=C bonds (IR, 1640 cm^{-1}), the oil was further reduced with H_2/10% Pd—C (1.00 g) in ethanol (100 ml) and benzene (20 ml) at 4 atm for 20 h. After filtration and evaporation, the reduction mixture was column-chromatographed over silica gel with benzene—ethyl acetate (20:1) to yield 1,1′-bis(2-ethoxycarbonylethyl)-ferrocene (II) [4], a yellow oil (3.8 g, 60%). IR spectrum (neat liq., cm^{-1}): 1735 [ν(C=O) of ester].

The ester II (4.00 g) was hydrolysed by refluxing with 2 *N* KOH—ethanol for 10 h. The reaction mixture was evaporated, and then dil. HCl was added to the residue to precipitate a yellow solid (2.50 g), which was 1,1′-bis(2-carboxy-ethyl)ferrocene (III) (73%), m.p. 140—141°C (lit. [4], m.p. 135—137°C). IR spectrum (KBr, cm^{-1}): 1710 [ν(C=O) of carboxyl].

Cyclization of 1,1′-bis(2-carboxyethyl)ferrocene (III)

The cyclization was carried out according to a modification of the procedure described by Schlögl and Peterlik [3]. PCl_3 (44 ml) was added dropwise during 20 min to a powder (2.19 g) of 1,1′-bis(2-carboxyethyl)ferrocene (III). The mixture was stirred at room temperature under a N_2 gas atmosphere for 4 h.

The excess PCl_3 was evaporated in vacuo below 20°C. The residue was dissolved in dichloromethane, and then the resulting supernatant solution was evaporated. The residue (2.50 g), an unstable brown oil, was 1,1′-bis(2-chloroformylethyl)-ferrocene (IV). IR spectrum (neat liq., cm^{-1}): 1800 [ν(C=O) of chloroformyl].

A dichloromethane solution (200 ml) of the chloride IV (2.50 g) was added dropwise during 2 h at 0°C to a dichloromethane suspension (200 ml) of $AlCl_3$ (6.00 g) under a N_2 gas atmosphere. The reaction mixture was stirred at room temperature for 3 h, and then poured into ice-water. The hydrolysate was phase-separated, and the organic layer was washed with aq. $NaHCO_3$ and aq. NaCl, dried and evaporated. The residue was column-chromatographed over silica gel to remove contaminant PCl_3, and then re-chromatographed over silica gel (Mallinckrodt silicic acid). In this way, the products were separated into five bands. The first (12 mg) and second bands (8 mg), eluted with benzene—ethyl acetate (10:1), were unknown products. The third band eluted with benzene—ethyl acetate (8:1) yielded [3](1,1′)[3](3,4)ferrocenophane-6,9-dione (VI) (17 mg, 0.9%), which was recrystallized from ethyl acetate to give orange-yellow plates, des. 192°C. (Found: M^+ 294.0318. $C_{16}H_{14}FeO_2$ calcd.: mol. wt. 294.0342.) IR spectrum (KBr, cm^{-1}): 1690 and 1668 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 2.35—3.35 (8H; m, $\rangle CH_2$), 3.95, 4.08, 4.36 and 4.50 (each 1H; m, H_2, $-H_5$, of Cp), 4.78 (1H; d, J = 2.2 Hz, H_5 of Cp), 4.92 (1H; d, J = 2.2 Hz, H_2 of Cp). Mass spectrum (*m/e*): 294 (M^+, 100), 266 [$(M - CO]^+$, 13), 238 ([$M - 2CO]^+$, 15), 216 ([$M - C_6H_6]^+$, 71), 188 ([$M - (C_6H_6 + CO)]^+$, 63), 160 ([$M - (C_6H_6 + 2CO)]^+$, 19).

The fourth band eluted with benzene—ethyl acetate (8:1) yielded [3](1,1′)-[3](3,3′)ferrocenophane-6,11-dione (V) (650 mg, 33%), which was recrystallized from benzene—ethyl acetate to give orange-yellow needles, m.p. 208—209°C (lit. [2], m.p. 206—210°C). (Found: C, 65.50; H, 4.98. $C_{16}H_{14}FeO_2$ calcd.: C, 65.33; H, 4.80%.) IR spectrum (KBr, cm^{-1}): 1650 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 2.44 (2H; dt, $\rangle CH_2$), 2.70-3.20 (4H; m, $\rangle CH_2$), 3.58 (2H; dt, $\rangle CH_2$), 4.45 (2H; dd, J = 1.5 and 2.5 Hz, H_4 and $H_{5'}$ of Cp), 4.66 (2H; dd, J = 1.5 and 2.5 Hz, H_5 and $H_{4'}$ of Cp), 5.59 (2H; t, J = 1.5 Hz, H_2 and $H_{2'}$ of Cp). Mass spectrum (*m/e*): 294 (M^+, 100), 266 ([$M - CO]^+$, 12), 238 ([$M - 2CO]^+$, 13).

The fifth band eluted with benzene—ethyl acetate (5:1) yielded 41 mg (2.1%) of [3](1,2)[3](1′,2′)ferrocenophane-6,9-dione (VII and/or VIII), which was recrystallized from ethyl acetate to give red plates, m.p. 187-187.5°C. (Found: M^+ 294.0328. $C_{16}H_{14}FeO_2$ calcd.: mol. wt. 294.0342.) IR spectrum (KBr, cm^{-1}): 1685 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 2.50—3.20 (8H, m, $\rangle CH_2$), 4.40—4.62 (6H; m, Cp). Mass spectrum (*m/e*): 294 (M^+, 100), 266 ([$M - CO]^+$, 19), 238 ([$M - 2CO]^+$, 20).

Bridge enlargement of [3](1,1′)[3](3,3′)ferrocenophane-6,11-dione (V)

An ether solution (80 ml) of CH_2N_2 was added to a methanol solution (5 ml) of [3](1,1′)[3](3,3′)ferrocenophane-6,11-dione (V) (350 mg). The reaction mixture was stirred at 0°C in the dark. A further amount of ethereal CH_2N_2 (80 ml) was added after 4 h. Stirring was continued for 16 h, and the solvents and excess CH_2N_2 were then evaporated in vacuo. The residue was column-chromatographed over silica gel to separate the three bridge enlarge-

ment products, IX, X and XI. The first band eluted with benzene yielded [4](1,1′)[4](3,3′)ferrocenophane-7,12-dione (IX) (162 mg, 43%), which was recrystallized from benzene—ethyl acetate to give yellow needles, m.p. 147—148°C. (Found: C, 66.99; H, 5.79. $C_{18}H_{18}FeO_2$ calcd.: C, 67.10; H, 5.63%.) IR spectrum (KBr, cm^{-1}): 1678 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 2.73 (8H, s, $\rangle CH_2$), 3.24 (4H; s, isolated methylene at 6- and 13-positions), 4.07 (4H, m, Cp), 4.14 (2H; t, J = 1.4 Hz, H_2 and H_2′ of Cp). Mass spectrum (*m/e*): 322 (M^+, 100), 294 ([M — CO]$^+$, 8), 266 ([M — 2CO]$^+$, 78).

The second band eluted with benzene—ethyl acetate (10:1) yielded [4]-(3,3′)[3](1,1′)ferrocenophane-6,11-dione (X) (8 mg, 2.2%), which was recrystallized from benzene—ethyl acetate to give orange-yellow needles, m.p. 154—155°C. (Found: C, 66.02; H, 5.38; M^+ 308.0514. $C_{17}H_{16}FeO_2$ calcd.: C, 66.23; H, 5.23%, mol. wt. 308.0498.) IR spectrum (KBr, cm^{-1}): 1696 and 1658 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 2.70—2.95 (8H, m, $\rangle CH_2$), 3.08 and 3.17 (2H; an *AB* system, J = 12 Hz, $\rangle CH_2$ at 12-position), 4.10, 4.41 and 4.48 (each 1H; m, Cp), 4.69 (2H; m, Cp), 4.92 (1H; t, J = 1.3 Hz, H_2 of Cp). Mass spectrum (*m/e*): 308 (M^+, 100), 280 ([M — CO]$^+$, 71), 252 ([M — 2CO]$^+$, 30).

The amounts of the third, fourth and fifth bands were so small that the structure of the compounds could not be determined. The sixth band eluted with benzene—ethyl acetate (4:1) yielded [4](1,1′)[4](3,3′)ferrocenophane-6,7,12-trione (XI) (18 mg, 4.5%), m.p. 149—150°C (orange-yellow plates, from benzene—ethyl acetate). (Found: M^+ 336.0487. $C_{18}H_{16}FeO_3$ calcd.: mol. wt. 336.0448.) IR spectrum (KBr, cm^{-1}): 1700 and 1644 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 2.55—2.95 (8H; m, $\rangle CH_2$), 3.21 (2H; s, isolated methylene at 13-position), 4.10—4.22 (3H, m, Cp), 4.60—4.72 (3H, m, Cp). Mass spectrum (*m/e*): 336 (M^+, 100), 308 ([M — CO]$^+$, 29), 280 ([M — 2CO]$^+$, 94), 252 ([M — 3CO]$^+$, 38).

The bridge enlargement of the diketone V was also carried out at low temperature. A mixture of a methanol solution (5 ml) of V (600 mg) and an ether solution of CH_2N_2 (80 ml) was kept at —50 to —80°C with stirring. After 10 h, a further amount of ethereal CH_2N_2 (40 ml) was added to the reaction mixture. The total reaction time was 48 h. The residue obtained after evaporation of the reaction mixture was column-chromatographed over silica gel to afford the three compounds IX, X and XI in yields of 5% (30 mg), 14% (88 mg) and 35% (240 mg), respectively.

The quinoxaline derivative (XII) of [4](1,1′)[4](3,3′)ferrocenophane-6,7,12-trione (XI)

o-Phenylenediamine (40 g) and saturated aq. $NaHCO_3$ (3 mg) were added to a methanol solution (0.5 ml) of the triketone XI (90 mg). After heating for several seconds over an open flame, the reaction mixture was extracted with benzene. The organic layer was washed with dil. HCl, aq. $NaHCO_3$ and then aq. NaCl, dried and evaporated. On column chromatography over silica gel with benzene as eluent, the quinoxaline derivative (XII) of the triketone (XI) was obtained in 85% yield (93 mg). Recrystallization from hexane—ethyl acetate afforded orange-yellow needles, m.p. 208—208.5°C. (Found: C, 69.92; H, 5.04; N, 6.80; M^+ 408.0942. $C_{24}H_{20}FeN_2O$ calcd.: C, 70.60; H, 4.94; N, 6.86%; mol.

wt. 408.0923.) IR spectrum (KBr, cm^{-1}): 1695 [ν(C=O)], 1682 [ν(C=N)]. Mass spectrum (*m/e*): 408 (M^+, 100), 380 ([M — CO]$^+$, 55).

[4](1,1′)[4](3,3′)Ferrocenophane (XIII)

(1) According to the procedure described by Rinehart et al. [9] for the preparation of [3](1,1′)ferrocenophane, an ether solution (8 ml) of [4](1,1′)-[4](3,3′)ferrocenophane-7,12-dione (IX) (20 mg) was added to a suspension of $LiAlH_4$ (20 mg) and $AlCl_3$ (100 mg) in ether (2 ml). After refluxing for 3 h, excess reagent was decomposed with moist ether, and then water. The resulting reaction mixture was extracted with ether. The extracts were washed with aq. NaCl, dried and evaporated. The crude residue was purified by column chromatography over silica gel to give 15 mg (82%) of [4](1,1′)[4](3,3′)ferrocenophane (XIII), which was recrystallized from hexane—ethyl acetate to give yellow plates, m.p. 117°C. (Found: C, 73.46; H, 7.41. $C_{18}H_{22}Fe$ calcd.: C, 73.48; H, 7.54%.) PMR spectrum ($CDCl_3$, δ): 1.60—1.90 (8H; m, $\rangle CH_2$), 2.20—2.55 (8H; m, $\rangle CH_2$), 3.95 (4H; bs, Cp), 4.03 (2H; bs, Cp). Mass spectrum (*m/e*): 294 (M^+, 100).

(2) [4](1,1′)[4](3,3′)Ferrocenophane-7-one (XXIII) (3.50 g) was reduced with $LiAlH_4$ (550 mg) and $AlCl_3$ (3.00 g) in ether (360 ml) according to the above procedure to give yellow plates (3.10 g, 93%), which were identified as [4](1,1′)[4](3,3′)ferrocenophane (XIII) by a mixed melting point determination and spectral comparisons.

Formylation of [4](1,1′)ferrocenophane (XVII)

[4](1,1′)Ferrocenophane (XVII) (m.p. 60—61°C, lit. [11], m.p. 63—64°C) was prepared according to the procedure described by Rosenblum et al. [11]. Formylation of XVII was carried out with dimethylformamide—$POCl_3$ according to Hata's method [16] for the formylation of ferrocene. A dry chloroform solution (7 ml) of the ferrocenophane XVII (2.00 g) and dimethylformamide (1.23 g) was stirred at 0°C for 10 min under a N_2 gas atmosphere. Then $POCl_3$ (2.57 g) was added dropwise during 30 min to the above solution at 0°C. The reaction mixture was stirred at 55°C for 12 h. After evaporation in vacuo to remove excess $POCl_3$ and chloroform, saturated aq. Na_2CO_3 was added to the resulting residue. The hydrolysate was phase-separated, and the organic layer was washed with aq. NaCl, dried and evaporated. By column chromatography over silica gel (Mallinckrodt silicic acid), the reaction products were separated into two bands with benzene as eluent. The first band yielded 2-formyl[4](1,1′)ferrocenophane (XIX) (115 mg, 14%), which was recrystallized from hexane to give deep-red crystals, m.p. 125—130°C. IR spectrum (KBr, cm^{-1}): 1670 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.70—3.15 (8H; m, $\rangle CH_2$), 3.98 (1H; m, Cp), 4.04 (1H; t, Cp) 4.22 (2H; m, Cp), 4.46 (1H, t, J = 2.7 Hz, H_4 of Cp), 4.57 (1H; dd, J = 1.5 and 2.7 Hz, H_5 of Cp), 4.66 (1H; dd, J = 1.5 and 2.7 Hz, H_3 of Cp), 10.10 (1H; s, —CHO). Mass spectrum (*m/e*): 268 (M^+, 100), 239 ([M — CHO]$^+$, 35). The semicarbazone derivative of the 2-formyl isomer (XIX) was obtained as orange needles, m.p. 183—184°C. (Found: C, 58.56; H, 6.20; N, 11.87, M^+ 325.0895. $C_{16}H_{19}FeN_3O$ calcd.: C, 59.10; H, 5.89; N, 12.92%; mol. wt. 325.0876.)

The second band in the column chromatography of the formylation products yielded 3-formyl[4](1,1′)ferrocenophane (XVIII) (1.54 g, 69%), which was

recrystallized from hexane to give deep-red crystals, m.p. 51—52°C. (Found: C, 67.21; H, 6.26. $C_{15}H_{16}FeO$ calcd.: C, 67.19; H, 6.01%.) IR spectrum (KBr, cm^{-1}): 1670 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.65—2.05 (4H; m, $\rangle CH_2$), 2.25—2.65 (4H; m, CH_2), 4.04 (1H; m, Cp), 4.22 (3H; m, Cp), 4.50 (1H; dd, J = 1.4 and 2.6 Hz, H_5 of Cp), 4.65 (1H; dd, J = 1.4 and 2.6 Hz, H_4 of Cp), 4.73 (1H; t, J = 1.4 Hz, H_2 of Cp), 9.85 (1H; s, —CHO). Mass spectrum (m/e): 268 (M^+, 100), 239 ([M — CHO]$^+$, 34). The semicarbazone derivative of the 3-formyl isomer (XVIII) was obtained as orange needles, m.p. 170—171°C. (Found: C, 58.87; H, 6.21; N, 12.54. $C_{16}H_{19}FeN_3O$ calcd.: C, 59.10; H, 5.89; N, 12.92%.)

3-(2-Carboxyvinyl)[4](1,1′)ferrocenophane (XX)

3-Formyl[4](1,1′)ferrocenophane (XVIII) (1.10 g), malonic acid (1.10 g) and piperidine (1.0 ml) were dissolved in 27 ml of pyridine. The reaction mixture was refluxed under a N_2 gas atmosphere for 4 h. After neutralization with dil. HCl, the product was extracted with benzene. The extracts were washed with aq. NaCl, dried and evaporated. The residual product was purified by column chromatography over silica gel with benzene—ethyl acetate (10:1) as eluent (1.13 g, 88%). On recrystallization from ethanol, the resulting deep-red needles proved to be 3-(2-carboxyvinyl)[4](1,1′)ferrocenophane (XX), m.p. 159.5—160°C. (Found: C, 65.84; H, 5.94. $C_{17}H_{18}FeO_2$ calcd.: C, 65.83; H, 5.85%.) IR spectrum (KBr, cm^{-1}): 1674 [ν(C=O)], 1610 [ν(C=C)]. PMR spectrum ($CDCl_3$, δ): 1.70—1.90 (4H; m, $\rangle CH_2$), 2.25—2.55 (4H; m, $\rangle CH_2$), 3.86 (1H, m, Cp), 3.94 (1H; m, Cp), 4.19 (2H; m, Cp), 4.35 (2H; m, Cp), 4.43 (1H, m, Cp), 5.97 and 7.65 (2H; an AB system, J = 15 Hz, *trans* olefinic protons), 11.51 (1H; s, —COOH). Mass spectrum (m/e): 310 (M^+, 100), 266 ([$M - CO_2$]$^+$, 7.7), 265 ([$M - CO_2H$]$^+$, 11).

3-(2-Carboxyethyl)[4](1,1′)ferrocenophane (XXI)

3-(2-Carboxyvinyl)[4](1,1′)ferrocenophane (XX) (1.00 g) was hydrogenated with 10% Pd—C (300 mg) in acetone (72 mg) under 4 atm for 4 h. The reaction mixture was filtered to remove the catalyst, and the filtrate was evaporated. The residue was column-chromatographed over silica gel with benzene—acetone (10:1) to yield almost quantitatively 3-(2-carboxyethyl)[4](1,1′)ferrocenophane (XXI) (990 mg), m.p. 89—90°C (yellow crystals). (Found: M^+ 312.0808. $C_{17}H_{20}FeO_2$ calcd.: mol. wt. 312.0811.) IR spectrum (KBr, cm^{-1}); 1699 [ν(C=O) of carboxyl]. PMR spectrum ($CDCl_3$, δ): 1.70—1.90 (4H; m, $\rangle CH_2$), 2.30—2.50 (4H, m, $\rangle CH_2$), 2.58 (4H; s, $\rangle CH_2$), 3.78 (1H; m, Cp), 3.90—4.10 (6H; m, Cp), 11.08 (1H; s, —COOH). Mass spectrum (m/e): 312 (M^+, 100).

[4](3,3′)[3](1,1′)Ferrocenophane-6-one (XXII)

A dry dichloromethane solution (100 ml) of 3-(2-carboxyethyl)[4](1,1′)-ferrocenophane (XXI) (5.00 g) was added slowly dropwise to a dry dichloromethane solution (100 ml) of $(CF_3CO)_2O$ (8.00 g) with stirring at 0°C under a N_2 gas atmosphere. After sitting at 0°C for 4 h, the reaction mixture was poured into water. The extracts with dichloromethane were washed with dil. HCl, aq. $NaHCO_3$ and aq. NaCl, dried and evaporated. Purification of the residual product by column chromatography on silica gel with benzene—ethyl acetate (8:1) afforded 4.51 g (96%) of [4](3,3′)[3](1,1′)ferrocenophane-6-one (XXII), which was

recrystallized from hexane—ethyl acetate to give orange plates, m.p. 86—86.5°C. (Found: C, 69.34; H, 6.01. $C_{17}H_{18}FeO$ calcd.: 69.41; H, 6.17%.) IR spectrum (KBr, cm^{-1}): 1662 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.60—2.40 (8H, m, $\rangle CH_2$), 2.87 (4H; m, $\rangle CH_2$), 3.95 (1H; dd, $H_{5'}$ of Cp), 4.34 (1H; dd, J = 1,4 and 2.6 Hz, H_4 of Cp), 4.42 (1H; dd, J = 1.4 and 2.3 Hz, $H_{4'}$ of Cp), 4.64 (2H, m, H_5 and $H_{2'}$ of Cp), 4.86 (1H; t, J = 1.4 Hz, H_2 of Cp). Mass spectrum (*m/e*): 294 (M^+, 100), 266 ([M — CO]$^+$, 18).

Bridge enlargement of [4](3,3')[3](1,1')ferrocenophane-6-one (XXII)

An ether solution of CH_2N_2 (120 ml) was added to a methanol solution (75 ml) of [4](3,3')[3](1,1')ferrocenophane-6-one (XXII) (770 mg). After stirring at 0°C in the dark for 10 h, the reaction mixture was evaporated in vacuo. The residue was column-chromatographed over silica gel (200 mesh), whereby it was separated into the two bridge-enlarged isomeric ketones. The first band eluted with benzene yielded 735 mg (90%) of [4](1,1')[4](3,3')ferrocenophane-7-one (XXIII), which was recrystallized from hexane—ethyl acetate to give yellow needles, m.p. 95—96°C. (Found: C, 70.05; H, 6.47. $C_{18}H_{20}FeO$ calcd.: C, 70.15; H, 6.54%.) IR spectrum (KBr, cm^{-1}): 1696 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.60—1.85 (4H; m, $\rangle CH_2$), 2.15—2.40 (4H; m, $\rangle CH_2$), 2.68 (4H; bs, $\rangle CH_2$), 3.20 (2H; s, isolated methylene at 6-position), 3.85—4.10 (6H; m, Cp). Mass spectrum (*m/e*): 308 (M^+, 100), 280 ([M — CO]$^+$, 24), 252 ([M — (CO + C_2H_4)]$^+$, 19).

The second band eluted with benzene—ethyl acetate (8:1) yielded 30 mg (3.7%) of [4](1,1')[4](3,3')ferrocenophane-6-one (XXIV), which was recrystallized from hexane—ethyl acetate to give yellow plates, m.p. 112.5—114°C. (Found: M^+ 308.0853. $C_{18}H_{20}FeO$ calcd.: mol. wt. 308.0861.) IR spectrum (KBr, cm^{-1}): 1646 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.60—2.75 (14H; m, CH_2), 3.89 (2H; d, J = 2.0 Hz, $H_{4'}$ and $H_{5'}$ of Cp), 4.05 (1H; t, J = 2.0 Hz, $H_{2'}$ of Cp), 4.44 (1H; dd, J = 1.5 and 2.5 Hz, H_4 of Cp), 4.54 (1H; dd, J = 1.5 and 2.5 Hz, H_5 of Cp), 4.64 (1H; t, J = 1.5 Hz, H_2 of Cp). Mass spectrum (*m/e*): 308 (M^+, 100), 280 ([M — CO]$^+$, 6.6), 265 ([M — $COCH_3$]$^+$, 27).

Bridge enlargement of 3-(2-carboxyethyl)[3](1,1')ferrocenophane-6-one (XXVI)

Heteroannular cyclization of 1,1'-bis(2-carboxyethyl)ferrocene (III) (1.11 g) with $(CF_3CO)_2O$ (10.5 g) according to the procedure described by Rinehart et al. [4], afforded a mixture of 2-(2-carboxyethyl)ferrocenephane-6-one (XXV) and 3-(2-carboxyethyl)ferrocenophane-6-one (XXVI), which compounds were so unstable that they had to be immediately converted into the methyl esters with CH_2N_2. A mixture of the esters was column-chromatographed on silica gel with benzene—ethyl acetate (50:1), three bands being obtained. The first band was the diester of the starting material. The second band yielded 215 mg (20%) of the ester of the 2-substituted ferrocenophane (XXV), an orange-red oil. IR spectrum (neat liq., cm^{-1}); 1725 [ν(C=O) of ester], 1660 [ν(C=O) of bridge]. PMR spectrum ($CDCl_3$, δ): 2.30—3.50 (8H, m, $\rangle CH_2$), 3.69 (3H; s, —CH_3), 4.08 (3H, m, Cp), 4.28 (2H; d, Cp), 4.68 (1H; m, Cp), 4.95 (1H; m, Cp).

The third band yielded 538 mg (49%) of the methyl ester of the 3-substituted ferrocenophane (XXVI), an orange-red oil. IR spectrum (neat liq., cm^{-1}): 1730 [ν(C=O) of ester], 1660 [ν(C=O) of bridge]. PMR spectrum ($CDCl_3$, δ):

2.53 (4H, s, $\rangle CH_2$), 2.85 (4H; s, $\rangle CH_2$), 3.62 (3H; s, $-CH_3$), 3.79 (1H; dd, Cp), 4.03 (1H; dd, Cp), 4.23 (1H; t, Cp), 4.50 (1H; dd, Cp), 4.57 (1H; dd, Cp), 4.68 (2H; d, Cp).

An ether solution of CH_2N_2 (70 ml) was added to a methanol (10 ml) solution of the methyl ester of the 3-substituted isomer (XXVI) (538 mg). After stirring at room temperature for 23 h, the reaction mixture was evaporated in vacuo. On column chromatography of the crude residual product over silica gel (Mallinckrodt silicic acid), the first band eluted with benzene yielded 327 mg (58%) of 3-[2-(methoxycarbonyl)ethyl][4](1,1′)ferrocenophane-7-one (XXVII), a bridge enlargement product, which was recrystallized from hexane—ethyl acetate to give yellow granules, m.p. 71—72°C. (Found: M^+ 340.0740. $C_{18}H_{20}FeO_3$ calcd.: mol. wt. 340.0760.) IR spectrum (KBr, cm^{-1}): 1725 [ν(C=O) of ester], 1680 [ν(C=O) of bridge]. PMR spectrum ($CDCl_3$, δ): 2.54 (4H; m, $\rangle CH_2$), 2.75 (4H; s, $\rangle CH_2$), 3.26 (2H; s, isolated methylene at 6-position), 3.65 (3H; s, $-CH_3$), 3.81 (1H; dt, J = 1.3 and 2.5 Hz, Cp), 4.02 (3H; m, Cp), 4.10 (1H; m, Cp), 4.15 (1H; m, Cp), 4.21 (1H; td, J = 1.3 and 2.5 Hz, Cp). Mass spectrum (m/e): 340 (M^+, 100).

Bridge enlargement of the methyl ester of the 2-substituted [3]ferrocenophane (XXV) under the same conditions as the above reaction was unsuccessful, the recovered starting material and a small amount of an unknown product being obtained.

The [4]ferrocenophane XXVII (50 mg) was reduced under Clemmensen conditions according to the procedure for the reduction of the keto-ester I already described. Column chromatography over silica gel separated the reduction product and the starting material into two bands. The first band eluted with benzene yielded 21 mg (43%) of 3-[2-(methoxycarbonyl)ethyl][4](1,1′)ferrocenophane (XXVIII), an orange-yellow oil. IR spectrum (neat liq., cm^{-1}): 1740 [ν(C=O) of ester]. PMR spectrum ($CDCl_3$, δ): 1.70—2.00 (4H; m, $\rangle CH_2$), 2.25—2.65 (4H; m, $\rangle CH_2$), 2.59 (4H; s, $\rangle CH_2$), 3.73 (3H; s, $-CH_3$), 3.88 (1H; t, Cp), 4.00—4.25 (6H; m, Cp).

Hydrolysis of the methyl ester XXVIII with NaOH in benzene—methanol—water afforded the corresponding carboxylic acid, which was identical with the acid XXI, in 94% yield.

Bridge enlargement of [3](1,1′)[3](3,3′)ferrocenophane-6-one (XXIX)

[3](1,1′)[3](3,3′)Ferrocenophane-6-one (XXIX) (m.p. 114—115°C, lit. [4], m.p. 111—112.5°C) was prepared by cyclization of the diacid III followed by Clemmensen reduction, cyclization with $(CF_3CO)_2O$ and then chromatographic separation over silica gel, according to the modification of the procedure described by Rinehart et al. [4].

An ether solution of CH_2N_2 (2 ml) was added to a methanol solution (2 ml) of the [3][3]ferrocenophane XXIX (50 mg). The solution was stirred at 0°C in the dark for 3.5 h, and then evaporated in vacuo. The residue was column-chromatographed over silica gel to afford a yellow band which was eluted with benzene. The band yielded 47 mg (89%) of [4](1,1′)[3](3,3′)ferrocenophane-7-one (XXXI), a bridge enlargement product, which was recrystallized from hexane to give yellow plates, m.p. 71—72°C. (Found: C, 69.13; H, 6.14; M^+ 294.0706. $C_{17}H_{18}FeO$ calcd.: C, 69.41; H, 6.17%; mol. wt. 294.0706).

IR spectrum (KBr, cm^{-1}): 1698 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.86 (6H; s, $\rangle CH_2$), 2.60—2.90 (4H; m, $\rangle CH_2$), 3.16 (2H; s, isolated methylene at 6-position), 3.84 (1H; t, J = 1.8 Hz, Cp), 3.89 (1H; t, J = 1.8 Hz, Cp), 4.11 (4H; d, J = 1.8 Hz, Cp).

In the column chromatography, the fifth band eluted with benzene—ethyl acetate (20:1) yielded 6-hydroxy-6-(hydroxymethyl)[3](1,1')[3](3,3')ferrocenophane (XXXII) (3.6 mg, 7%), m.p. 180°C. (Found: M^+ 312.0804. $C_{17}H_{20}FeO_2$ calcd.: mol. wt. 312.0811.) IR spectrum (KBr, cm^{-1}): 3380 [ν(OH)]. Mass spectrum (*m/e*): 312 (M^+, 100), 294 ([$M - H_2O$]$^+$, 44), 281 ([$M - CH_2OH$]$^+$, 77), 265 ([$M - (H_2O + CHO)$]$^+$, 67), 253 ([$M - (CH_2OH + CO)$]$^+$, 57).

The other bands were the starting material (4.0 mg) and unknown products.

[4](1,1')[3](3,3')Ferrocenophane (XXXIII)

[4](1,1')[3](3,3')Ferrocenophane-7-one (XXXI) (30 mg) was reduced with $LiAlH_4$ (49 mg) and $AlCl_3$ (28 mg) in ether (4 ml) according to the procedure already described in the preparation of the [4][4]ferrocenophane XIII. The crude reaction products were column-chromatographed over silica gel, two bands being obtained. The first band eluted with hexane—benzene (1:4) yielded 23 mg (79%) of [4](1,1')[3](3,3')ferrocenophane (XXXIII), which was recrystallized from ethanol to give yellow plates, m.p. 73—74°C. (Found: M^+ 280.0920. $C_{17}H_{20}Fe$ calcd.: 280.0913.) PMR spectrum ($CDCl_3$, δ): 1.65—2.25 (14 H; m, $\rangle CH_2$), 3.81 (2H; t, J = 1.8 Hz, H_2 and $H_{2'}$ of Cp), 4.00 (4H; m, Cp).

The second band eluted with benzene—ethyl acetate (1:5) yielded a small amount of 7-hydroxy[4](1,1')[3](3,3')ferrocenophane (XXXIV) (1 mg, 3.3%).

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References

1 M. Hisatome, T. Namiki and K. Yamakawa, J. Organometal. Chem., 96 (1975) C55.
2 W.E. Watts, Organometal. Chem. Rev., 2 (1967) 231.
3 K. Schlögl and M. Peterlik, Tetrahedron Lett., (1962) 573; Monatsch. Chem., 93 (1962) 1328.
4 K.L. Rinehart, D.E. Bublitz and D.H. Gustafson, J. Amer. Chem. Soc., 85 (1963) 970.
5 D.E. Bublitz and K.L. Rinehart, Tetrahedron Lett., (1964) 827.
6 N.D. Jones, R.E. Marsh and J.H. Richards, Acta Crystallogr., 19 (1965) 330.
7 F. Vögle and P. Neumann, Tetrahedron, 26 (1970) 5847.
8 K.L. Rinehart and R.J. Curby, J. Amer. Chem. Soc., 79 (1957) 3290.
9 K.L. Rinehart, R.J. Curby, D.H. Gustafson, K.G. Harrison, R.E. Bozak and D.E. Bublitz, J. Amer. Chem. Soc., 84 (1962) 3263.
10 K. Schlögl and M. Fried, Tetrahedron Lett., (1963) 1473.
11 M. Rosenblum, A.K. Banerjee, N. Danieli, R.W. Fish and V. Schlatter, J. Amer. Chem. Soc., 85 (1963) 316.
12 T. Shirafuji, A. Odaira, Y. Yamamoto and H. Nozaki, Bull. Chem. Soc. Jap., 45 (1972) 2884.
13 H. Falk and K. Schlögl, Monatsh. Chem., 96 (1965) 266; H. Egger and H. Falk, Tetrahedron Lett., (1966) 437.

14 M. Hisatome and K. Yamakawa, unpublished result.
15 R.S. Bly, C.M. DuBose, and G.B. Konizer, J. Org. Chem., 33 (1968) 2188.
16 K. Hata, Yuki-Gosei Kagaku (Tokyo), 29 (1971) 541.
17 M.I. Levenberg and J.H. Richards, J. Amer. Chem. Soc., 86 (1964) 2634.
18 D.W. Slocum and C.R. Ernst, Organometal. Chem. Rev. A, 6 (1970) 337.
19 R.R. McGuire, R.E. Cochoy and J.A. Winstead, J. Organometal. Chem., 84 (1975) 269.