Journal of Organometallic Chemistry, 125 (1977) 79—93

ORGANOMETALLIC COMPOUNDS

XXIII *. FORMATION OF NOVEL DI- AND TRI-BRIDGED FERROCENOPHANES

MASAO HISATOME *, NAOYUKI WATANABE, TAKAO SAKAMOTO and KOJI YAMAKAWA

Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162 (Japan)

(Received July 2nd, 1976)

Summary

Treatment of 2-(2-carboxyethyl)[4](1,1′)ferrocenophane with trifluoroacetic anhydride gave three isomeric products IV, V and VI; cyclized at the 3-, 3′- and 2′-positions, respectively. The same reaction of 4-(2-carboxyethyl)[4](1,1′)[4]-(3,3′)ferrocenophane also gave three multibridged products XXVII, XXVIII and XXIX, cyclized at the 5-, 5′- and 4′-positions, respectively. The di- and tri-bridged ferrocenes V and XXVIII linked between dissymmetric positions, "twist ferrocenophanes", are novel ferrocenophanes. Some reactions of the multi-bridged ferrocenophanes are described.

Studies on multibridged ferrocenophanes with three-carbon chains were reported by Schlögl and Peterlik [2], and by Rinehart et al. [3]. However, there has been no investigation of multibridged ferrocenophanes containing links with four-carbon chains, except for our recent paper [4], in which preparation of [4]-(1,1′)[4](3,3′)- and [4](1,1′)[3](3,3′)ferrocenophanes was described. Bis-cyclopentylene-(1,1′)(3,3′)ferrocenes reported by Dabard et al. [5] seem to be classified into the category of [3][3]ferrocenophanes. Since ferrocenophanes bridged with a four-carbon chain have different flexibility from the corresponding [3]-ferrocenophanes, it is considered that additional heteroannular cyclization and other reactions of the [4]ferrocenophanes show characteristic behavior.

In the present study, it was found that cyclization of propionic acid derivatives of [4]- and [4][4]-ferrocenophanes gave "twist ferrocenophanes", together with normal cyclized products. The twist ferrocenophanes are novel multibridged

* For Part XXII, see ref. 1.

ferrocenes linked between dissymmetric positions of cyclopentadienyl (Cp) rings. Further, the reactivity of the resultant di- and tri-bridged ferrocenophanes was investigated and yielded some multibridged ferrocenophane derivatives.

Results and discussion

Dibridged ferrocenophanes

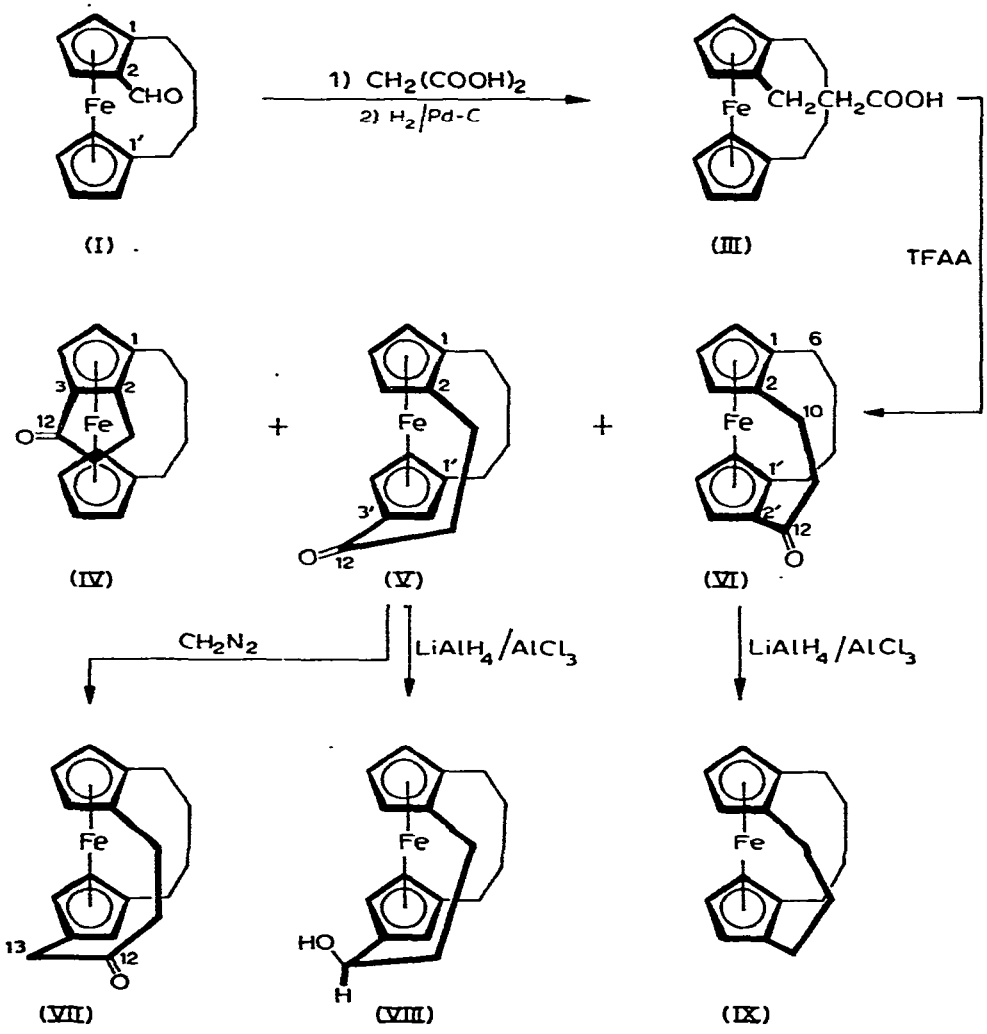
In the first place, bridging of [4]ferrocenophane between the 2- and 2'-positions * was attempted. Since intramolecular electrophilic substitution of (3-carboxypropyl)ferrocene derivatives selectively gives homoannular cyclization products [6—8], as also described below, a bridge with a four-carbon chain cannot be formed by one-step cyclization. Additional bridging of ferrocenophanes in the present study was carried out by cyclization of (2-carboxyethyl)ferrocene derivatives with a three-carbon side chain. The carboxylic acids were prepared by the Knoevenagel condensation of formyl derivatives, followed by catalytic reduction. This process was more advantageous in yield than other routes [4].

Condensation of 2-formyl[4](1,1')ferrocenophane[4] (I) with malonic acid gave in good yield (90%) 2-(2-carboxyvinyl)[4]ferrocenophane (II), which was reduced by H_2/Pd—C to afford quantitatively saturated carboxylic acid (III). Treatment of the acid III with trifluoroacetic anhydride (TFAA) gave three cyclization products IV, V and VI in 9, 44 and 35% yields, respectively. The IR and PMR spectra of the compound IV indicated, respectively, a conjugated carbonyl group band of a 5-membered ring [3,4,9] at 1688 cm^{-1} and a pair of proton signals of acylated Cp ring at δ 4.42 and 4.48 ppm as an AB system (J 2.5 Hz). The isomer IV was then assigned the homoannular cyclization product, [4](1,1')-[3](2,3)ferrocenophan-12-one. The acylated Cp ring proton signals of the ketone VI appeared as a triplet with J 2.5 Hz at δ 4.25 and two doublet of doublets (δ 4.12 and 4.83, J 1.5 and 2.5 Hz), while the signals of the other ketone V appeared as a triplet with J 1.5 Hz at δ 4.81 and two doublet of doublets (δ 4.22 and 4.37, J 1.5 and 2.5 Hz). The usual *ortho* and *meta* coupling constants in the Cp ring of acylferrocenes are 2.4—2.7 and 1.3—1.5 Hz, respectively [4,10]. Thus, the isomeric ketones V and VI were assigned [4](1,1')[3](2,3')- and [4](1,1')-[3](2,2')ferrocenophan-12-one, respectively.

Bridge enlargement of the two ketones V and VI with CH_2N_2 was attempted in order to obtain [4][4]ferrocenophane derivatives. The abnormal ferrocenophane V was converted into [4][4]ferrocenophane (VII), while in the reaction of VI with CH_2N_2, only the starting material was recovered. On the other hand, the ketone VI, as well as usual acylferrocene derivatives [2—4,11,12], underwent complete reduction with the $LiAlH_4/AlCl_3$ system to give saturated [4]-(1,1')[3](2,2')ferrocenophane (IX) in 90% yield. However, the reaction of the other isomer V under the same conditions afforded only an incomplete reduction product, a hydroxyl derivative VIII. The *endo*-configuration of the alcohol VIII was confirmed by the appearance of an intramolecular hydrogen bonding band with the iron atom [13] at 3580 cm^{-1} (free OH: 3621 cm^{-1}) in dilute CCl_4

* The numbering system of multibridged ferrocenophanes in this study is based on that of precursor ferrocenophanes, as illustrated in the schemes. Most of the compounds were obtained as racemic mixtures; only one enantiomorph is shown.

SCHEME 1. Synthesis of dibridged ferrocenophanes.



solution (1.4×10^{-3} mol/l). Accordingly, hydrogenolysis of the *endo*-alcohol VIII is probably much harder than hydrogenolysis of the corresponding alcohol derivative of VI.

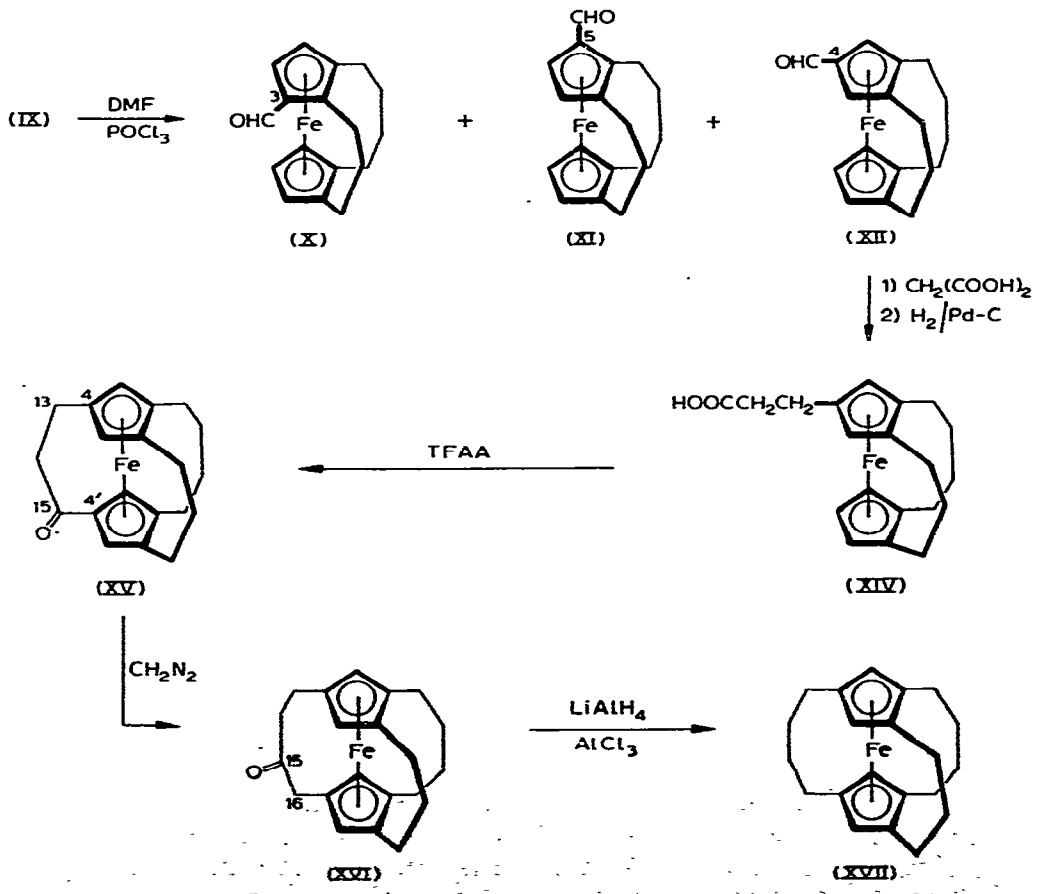
The reactivities of the two ketones V and VI can be interpreted by a difference in the following steric factor for the attack of the reagents on the carbonyl group. The C=O group of VI is adjacent to the other bridging chain, while that of V is not. Furthermore, in their predominant conformations, the dihedral angle of VI between the planes of the Cp ring and the C=O group is larger than that of V, this is supported by the frequencies of ν(C=O) in the ketones (V: 1648 cm^{-1}; VI: 1663 cm^{-1}).

Tribridged ferrocenophanes

In the next stage, syntheses of tribridged ferrocenophanes containing four-carbon chains were achieved by two routes.

Three formyl[4][3]ferrocenophanes (X, XI and XII) were obtained by formylation of IX with dimethylformamide (DMF) and $POCl_3$. The formylated Cp ring protons of the main product XII appeared at δ 4.42 and 4.56 as an AX system with J 1.3 Hz, corresponding to a *meta* coupling constant [4,10]. The minor products X and XI, which showed AX system signals with J 2.5 and 2.7 Hz (*ortho* coupling constant), respectively, were assigned as 3- and 5-formyl[4]-(1,1')[3](2,2')ferrocenophanes. Propionic acid (XIV) was derived from the 4-formyl[4](1,1')[3](2,2')ferrocenophane (XII) by condensation followed by catalytic reduction. Cyclization of the acid XIV with TFAA gave only one product (90%), in which the acylated Cp ring protons appeared at δ 4.54 and 4.65 as

SCHEME 2. Synthesis of tribridged ferrocenophanes from [4](1,1')[3](2,2')ferrocenophane (IX).

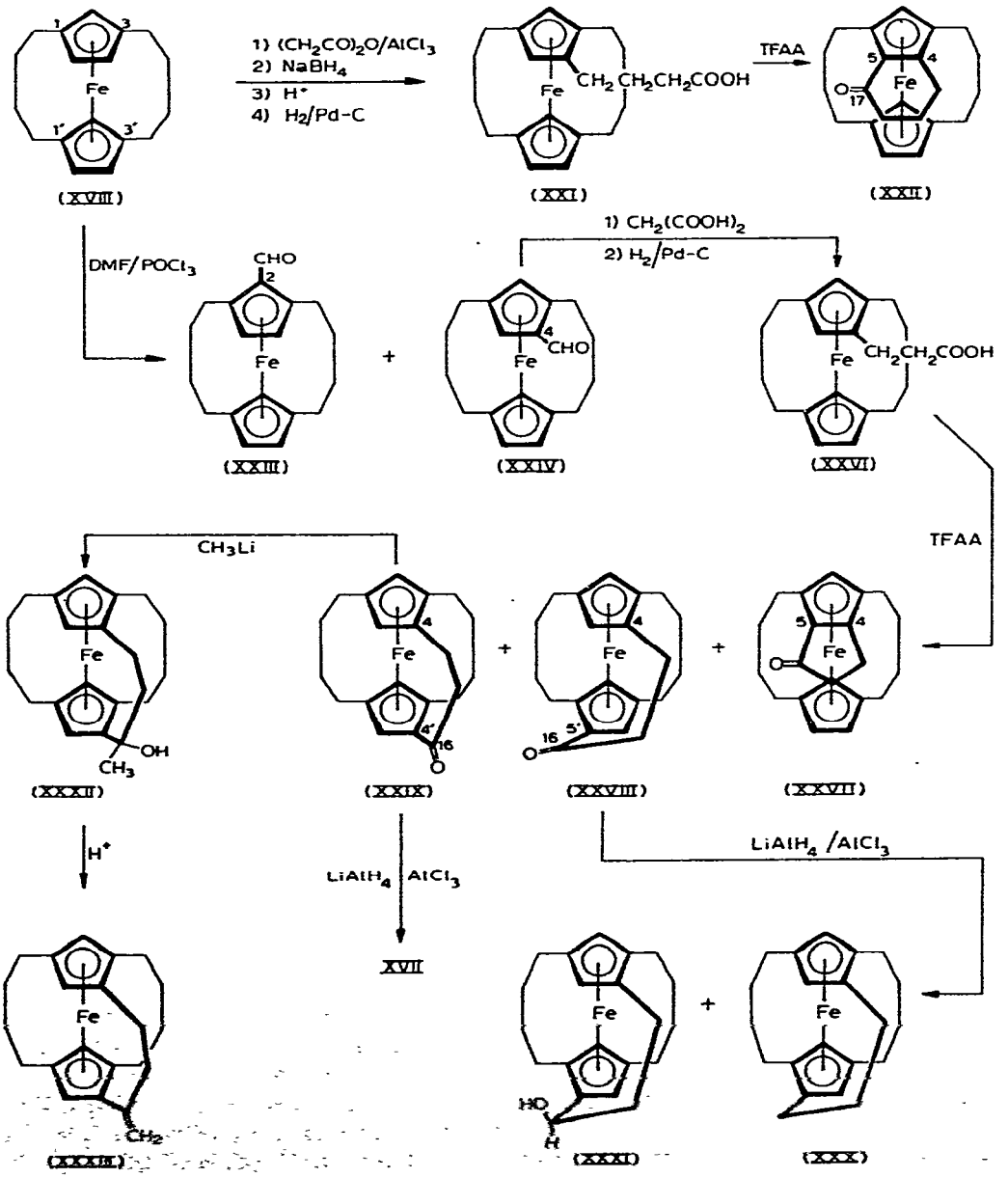


an AX system with a *meta* coupling constant (1.4 Hz). This [4](1,1')[3](2,2')-[3](4,4')ferrocenophan-15-one (XV) was converted into the bridge-enlargement product XVI in 80% yield by treatment with CH_2N_2. Saturated [4][4][3]ferro-

cenophane (XVII)*(m.p. 110—111°C) was obtained by reduction of the ketone XVI with the $LiAlH_4/AlCl_3$ system.

On the other hand, derivation of tribridged ferrocenophanes from [4](1,1')-[4](3,3')ferrocenophane described in our recent paper [4] was carried out. An attempt at direct preparation of tribridged [4][4][4]ferrocenophane by the cy-

SCHEME 3. Synthesis of tribridged ferrocenophanes from [4](1,1')[4](3,3')ferrocenophanes (XVIII).



clization of the butyric acid derivative of XVIII was unsuccessful. Treatment of the acid XXI, which was derived from XVIII by acylation with a four-carbon unit, gave only a homoannular cyclization product XXII at the 5-position in 86% yield. The spectra of XXII showed an acylated Cp ring proton at δ 4.40 as a singlet and an effectively conjugated C=O group band at 1663 cm^{-1}.

Formylation of [4][4]ferrocenophane (XVIII) gave two isomers XXIII and XXIV, which were assigned as the 2- and 4-formyl derivatives, respectively, by consideration of the patterns of acylated Cp ring proton signals; those of XXIII and XXIV were singlets (δ 4.39, 2H) and two doublets (δ 4.49 and 4.66, *J* 1.5 Hz). The main product XXIV was converted into propionic acid (XXVI) by the general method. Three cyclization products were obtained by treatment of the acid XXVI with TFAA. The compound XXVII possessing a conjugated C=O group of a 5-membered ring (1690 cm^{-1}) and an isolated proton of an acylated Cp ring (δ 4.38, singlet, 1H) is a homoannular cyclization product. The other possible bridged products in the reaction are 4'- and 5'-isomeric ketones. Reduction of the ketone XXIX [ν(C=O): 1670 cm^{-1}] with the $LiAlH_4/AlCl_3$ system gave a product (94%, m.p. 109—110.5°C) identical with the [4][4][3]ferrocenophane (XVII) described above by a mixed melting point determination and by spectral comparisons. The structure of the major product XXIX was then determined. The frequency (1650 cm^{-1}) of ν(C=O) in the other ketone XXVIII is analogous to that of dissymmetrically dibridged ferrocenophane V. Reduction of the ketone XXVIII with $LiAlH_4/AlCl_3$ for 68 h gave *endo*-alcohol XXXI, an incomplete reduction product, in 35% yield, together with deoxygenated ferrocenophane XXX (24%). Accordingly, the isomeric ketone XXVIII could be assigned as the tribridged product at 5'-position.

The dissymmetrically bridged ferrocenophanes, V and XXVIII, and their derivatives, were stable, in spite of their unusual structure. The Cp—Fe—Cp bond angle of both ketones V and XXVIII is presumed to be in the range of 140° to 150°, when the conformation is examined with a Dreiding stereo molecular model. We propose that the highly strained ferrocenophanes be called "twist ferrocenophanes".

Synthesis of [4][4][4]ferrocenophane from the ketone XXIX by treatment with CH_2N_2 under various conditions has not yet materialized. However, the ketone group of XXIX, when allowed to react with CH_3Li, was converted into the hydroxyl group XXXII. Treatment of this alcohol XXXII with hydrochloric acid gave an *exo*-methylene derivative XXXIII. Further investigations are in progress to obtain the tribridged [4][4][4]ferrocenophanes by rearrangement of the olefin XXXIII.

Experimental

All melting points are uncorrected. Column-chromatographic separations were carried out with Wako activated alumina (300 mesh), Wakogel C-200 (200 mesh), Kanto-kagaku silica gel (100 mesh), and Mallinckrodt silicic acid (100 mesh). 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 or a Hitachi R-24 spectrometer at 60 MHz at room temperature with tetramethylsilane as internal standard. The data of the PMR

spectra measured at 100 MHz are described unless otherwise stated. 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 in the 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.

General procedure

Formylation. A dry chloroform solution of ferrocenophane and dry dimethylformamide (DMF) was stirred at 0°C for 10 min under an N_2 gas atmosphere. Then $POCl_3$ was slowly added dropwise to the above solution at 0°C. The reaction mixture was stirred at room temperature. After evaporation in vacuo to remove excess reagents and solvent, 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. The residue was column-chromatographed over silica gel to yield several formyl products.

Condensation with malonic acid. Formylferrocenophane, malonic acid and piperidine were dissolved in dry pyridine. The reaction mixture was refluxed under an N_2 gas atmosphere. After neutralization with dil. aq. HCl, the product was extracted with benzene. The extracts were washed with aq. NaCl, dried and evaporated. The residue was purified by column chromatography over silica gel.

Catalytic reduction. An acetone solution of α,β-unsaturated carboxylic acids was hydrogenated with 10% Pd—C at room temperature under 3—4 atm. The reaction mixture was filtered to remove the catalyst, and the filtrate was evaporated. The residue was column-chromatographed over silica gel.

Cyclization. A dry dichloromethane solution of (carboxyalkyl)ferrocenophane was slowly added dropwise to a dry dichlomethane solution of trifluoroacetic anhydride (TFAA) with stirring at 0°C under an N_2 gas atmosphere. After stirring at room temperature, the reaction mixture was poured into water. The extracts with dichloromethane were washed with dil. aq. HCl, aq. $NaHCO_3$ and aq. NaCl, dried and evaporated. The residue was column-chromatographed over silica gel.

Bridge enlargement. An ether solution of CH_2N_2 was added to a methanol solution of ketoferrocenophane. The reaction mixture was stirred at 0°C or at room temperature in the dark. The solvent and the excess CH_2N_2 were evaporated in vacuo. The residue was column-chromatographed over silica gel.

Reduction with $LiAlH_4/AlCl_3$ system. $LiAlH_4$ powder was suspended in a dry ether solution of $AlCl_3$. A dry ether solution of ketoferrocenophane was added dropwise to the suspension. After stirring, excess reagent was decomposed with moist ether, and then water. The resulting reaction products were extracted with ether. The extracts were washed with aq. NaCl, dried and evaporated. The residue was column-chromatographed over silica gel or alumina.

Cyclization of 2-(2-carboxyethyl)[4](1,1')ferrocenophane (III)

2-Formyl[4](1,1')ferrocenophane[4] (I) (845 mg) was treated with malonic acid (850 mg) and piperidine (1 ml) in 20 ml of pyridine at 90—95°C for 3.5 h. The reaction product was purified by column chromatography over silica gel with benzene/ethyl acetate (20 : 1) as eluent to give crude crystals (880 mg, 90%). On recrystallization from ethanol, the resulting deep-red needles proved to be

2-(2-carboxyvinyl)[4](1,1')ferrocenophane (II), m.p. 183—184°C. (Found: M^+ 310.0679. $C_{17}H_{18}O_2Fe$ calcd.: mol.wt. 310.0655.) IR spectrum (KBr, cm^{-1}): 1675 [ν(C=O)], 1603 [ν(C=C]. PMR spectrum ($CDCl_3$, δ): 1.70—2.10 (4H, m, $\succ CH_2$), 2.30—2.65 (4H, m, $=CH_2$), 3.90 (1H, m, Cp), 4.00 (2H, m, Cp), 4.11 (1H, m, Cp), 4.39 (1H, t, J 2.5 Hz, H(4) of Cp), 4.43 (1H, m, Cp), 4.54 (1H, m, Cp), 6.05 and 7.91 (2H, an AX system, J 15 Hz, *trans* olefinic protons). Mass spectrum (*m/e*): 310 (M^+, 100), 266 ($[M - CO_2]^+$, 7), 265 ($[M - CO_2H]^+$, 9).

The α,β-unsaturated carboxylic acid (II) (625 mg) was hydrogenated with Pd—C (100 mg) in acetone (100 ml) for 20 h. The crude product was column-chromatographed over silica gel with benzene/acetone (40 : 1) to yield almost quantitatively 2-(2-carboxyethyl)[4](1,1')ferrocenophane (III) (622 mg), m.p. 85—101°C (yellow needles). (Found: M^+ 312.0840. $C_{17}H_{20}O_2Fe$ calcd.: mol.wt. 312.0811.) IR spectrum (KBr, cm^{-1}): 1703 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.70—2.05 (4H, m, $\succ CH_2$), 2.30—2.80 (8H, m, $=CH_2$), 3.79 (1H, m, Cp), 3.98 (4H, m, Cp), 4.06 (2H, m, Cp). Mass spectrum (*m/e*): 312 (M^+, 100), 253 ($[M - CH_2CO_2H]^+$, 8), 239 ($[M - C_2H_4CO_2H]^+$, 11).

The carboxylic acid (III) (202 mg) was cyclized with TFAA (1.96 g) in 40 ml of dichloromethane for 4 h. The reaction products were separated into three bands by column chromatography over silica gel. The first band eluted with benzene/ethyl acetate (50 : 1) yielded [4](1,1')[3](2,2')ferrocenophan-12-one (VI) (67 mg, 35%), which was recrystallized from hexane/ethyl acetate to give orange-red prisms, m.p. 219—222°C. (Found: C, 69.45; H, 6.19; M^+ 294.0726. $C_{17}H_{18}OFe$ calcd.: C, 69.41; H, 6.17%; mol.wt. 294.0706.) IR spectrum (KBr, cm^{-1}): 1663 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.80—2.00 (4H, m, $\succ CH_2$) 2.20—3.70 (8H, m, $\succ CH_2$), 3.90 (1H, dd, J 1.3 and 2.3 Hz, H(5) of Cp), 3.99 (1H, t, J 2.3 Hz, H(4) of Cp), 4.12 (1H, dd, J 1.5 and 2.5 Hz, H(5') of Cp), 4.25 (1H, t, J 2.5 Hz, H(4') of Cp), 4.57 (1H, dd, J 1.3 and 2.3 Hz, H(3) of Cp), 4.83 (1H, dd, J 1.5 and 2.5 Hz, H(3') of Cp). Mass spectrum (*m/e*): 294 (M^+, 100), 266 ($[M - CO]^+$, 6), 251 ($[M - COCH_3]^+$, 11).

The second band eluted with benzene/ethyl acetate (50 : 1) yielded [4](1,1')-[3](2,3')ferrocenophan-12-one (V) (84 mg, 44%), which was recrystallized from hexane/ethyl acetate to give orange-yellow plates, m.p. 130—131.5°C. (Found: C, 69.25; H, 6.25; M^+ 294.0716. $C_{17}H_{18}OFe$ calcd.: C, 69.41; H, 6.17%; mol.wt. 294.0706.) IR spectrum (KBr, cm^{-1}): 1648 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.75—3.10 (11H, m, $\succ CH_2$), 3.45 (1H, m, $\succ CH_2$), 3.82 (1H, t, J 2.0 Hz, H(4) of Cp), 4.16 (2H, m, H(3) and H(5) of Cp) 4.22 (1H, dd, J 1.5 and 2.5 Hz, H(5') of Cp), 4.37 (1H, dd, J 1.5 and 2.5 Hz, H(4') of Cp), 4.81 (1H, t, J 1.5 Hz, H(2') of Cp). Mass spectrum (*m/e*): 294 (M^+, 100), 266 ($[M - CO]^+$, 13), 251 ($[M - COCH_3]^+$, 8), 238 ($[M - COC_2H_4]^+$, 12).

The third band eluted with benzene/ethyl acetate (50 : 1) yielded 17 mg (8.9%) of [4](1,1')[3](2,3)ferrocenophan-12-one (IV), which was recrystallized from hexane/ethyl acetate to give red prisms, m.p. 104—105°C. (Found: C, 69.26; H, 6.31; M^+ 294.0696. $C_{17}H_{18}OFe$ calcd.: C, 69.41; H, 6.17%; mol.wt. 294.0706). IR spectrum (KBr, cm^{-1}): 1688 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.70—2.00 (4H, m, $\succ CH_2$), 2.30—3.15 (8H, m, $\succ CH_2$), 3.75 (1H, m, Cp), 3.90 (2H, m, Cp), 4.24 (1H, m, Cp), 4.42 (1H, d, J 2.5 Hz, H(5) of Cp), 4.48 (1H, d, J 2.5 Hz, H(4) of Cp). Mass spectrum (*m/e*): 294 (M^+, 100), 266 ($[M - CO]^+$, 24).

Bridge enlargement of [4](1,1')[3](2,3')ferrocenophan-12-one (V)

A methanol solution (6 ml) of [4](1,1')[3](2,3')ferrocenophan-12-one (V) (55 mg) was added into an ether solution (50 ml) of CH_2N_2. The mixture was stirred at room temperature for 46 h. The product was column-chromatographed over silica gel with benzene as eluent. The first band yielded 16 mg (28%) of [4](1,1')[4](2,3')ferrocenophan-12-one (VII), which was recrystallized from hexane/ethyl acetate to give yellow plates, m.p. 129—130°C. (Found: M^+ 308.0838. $C_{18}H_{20}OFe$ calcd.: mol.wt. 308.0862.) IR spectrum (KBr, cm^{-1}): 1692 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.50—3.00 (12H, m, $\rangle CH_2$), 3.30 and 3.40 (2H, an AB system, J 12.5 Hz, $\rangle CH_2$ at 13-position), 3.98 (3H, m, Cp), 4.08 (2H, m, Cp), 4,17 (1H, m, Cp). Mass spectrum (*m/e*): 308 (M^+, 100), 280 ([M — CO]$^+$, 34), 252 ([M — COC_2H_4]$^+$, 15).

On the other hand, the starting material was recovered unchanged in the bridge enlargement reaction of [4](1,1')[3](2,2')ferrocenophan-12-one (VI) (19 mg) with CH_2N_2 at room temperature for 44 h.

Reduction of [4](1,1')[3](2,3')ferrocenophan-12-one (V)

[4](1,1')[3](2,3')Ferrocenophan-12-one (V) (23 mg) was reduced with $LiAlH_4$ (35 mg) and $AlCl_3$ (18 mg) in ether (5 ml) at room temperature for 3 h. Column chromatography of the reactant over alumina yielded no complete reduction product, but *endo*-12-hydroxy[4](1,1')[3](2,3')ferrocenophane (VIII) in 86% yield (20 mg) with benzene/ethyl acetate (50 : 1) as eluent. The crude product was recrystallized from hexane/ethyl acetate to give yellow needles, m.p. 128—129°C. (Found: C, 69.24; H, 6.71; M^+ 296.0870. $C_{17}H_{20}OFe$ calcd.: C, 68.94; H, 6.81%; mol.wt. 296.0862.) IR spectrum (KBr, cm^{-1}): 3412 and 3380 [ν(O—H)]. PMR spectrum ($CDCl_3$, δ): 1.60—2.90 (13H, m, $\rangle CH_2$ and —OH), 3.77 (1H, bt, Cp), 3.97 (3H, m, Cp), 4.10 (1H, m, Cp), 4.27 (1H, m, Cp), 4.55 (1H, m, $\geqslant CH$ at 12-position). Mass spectrum (*m/e*): 296 (M^+, 100), 278 ([M — H_2O]$^+$, 5), 267 ([M — CHO]$^+$, 9).

Reduction of [4](1,1')[3](2,2')ferrocenophan-12-one (VI)

[4](1,1')[3](2,2')Ferrocenophan-12-one (VI) (22 mg) was reduced with $LiAlH_4$ (35 mg) and $AlCl_3$ (18 mg) in 5 ml of ether at 25°C for 3 h. The crude product was column-chromatographed over alumina to yield only 19 mg (90%) of [4](1,1')[3](2,2')ferrocenophane (IX), which was recrystallized from methanol to give yellow plates, m.p. 158—160°C. (Found: M^+ 280.0920. $C_{17}H_{20}Fe$ calcd.: mol.wt. 280.0913.) PMR spectrum ($CDCl_3$, δ): 1.70—2.00 (7H, m, $\rangle CH_2$), 2.10—2.35 (7H, m, $\rangle CH_2$), 3.84 (2H, dd, J 1.5 and 2.3 Hz, H(3) and H(3') of Cp), 3.94 (2H, dd, J 1.5 and 2.3 Hz, H(5) and H(5') of Cp), 3.98 (2H, t, J 2.3 Hz, H(4) and H(4') of Cp). Mass spectrum (*m/e*): 280 (M^+, 100), 266 ([M — CH_2]$^+$, 8), 252 [(M — C_2H_4]$^+$, 30), 239 ([M — C_3H_5]$^+$, 13).

Formylation of [4](1,1')[3](2,2')ferrocenophane (IX)

Formylation of [4](1,1')[3](2,2')ferrocenophane (IX) (182 mg) was carried out with DMF (200 mg) and $POCl_3$ (320 mg) in 3 ml of chloroform at room temperature for 15 h. On column chromatography over silica gel, the reaction products were separated into three bands with benzene as eluent. The first band yielded 3-formyl[4](1,1')[3](2,2')ferrocenophane (X) (7 mg, 3.5%). Purification

by rechromatography of the crude gave orange-red crystallines, m.p. 140—141°C. (Found: M^+ 308.0851. $C_{18}H_{20}OFe$ calcd.: mol.wt. 308.0862.) IR spectrum (KBr, cm^{-1}): 1664 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.65—2.60 (14H, m, $\geq CH_2$), 3.83 (1H, dd, J 1.5 and 2.5 Hz, H(3') of Cp), 3.91 (1H, dd, J 1.5 and 2.5 Hz, H(5') of Cp), 4.36 (1H, t, J 2.5 Hz, H(4') of Cp), 4.51 (1H, d, J 2.5 Hz, H(5) of Cp), 4.79 (1H, d, J 2.5 Hz, H(4) of Cp), 9.89 (1H, s, —CHO). Mass spectrum (*m/e*): 308 (M^+, 100), 282 ([$M - C_2H_2$]$^+$, 11), 280 ([M — CO]$^+$, 14).

The second band yielded 5-formyl[4](1,1')[3](2,2')ferrocenophane (XI) (22 mg, 11%), which was rechromatographed several times to give orange-red crystals, which sublimed at 210°C. (Found: M^+308.0844. $C_{18}H_{20}OFe$ calcd.: mol. wt. 308.0862.) IR spectrum (KBr, cm^{-1}): 1661 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.60—2.45 (14H, m, $\geq CH_2$), 3.76 (1H, t, J 2.0 Hz, H(4') of Cp), 4.17 (2H, d, J 2.0 Hz, H(3') and H(5') of Cp), 4.25 (1H, d, J 2.7 Hz, H(3) of Cp), 4.59 (1H, d, J 2.7 Hz, H(4) of Cp), 10.06 (1H, s, —CHO). Mass spectrum (*m/e*): 308 (M^+, 100), 282 ([$M - C_2H_2$]$^+$, 14), 280 ([M — CO]$^+$, 15), 279 ([M — CHO]$^+$, 14).

The deep-red oily compound obtained from the third band (142 mg, 71%) was purified by rechromatography several times to provide 4-formyl[4]-(1,1')[3](2,2')ferrocenophane (XII). (Found: M^+ 308.0843. $C_{18}H_{20}OFe$ calcd.: mol.wt. 308.0862.) IR spectrum (neat liq., cm^{-1}): 1662 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.65—2.40 (14H, m, $\geq CH_2$), 4.06 (1H, m, Cp), 4.18 (2H, m, Cp), 4.42 (1H, d, J 1.3 Hz, H(3) of Cp), 4.56 (1H, d, J 1.3 Hz, H(5) of Cp), 9.75 (1H, s, —CHO). Mass spectrum (*m/e*): 308 (M^+, 100), 280 ([M — CO]$^+$, 24), 279 ([M — CHO]$^+$, 17).

[4](1,1')[3](2,2')[3](4,4')Ferrocenophan-15-one (XV)

The Knoevenagel condensation of 4-formyl[4](1,1')[3](2,2')ferrocenophane (XII) (25 mg) with malonic acid (28 mg) and piperidine (0.1 ml) in 2 ml of pyridine at 95°C for 4 h afforded 26 mg (92%) of 4-(2-carboxyvinyl)[4](1,1')[3]-(2,2')ferrocenophane (XIII), which was purified by column chromatography over silica gel, followed by recrystallization from ethanol to give deep-red prisms, m.p. 196—197.5°C. (Found: M^+ 350.0972. $C_{20}H_{22}O_2Fe$ calcd.: 350.0967.) IR spectrum (KBr, cm^{-1}): 1680 [ν(C=O)], 1620 [ν(C=C)]. PMR spectrum ($CDCl_3$, δ): 1.60—2.35 (14H, m, $\geq CH_2$), 3.90 (1H, t, J 2.5 Hz, H(4') of Cp), 4.06 (1H, dd, J 1.5 and 2.5 Hz, H(3') of Cp), 4.17 (1H, dd, J 1.5 and 2.5 Hz, H(5') of Cp), 4.25 (1H, d, J 1.5 Hz, H(3) of Cp), 4.32 (1H, d, J 1.5 Hz, H(5) of Cp), 5.98 and 7.65 (2H, an AX system, J 15 Hz, *trans* olefinic protons). Mass spectrum (*m/e*): 350 (M^+, 100), 306 ([$M - CO_2$]$^+$, 37).

The α,β-unsaturated carboxylic acid (XIII) (92 mg) was reduced by H_2/Pd—C in acetone under 3 atm for 7 h. Column chromatography of the product over silica gel gave 81 mg (88%) of 4-(2-carboxyethyl)[4](1,1')[3](2,2')ferrocenophane (XIV), orange-yellow solid, m.p. 125—132°C. (Found: M^+ 352.1101. $C_{20}H_{24}O_2Fe$ calcd.: mol.wt. 352.1123.) PMR spectrum ($CDCl_3$, δ): 1.65—1.90 (8H, m, $\geq CH_2$), 2.05—2.30 (6H, m, $\geq CH_2$), 2.55 (4H, s, $\geq CH_2$), 3.78 (2H, m, Cp), 3.88 (2H, m, Cp), 3.97 (1H, m, Cp). Mass spectrum (*m/e*): 352 (M^+, 100), 326 ([$M - C_2H_2$]$^+$, 14), 293 ([$M - CH_2CO_2H$]$^+$, 19).

The acid (XIV) (68 mg) was reacted with TFAA (480 mg) in dichloromethane (14 ml) at room temperature for 3 h. The reaction product was column-chromatographed over silica gel with benzene/ethyl acetate (100 : 1) to yield 59 mg

(91%) of [4](1,1')[3](2,2')[3](4,4')ferrocenophan-15-one (XV). On recrystallization of the crude from ethyl acetate orange-yellow prisms, m.p. 145—146°C, was obtained. (Found: C, 71.97; H, 6.65; M^+ 334.1007. $C_{20}H_{22}OFe$ calcd.: C, 71.87; H, 6.63%; mol.wt. 334.1018.) IR spectrum (KBr, cm^{-1}): 1657 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.50—2.50 (15H, m, $\geq CH_2$), 2.80—3.30 (3H, m, $\geq CH_2$), 4.44 (2H, s, H(3) and H(5) of Cp), 4.54 (1H, d, J 1.4 Hz, H(3') of Cp), 4.65 (1H, d, J 1.4 Hz, H(5') of Cp). Mass spectrum (*m/e*): 334 (M^+, 100), 306 ($[M - CO]^+$, 13), 278 ($[M - COC_2H_4]^+$, 20).

[4](1,1')[3](2,2')[4](4,4')Ferrocenophan-15-one (XVI)

Bridge enlargement of [4](1,1')[3](2,2')[3](4,4')ferrocenophan-15-one (XV) (36 mg) with CH_2N_2 in ether (50 ml) and methanol (8 ml) at room temperature for 24 h afforded 29 mg (80%) of [4](1,1')[3](2,2')[4](4,4')ferrocenophan-15-one (XVI) which was column-chromatographed over silica gel with benzene as eluent. Recrystallization of the crude from hexane gave yellow needles, m.p. 78—80°C. (Found: M^+ 348.1179. $C_{21}H_{24}OFe$ calcd.: mol.wt. 348.1176.) IR spectrum (KBr, cm^{-1}): 1702 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.50—2.30 (14H, m, $\geq CH_2$), 2.70 (4H, m, $\geq CH_2$), 3.13 (2H, s, $\geq CH_2$ at 16-position), 3.93 and 4.03 (each 2H, bs, Cp). Mass spectrum (*m/e*): 348 (M^+, 100), 320 ($[M - CO]^+$ 62), 292 ($[M - COC_2H_4]^+$, 32).

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

(1) [4](1,1')[3](2,2')[4](4,4')Ferrocenophan-15-one (XVI) (5 mg) was reduced with $LiAlH_4$ (8 mg) and $AlCl_3$ (5 mg) in ether (3.5 ml) at room temperature for 6 h. The reduction product was column-chromatographed over alumina with hexane/benzene (1 : 4) to yield 4 mg (83%) of [4](1,1')[4](3,3')[3](4,4')-ferrocenophane (XVII), which was recrystallized from ethanol to give yellow plates, m.p. 110—111°C. (Found: C, 75.48; H, 7.77; M^+ 334.1360. $C_{21}H_{26}Fe$ calcd.: C, 75.45; H, 7.84%; mol.wt. 334.1381.) PMR spectrum ($CDCl_3$, δ): 1.55—2.30 (22H, m, $\geq CH_2$), 3.87 (2H, d, J 1.3 Hz, H(3) and H(3') of Cp), 3.95 (2H, d, J 1.3 Hz, H(5) and H(5') of Cp). Mass spectrum (*m/e*): 334 (M^+, 100), 306 ($[M - C_2H_4]^+$, 13).

(2) Reduction of [4](1,1')[4](3,3')[3](4,4')ferrocenophan-16-one (XXIX) (200 mg) with $LiAlH_4$ (300 mg) and $AlCl_3$ (165 mg) in ether (34 ml) at room temperature for 3 h yielded 181 mg (94%) of the reduction product (m.p. 109—110.5°C, from methanol), which was identified as [4](1,1')[4](3,3')[3](4,4')-ferrocenophane (XVII) by a mixed melting point determination (m.p. 110—111°C) and by spectral comparisons.

Cyclization of 4-(3-carboxypropyl)[4](1,1')[4](3,3')ferrocenophane (XXI)

A dichloromethane solution (3 ml) of [4](1,1')[4](3,3')ferrocenophane [4] (XVIII) (50 mg) was added with vigorous stirring into a suspension of anhydrous $AlCl_3$ (68 mg) in a dichloromethane solution (2 ml) of succinic anhydride (86 mg). The reaction mixture was stirred at room temperature for 18 h, and was then poured into ice-water. The resulting hydrolysate was phase separated after the reduction of ferricinium ion with added ascorbic acid. The organic layer was washed with saturated aq. Na_2CO_3 and then water, dried with $CaCl_2$ and evaporated. The residue was column-chromatographed over silica gel. The red band

eluted with benzene/ethyl acetate (50 : 1) yielded 40 mg (60%) of 4-(3-carboxypropanoyl)[4](1,1')[4](3,3')ferrocenophane (XIX), orange-red crystals. PMR spectrum ($CDCl_3$, at 60 MHz, δ): 1.60—2.50 (20H, m, $\geq CH_2$) 3.92 (2H, m, H(4') and H(5') of Cp), 4.11 (1H, t, H(2') of Cp), 4.43 (1H, d, H(2) of Cp), 4.58 (1H, d, H(5) of Cp).

Powder of $NaBH_4$ (20 mg) was added to an isopropyl alcohol (3.5 ml) solution of the keto-carboxylic acid (XIX) (40 mg). The reaction mixture was stirred at room temperature for 3 h. After addition of NH_4Cl and then water, the product was extracted with dichloromethane. The extracts were washed with 10% aq. HCl and then water, dried and evaporated in vacuo. The residue was column-chromatographed over silica gel with benzene as eluent to yield 25 mg (65%) of γ-lactone derivative XX (yellow oil) of [4][4]ferrocenophane. IR spectrum (neat liq., cm^{-1}): 1765 (ν(C=O) of γ-lactone ring).

The γ-lactone (XX) (25 mg) was reduced with H_2/Pd—C (10 mg) in acetic acid (6 ml) under 4.6 atm. for 20 h. After filtration of the reaction mixture through celite, water was added into the filtrate. The dichloromethane extracts of the product were washed with water, dried and evaporated. The crude residue was purified by column chromatography over silica gel with benzene/acetone (20 : 1) to yield 23 mg (92%) of 4-(3-carboxypropyl)[4](1,1')[4](3,3')ferrocenophane (XXI), a yellow oil. PMR spectrum ($CDCl_3$, at 60 MHz, δ): 1.60—2.10 (10H, m, $\geq CH_2$), 2.25—2.60 (12H, m, $\geq CH_2$), 3.76 (1H, bd, Cp), 4.06 (4H, bs, Cp), 9.35 (1H, bs, —COOH).

The carboxylic acid (XXI) (23 mg) was cyclized with TFAA (150 mg) in dichloromethane (5 ml) at room temperature for 2 h. The crude product was purified by column chromatography over silica gel with benzene to yield 19 mg (86%) of [4](1,1')[4](3,3')[4](4,5)ferrocenophan-17-one (XXII), a red oil. (Found: M^+ 362.1324. $C_{22}H_{26}OFe$ calcd.: mol.wt. 362.1331.) IR spectrum (neat liq., cm^{-1}): 1663 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.60—2.80 (22H, m, $\geq CH_2$), 3.82 (1H, m, H(5') of Cp), 3.91 (1H, t, *J* 2.0 Hz, H(2') of Cp), 3.97 (1H, m, H(4') of Cp), 4.40 (1H, s, H(2) of Cp). Mass spectrum (*m/e*): 362 (M^+, 100), 334 ($[M - CO]^+$, 1), 306 ($[M - COC_2H_4]^+$, 2).

Formylation of [4](1,1')[4](3,3')ferrocenophane (XVIII)

[4](1,1')[4](3,3')Ferrocenophane [4] (XVIII) (2.50 g) was formylated with DMF (3.74 g) and $POCl_3$ (7.50 g) in chloroform (53 ml) at 55°C for 12 h. On column chromatography of the crude products over silica gel with benzene, two formylated isomers were separated. The first band yielded 0.09 g (3%) of 2-formyl[4](1,1')[4](3,3')ferrocenophane (XXIII), which was recrystallized from hexane to afford deep-red prisms, m.p. 78—79°C. (Found: C, 70.95; H, 7.09. $C_{19}H_{22}OFe$ calcd.: C, 70.82; H, 6.88%.) IR spectrum (KBr, cm^{-1}): 1670 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.00—2.05 (8H, m, $\geq CH_2$), 2.25—2.55 (6H, m, $\geq CH_2$), 2.75—3.05 (2H, m, $\geq CH_2$), 3.94 (2H, d, *J* 1.4 Hz, H(4') and H(5') of Cp), 4.17 (1H, t, *J* 1.4 Hz, H(2') of Cp), 4.39 (2H, s, H(4) and H(5) of Cp), 10.45 (1H, s, —CHO). Mass spectrum (*m/e*): 322 (M^+, 100), 293 ($[M - CHO]^+$, 38).

The second band yielded 2.36 g (86%) of 4-formyl[4](1,1')[4](3,3')ferrocenophane (XXIV) (red oil), which was purified by column chromatography several times. (Found: M^+ 322.1011. $C_{19}H_{22}OFe$ calcd.: mol.wt. 322.1018.) IR spectrum (neat liq., cm^{-1}): 1670 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.50—

2.10 (8H, m, $\geq CH_2$), 2.10—2.90 (8H, m, $\geq CH_2$), 3.93 (1H, t, J 1.3 Hz, H(2') of Cp), 4.10 (1H, m, H(5') of Cp), 4.16 (1H, m, H(4') of Cp), 4.49 (1H, d, J 1.5 Hz, H(2) of Cp), 4.66 (1H, d, J 1.5 Hz, H(5) of Cp), 10.06 (1H, s, —CHO). Mass spectrum (*m/e*): 322 (M^+, 100), 293 ([M — CHO]$^+$, 34). The semicarbazone derivative of the 4-formyl isomer (XXIV) was obtained as orange needles, m.p. 120—123°C, on recrystallization from hexane/ethyl acetate.

Cyclization of 4-(2-carboxyethyl)[4](1,1')[4](3,3')ferrocenophane (XXVI)

Condensation of 4-formyl[4](1,1')[4](3,3')ferrocenophane (XXIV) (2.03 g) with malonic acid (2.03 g) and piperidine (1.2 ml) in 42 ml of pyridine on refluxing for 9 h gave 2.13 g (93%) of 4-(2-carboxyvinyl)[4](1,1')[4](3,3')ferrocenophane (XXV). Recrystallization from methanol gave red needles, m.p. 198—198.5°C. (Found: C, 68.82; H, 6.72. $C_{21}H_{24}O_2Fe$ calcd.: C, 69.24; H, 6.64%.) IR spectrum (KBr, cm^{-1}): 1676 [ν(C=O)], 1610 [ν(C=C)]. PMR spectrum ($CDCl_3$, δ): 1.55—2.00 (8H, m, $\geq CH_2$), 2.15—2.65 (8H, m, $\geq CH_2$), 3.85 (1H, m, Cp), 3.94 (2H, m, Cp), 4.35 (1H, m, Cp), 4.53 (1H, m, Cp), 6.01 and 7.87 (2H, an AX system, J 15 Hz, *trans* olefinic protons). Mass spectrum (*m/e*): 364 (M^+, 100), 320 ([M — CO_2]$^+$, 37).

The α,β-unsaturated carboxylic acid (XXV) (2.13 g) was reduced with H_2 and 10% Pd—C (0.5 g) in acetone (150 ml) under 4 atm. to yield quantitatively 4-(2-carboxyethyl)[4](1,1')[4](3,3')ferrocenophane (XXVI) (2.16 g). The acid was purified by column chromatography over silica gel with benzene/acetone (10 : 1) as eluent to give yellow prisms, m.p. 108—110°C. (Found: M^+ 366.1300. $C_{21}H_{26}O_2Fe$ calcd.: mol.wt. 366.1281.) IR spectrum (KBr, cm^{-1}): 1710 [ν(C=O)]. Mass spectrum (*m/e*): 366 (M^+, 100).

The acid (XXVI) (1.365 g) was cyclized with TFAA (2.00 g) in dichloromethane (54 ml) at room temperature for 6 h. The reaction products were separated into three bands by column chromatography over silica gel with benzene. The first eluted band yielded 742 mg (58%) of [4](1,1')[4](3,3')[3](4,4')ferrocenophan-16-one (XXIX). Recrystallization from hexane-benzene gave orange-yellow needles, m.p. 124—125°C. (Found: C, 72.58; H, 6.93. $C_{21}H_{24}OFe$ calcd.: C, 72.42; H, 6.95%). IR spectrum (KBr, cm^{-1}): 1670 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.50—3.70 (20H, m, $\geq CH_2$), 3.89 (1H, d, J 1.4 Hz, H(2) of Cp), 4.17 (1H, d, J 1.4 Hz, H(5) of Cp), 4.65 (1H, d, J 1.5 Hz, H(2') of Cp), 4.83 (1H, d, J 1.5 Hz, H(5') of Cp). Mass spectrum (*m/e*): 348 (M^+, 100), 320 ([M — CO]$^+$, 14), 305 ([M — $COCH_3$]$^+$, 18).

The second band yielded 60 mg (4.7%) of [4](1,1')[4](3,3')[3](4,5')ferrocenophan-16-one (XXVIII), which was recrystallized from hexane/ethyl acetate to give orange-yellow plates, m.p. 172—174°C. (Found: M^+ 348.1153. $C_{21}H_{24}OFe$ calcd.: mol.wt. 348.1175.) IR spectrum (KBr, cm^{-1}): 1650 [ν(C=O)]. PMR spectrum ($CDCl_3$, δ): 1.20—3.50 (20H, m, $\geq CH_2$), 3.85 (1H, d, J 1.2 Hz, H(5) of Cp), 4.11 (1H, d, J 1.2 Hz, H(2) of Cp), 4.29 (1H, d, J 1.5 Hz, H(2') of Cp), 4.60 (1H, d, J 1.5 Hz, H(4') of Cp). Mass spectrum (*m/e*): 348 (M^+, 100), 320 ([M — CO]$^+$, 11), 305 ([M — $COCH_3$]$^+$, 22).

The third band yielded 344 mg (27%) of [4](1,1')[4](3,3')[3](4,5)ferrocenophan-16-one (XXVII). Recrystallization of the ketone from hexane gave red needles, m.p. 120—120.5°C. (Found: C, 72.08; H, 6.96. $C_{21}H_{24}OFe$ calcd.: C, 72.42; H, 6.95%.) IR spectrum (KBr, cm^{-1}): 1690 [ν(C=O)]. PMR spectrum

($CDCl_3$, δ): 1.60—3.15 (20H, m,$\geq CH_2$), 3.66 (1H, dd, *J* 1.5 and 2.3 Hz, H(5') of Cp), 3.84 (1H, dd, *J* 1.5 and 2.3 Hz, H(4') of Cp), 3.92 (1H, t, *J* 1.5 Hz, H(2') of Cp), 4.38 (1H, s, H(2) of Cp). Mass spectrum (*m/e*): 348 (M^+, 100), 320 ($[M - CO]^+$, 27), 305 ($[M - COCH_3]^+$, 8).

Reduction of [4](1,1')[4](3,3')[3](4,5')ferrocenophan-16-one (XXVIII)

[4](1,1')[4](3,3')[3](4,5')Ferrocenophan-16-one (XXVIII) (37 mg) was reduced with $LiAlH_4$ (60 mg) and $AlCl_3$ (30 mg) at room temperature for 68 h. The reaction products were separated into two bands by column chromatography over alumina. The first band eluted with hexane/benzene (1 : 1) yielded 8.5 mg (24%) of [4](1,1')[4](3,3')[3](4,5')ferrocenophane (XXX), which was recrystallized from ethanol to give yellow plates, m.p. 197—198°C. (Found: M^+ 334.1355. $C_{21}H_{26}Fe$ calcd.: mol.wt. 334.1382.) PMR spectrum ($CDCl_3$, δ): 1.40—2.90 (22H, m,$\geq CH_2$), 3.83 (2H, d, *J* 1.3 Hz, H(5) and H(4') of Cp), 3.96 (2H, d, *J* 1.3 Hz, H(2) and H(2') of Cp). Mass spectrum (*m/e*): 334 (M^+, 100), 319 ($[M - CH_3]^+$, 6), 306 ($[M - C_2H_4]^+$, 18).

The second band eluted with benzene/ethyl acetate (50 : 1) yielded 13 mg (35%) of *endo*-16-hydroxy[4](1,1')[4](3,3')[3](4,5')ferrocenophane (XXXI), which was recrystallized from hexane/ethyl acetate to give yellow granules, m.p. 194—195°C. (Found: M^+ 350.1316. $C_{21}H_{26}OFe$ calcd.: mol.wt. 350.1331.) IR spectrum (KBr, cm^{-1}): 3520 [ν(O—H)]. PMR spectrum ($CDCl_3$, δ): 1.45—3.95 (21H, m,$\geq CH_2$ and —OH), 3.55 (1H, m, H(4') of Cp), 3.96 (2H, m, H(2) and H(2') of Cp), 4.34 (1H, m, H(5) of Cp), 4.72 (1H, m,$\geqslant CH$). Mass spectrum (*m/e*): 350 (M^+, 100), 332 ($[M - H_2O]^+$, 6), 321 ($[M - CHO]^+$, 19).

16-Hydroxy-16-methyl[4](1,1')[4](3,3')[3](4,4')ferrocenophane (XXXII)

An ether solution of CH_3Li (6 ml, conc.: 1.6 mol/l) was added dropwise to a benzene solution (9 ml) of [4](1,1')[4](3,3')[3](4,4')ferrocenophan-16-one (XXIX) (200 mg) at 6—10°C under an N_2 atmosphere. The reaction mixture was stirred at room temperature for 30 min, and then poured into water. The product was extracted with benzene several times. The extracts were washed with aq. NaCl, dried and evaporated. The residue was column-chromatographed over alumina with benzene/ethyl acetate (50 : 1). The yellow band yielded 202 mg (96%) of 16-hydroxy-16-methyl[4](1,1')[4](3,3')[3](4,4')ferrocenophane (XXXII), which was recrystallized from hexane to give yellow needles, m.p. 110—112°C. (Found: M^+ 364.1478. $C_{22}H_{28}OFe$ calcd.: mol.wt. 364.1487.) IR spectrum (KBr, cm^{-1}): 3408 [ν(O—H)]. PMR spectrum ($CDCl_3$, δ): 1.54 (3H, s, $—CH_3$), 1.55—2.50 (20H, m,$>CH_2$ and —OH), 2.90 (1H, m,$>CH_2$), 3.86 (1H, d, *J* 1.5 Hz, Cp), 3.92 (2H, d, *J* 1.5 Hz, Cp), 3.97 (1H, d, *J* 1.5 Hz, Cp). Mass spectrum (*m/e*): 364 (M^+, 100), 346 ($[M - H_2O]^+$, 34), 321 ($[M - COCH_3]^+$, 16).

16-Methylene[4](1,1')[4](3,3')[3](4,4')ferrocenophane (XXXIII)

16-Hydroxy-16-methyl[4](1,1')[4](3,3')[3](4,4')ferrocenophane (XXXII) (15 mg) was dissolved in benzene (10 ml). A mixture of the benzene solution (conc.: 3×10^{-3} mol/l) and 6*N* HCl (10 ml) was vigorously stirred at room temperature for 19 h. The reaction mixture was phase separated after the reduction of ferricinium ion with added ascorbic acid. The organic layer was washed with saturated aq. $NaHCO_3$ and then aq. NaCl, dried and evaporated. The residue was

column-chromatographed over alumina. The first band eluted with hexane/benzene (1 : 1) yielded 9.5 mg (66%) of 16-methylene[4](1,1')[4](3,3')[3](4,4')-ferrocenophane (XXXIII), which was recrystallized from ethanol to give yellow plates, m.p. 68—72°C. (Found: M^+, 346.1362. $C_{22}H_{26}Fe$ calcd.: mol.wt. 346.1382.) IR spectrum (KBr, cm^{-1}): 1626 [ν(C=C)]. PMR spectrum ($CDCl_3$, δ): 1.60—1;90 (8H, m, $\rangle CH_2$), 2.10—2.50 (8H, m, $\rangle CH_2$), 2.55—2.75 (4H, m, $\rangle CH_2$), 3.92 (1H, d, J 1.3 Hz, Cp), 4.05 (1H, d, J 1.3 Hz, Cp), 4.12 (1H, d, J 1.3 Hz, Cp), 4.16 (1H, d, J 1.3 Hz, Cp), 5.01 and 5.30 (2H, an AX system, J 2.3 Hz, $=CH_2$). Mass spectrum (m/e): 346 (M^+, 100), 318 ($[M - C_2H_4]^+$, 7), 290 ($[M - C_4H_8]^+$, 5).

The starting material (3.5 mg) was recovered from the second eluted band with benzene as eluent.

Acknowledgements

The authors are grateful to Dr. M. Suzuki, Tanabe Seiyaku Co. Ltd., for elemental analyses. Thanks are also due to Mrs. S. Toshioka and Miss. K. Ohdachi, and Miss N. Sawabe of this laboratory for measurement of the mass and PMR spectra, respectively.

References

1 M. Hisatome, T. Namiki and K. Yamakawa, J. Organometal. Chem., in press.
2 K. Schlögl and M. Peterlik, Tetrahedron Lett., (1962) 573; ibid, Monatsh. Chem., 93 (1962) 1328.
3 K.L. Rinehart, D.E. Bublitz and D.H. Gustafson, J. Amer. Chem. Soc., 85 (1963) 970.
4 M. Hisatome, T. Sakamoto and K. Yamakawa, J. Organometal. Chem., 107 (1976) 87.
5 D. Astruc, R. Dabard, M. Martin, P. Batail and D. Grandjean, Tetrahedron Lett., (1976) 829.
6 K.L. Rinehart and R.J. Curby, J. Amer. Chem. Soc., 79 (1957) 3290.
7 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.
8 K. Schlögl and M. Fried, Tetrahedron Lett., (1963) 1473.
9 D.E. Bublitz and K.L. Rinehart, Tetrahedron Lett., (1964) 827.
10 R.R. McGuire, R.E. Cochoy and J.A. Winstead, J. Organometal. Chem., 84 (1975) 269.
11 K. Schlögl, A. Mohar and M. Peterlik, Monatsh. Chem., 92 (1961) 921.
12 J.M.O. Osgerby and P.L. Pauson, J. Chem. Soc., (1961) 4604.
13 D.S. Trifan and R. Bacskai, J. Amer. Chem. Soc., 82 (1960) 5010.