Bridge Contraction of [4]Ferrocenophanes by Wolff Rearrangement and Synthesis of [3$_4$](1,2,3,4)Ferrocenophane via the Contraction Reaction

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The bridge contraction of α-oxo[4]ferrocenophane via a Wolff rearrangement was examined; β-formylation with ethyl formate, diazotization with tosyl azide and then irradiation with a mercury lamp in ethanol gave α-ethoxycarbonyl[3]ferrocenophane. A sequence of the reactions was applied to di- and tribridged α-oxo[4]ferrocenophanes to afford the corresponding [3]ferrocenophanes. The same reaction of α-oxo[4][3$_3$]-(1,2,3,4)ferroceneophane yielded α-oxo[3][3$_3$](1,2,3,4)ferrocenophane (**20**), but no α-ethoxycarbonyl[3][3$_3$](1,2,3,4)ferrocenophane, which was an usual product in the Wolff rearrangement in ethanol. The production of an unexpected compound **20** is possibly brought about by the addition of dioxygen to an ketene intermediate in the rearrangement, followed by removal of carbon dioxide. Reduction of **20** has led to the first synthesis of **1**, tetrabridged ferrocenophane with trimethylene chains in a C_{2v} symmetric mode.

Although a number of multibridged ferrocenophanes have been found so far,[1] the synthesis of [3$_4$](1,2,3,4)ferrocenophane (**1**)# bridged with four trimethylene chains in a C_{2v} symmetric mode has not been achieved, despite attempts to do so by several groups.[4—6] A report concerning the successful preparation by Schlögl and Peterlik[4] was revised after scrutiny of their synthetic reaction.[7] Although the product given via an acid-catalyzed cyclization of [3](1,2,4)ferrocenophane-3-propanoic acid was assigned to the corresponding tetrabridged phane by Vigo,[5] Hillman et al.[6,8] proved by X-ray crystal analysis that this compound was a condensed-ring ferrocenophane produced by homoannular cyclization accompanied by a rearrangement of the existing adjacent bridge. Hillman et al.[6] mentioned that the unusual reaction occurred so as to prevent the introduction of an additional strain by bridging, because trimethylene chain is too short to bridge between the two cyclopentadienyl (Cp) rings without any deformation. These results suggest that synthesis of **1** by direct addition of a fourth trimethylene bridge to [3$_3$](1,2,4)-ferrocenophane is very difficult.

Accordingly, we designed a route for the synthesis of **1** via a Wolff rearrangement of a tetramethylene bridge to form the fourth trimethylene bridge. It is known that the preparation of multibridged ferrocenophanes containing a tetramethylene bridge is relatively ready,[1c] and that the Wolff rearrangement is useful in synthesis of strained small-ring compounds.[9] The preparation of [4][3$_3$](1,2,3,4)ferrocenophane (**2**) which are available as precursors of **1** for the bridge contraction has already been achieved,[10] and the structure of **2** was confirmed by the X-ray crystal analysis of its derivative.[11] Since there has been no example of application of Wolff rearrangement to ferrocenophanes, the bridge contraction and the related reactions in monobridged and some multibridged ferrocenophanes were examined in order to find appropriate conditions. The contraction of **2** under these reaction conditions was carried out and the first synthesis of **1** has been completed (Chart 1). Those experimental results are mentioned and discussed in this paper.

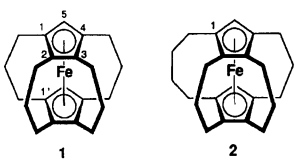
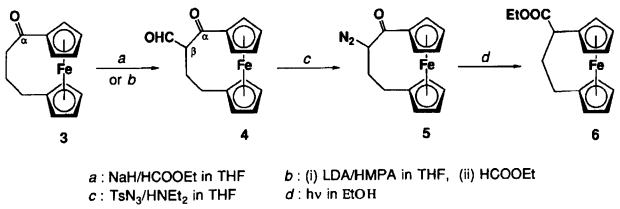


Chart 1.

#The nomenclature of the ferrocenophanes in papers published by the authors[2] was a modification of that proposed by Vögtle and Neumann.[3] The modified numbering system is also adopted for the compounds mentioned in this paper, because these are closely connected with the ferrocenophanes reported in a series of studies concerning multibridged ferrocenophanes.[1c,2] The numberings of the cyclopentadienyl rings and the bridges are denoted in the chart and schemes.

Results and Discussion

α-Oxo[4]ferrocenophane (**3**) was chosen as being the simplest model compound in order to find adequate conditions for the contraction of the tetramethylene bridge in ferrocenophanes (Scheme 1). Formylation of **3** with ethyl formate was conducted by using NaH or lithium diisopropylamide (LDA). The LDA method was superior in reproducibility, and the NaH method was easily handled. There was no significant difference in the yields between the two reaction conditions, and both

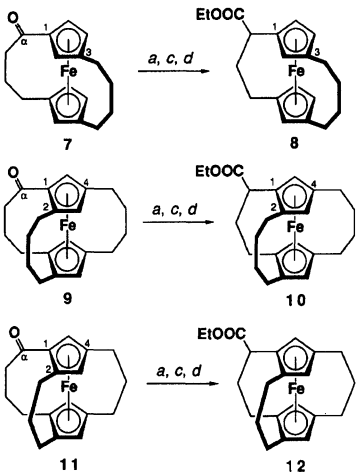


Scheme 1. Bridge contraction of α-oxo[4]ferrocenophane (**3**).

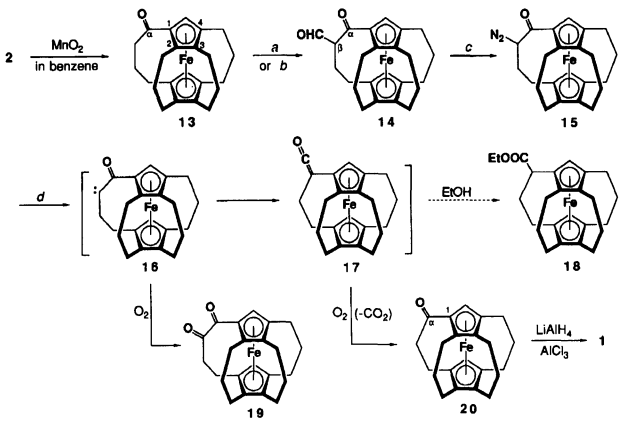
methods could be applied to formylation of other ferrocenophanes. Although the β-keto aldehyde derivatives of ferrocenophanes were usually unstable, **4** was sufficiently stable to be isolated and purified by column chromatography on silica gel (the maximal yield of 49%). The ^{1}H NMR spectrum of **4** in $CDCl_3$ indicated to be in an equilibrium mixture of keto and enol forms in a 10/1 ratio, respectively. Diazo ketone **5** given by reaction of **4** with *p*-toluenesulfonyl (tosyl) azide according to the usual procedure was so unstable that it could not be purified by chromatography; however, the diazo structure of the crude product, which was provided to the following rearrangement without further purification, was ascertained based on the appearance of the charasteric band of the diazo group in the IR spectrum (2130 cm^{-1}). Irradiation of **5** in ethanol with a high-pressure mercury lamp gave the corresponding rearrangement product (**6**) in 44% yield from **4**.

Bridge-contraction reactions of di- and tribridged ferrocenophanes were then carried out (Scheme 2). Formylation of **7**, **9**, and **11** with NaH and ethyl formate, followed by diazotization and then irradiation, without isolation of the keto aldehydes and diazoketones, afforded the corresponding bridge-contracted esters **8**, **10**, and **12** in 11, 10, and 25% yields, respectively.

Since it was demonstrated that bridge contraction by the Wolff rearrangement was applicable to multibridged ferrocenophanes, the synthesis of symmetrically tetrabridged [3$_4$]ferrocenophane (**1**) via the bridge contraction was attempted (Scheme 3). α-Oxo[4]-[3$_3$]ferrocenophane (**13**) were derived by the selective oxidation of the tetramethylene bridge of **2**[10] with $AgClO_4/CH_3ONa$[12] or manganese dioxide.[13] β-Keto aldehyde **14** yielded by formylation with LDA and ethyl formate was comparatively stable and could be purified to some extent by chromatography on silica gel. The ^{1}H NMR spectrum of **14** in $CDCl_3$ showed the formyl and enolic proton signals at δ=9.78 and 15.84 in a 1/4 intensity ratio, respectively. It is interesting that the enol form of **14** is more stable than the keto form, contrary to the situation of monobridged keto aldehyde (**4**). Diazotization of **14** followed by irradiation gave a bridge contraction product **20**. The mass spectrum of **20** showed the molecular ion peak at m/z 360, and the absorption of a conjugated carbonyl group with a Cp ring appeared at 1665 cm^{-1} in the IR spectrum. Furthermore, there was neither a signal of the ethoxycarbonyl group nor a signal of the methine group directly bound to ethoxycarbonyl group in the ^{1}H and ^{13}C NMR spectra. Namely, the product (**20**) was α-oxo[3][3$_3$]-ferrocenophane (8% yield from **13**), but not α-ethoxycarbonyl[3][3$_3$]ferrocenophane (**18**) that should be produced in a Wolff rearrangement of **15** in ethanol.



Scheme 2. Bridge contraction of di- and tribridged ferrocenophanes. Reaction conditions *a*—*d* are described in Scheme 1.



Scheme 3. Bridge contraction of [4][3$_3$](1,2,3,4)-ferrocenophane (**2**) and synthesis of [3$_4$](1,2,3,4)-ferrocenophane (**1**). Reaction conditions *a*—*d* are described in Scheme 1.

The other run of the photoreaction of the diazo compound **15** produced α,β-diketone **19**, whose structure was confirmed by observations of the characteristic diketone bands at 1700 and 1640 cm^{-1} and of the molecular ion peak at m/z 388 in the IR and mass spectra, respectively.

In the usual Wolff rearrangement of diazo ketones by irradiation in ethanol, ketene derivatives generated by a rearrangement of ketocarbenes undergo the addition of ethanol to give ethoxycarbonyl derivatives.[9a] If carbene **16** and ketene **17** are present as intermediates in the reaction system of **15**, it is presumed that diketone (**19**) is produced via the oxygenation of **16**, and that the addition of dioxygen to **17** followed by the removal of a carbon dioxide results in the production of ketone **20**. The formation of ferrocenylcarbenes[14—16] and oxygenation of the carbenes[14,15] to produce the corresponding ketones have been found. However, dioxygen in the reaction system should be almost removed by bubbling of an argon stream for ca. 30 min (as mentioned in the experimental section); the reaction of other ferrocenophanes under the same conditions afforded neither an α,β-dike-

tone nor a bridge-contracted α-oxo derivative. Therefore, the two oxygenation products (**19** and **20**) would be generated by reaction of the intermediates (**16**, **17**) with dioxygen exceptionally existing in the reaction system or with air when working up the reaction mixture. In either case of the oxygen source for the oxygenation, the production of **19** and **20** would demonstrate the unusual stability of the two intermediates, because the intermediates could not be quenched with the ethanol surrounding the species. The multibridged and congested structure of the phane may contribute to the stability, although the reason for the multibridging effect is not certain.

The production of **20** was fortunate for the preparation of **1**, because hydrolysis and decarboxylation of the usual product (**18**) became unnecessary. Reduction of ketone (**20**) gave tetrabridged phane (**1**) with four trimethylene chains in a C_{2v} symmetric mode. The ^{1}H and ^{13}C NMR spectra of **1** showed only one singlet signal of the Cp ring protons at $\delta=3.71$ and only four and three carbon signals assigned to the bridge methylenes and the Cp rings, respectively, in spite of the compound containing 22 carbons. The synthesis of [3$_4$](1,2,3,4)-ferrocenophane (**1**), the attempts of which by all other groups[4—6] failed, was achieved.

The phane **1** should be a highly strained compound because of the bridged structure with four trimethylene chains which are too short to bridge ferrocene nucleus without deformation. In general, although the methylene carbon signals of usual trimethylene bridges in the ^{13}C NMR spectra of ferrocenophanes do not appear beyond $\delta=20$ in the chemical shift,[17] the α-carbon signals of strained trimethylene bridges which are surrounded by other two bridges shift to high fields. For example, the α-carbon signals of the trimethylene bridges in [4]-[3][4][3](1,2,3,4)-, [4$_2$][3][4](1,2,3,4)-, and [4][3$_4$](1,2,3,4,5)ferrocenophanes appeared at $\delta=19.30$,[18] 18.91,[2c] and 17.97 and 18.62,[11] respectively. The ^{13}C NMR spectrum of **1** also showed the α-methylene signal of the 2,2′- and 3,3′-bridges at $\delta=18.43$, and the high field shift value was almost comparable with those of [4][3$_4$]ferrocenophane having five trimethylene bridges. Therefore, it is evidenced that **1** has the highly strained [3$_4$](1,2,3,4)-bridged structure.

Although the preparation of a single crystal that can be utilized for a measurement of the X-ray diffraction was attempted, such a crystal has not been obtained.

Experimental

All melting points were uncorrected. IR spectra were measured by using a Hitachi 215 infrared spectrophotometer. NMR spectra were measured on a JEOL JNM-FX100 (^{1}H nuclei, 100 MHz; ^{13}C nuclei, 25 MHz) or a JEOL JNM-GSX500 (^{1}H nuclei, 500 MHz; ^{13}C nuclei, 125 MHz) spectrometer. Mass spectra were obtained with a Hitachi M-80 double-focusing mass spectrometer by electron impact (EI) ionizing technique at 70 eV. high-resolution mass spectra were analyzed on a Hitachi M-003 data-processing system.

General Procedure of Formylation. (a) Reaction with NaH: To a solution of α-oxo[4]ferrocenophane derivative in tetrahydrofuran (THF) was added 60% NaH (ca. 2 mol equiv to the substrate) in mineral oil. After the suspension was stirred at room temperature for ca. 30 min under an argon atmosphere, ethyl formate (ca. 3 mol equiv of the substrate) was added to the suspension. The reaction mixture was refluxed for 10 h, and was then quenched by addition of methanol and then 6 M HCl (1 M=1 mol dm^{-3}). The resulting hydrolyzate was extracted with benzene, and the combined extracts were washed with saturated aq NaCl and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was rapidly eluted through a short column of silica gel with benzene/ethyl acetate (5/1) to remove any unknown highly polar compounds. After the appearance of two carbonyl bands in the IR spectrum was detected, the crude β-formyl-α-oxo[4]ferrocenophane was immediately used for the following diazotization without any further purification when being unstable.

(b) Reaction with Lithium Diisopropylamide (LDA): A solution of LDA and hexamethylphosphoric triamide (HMPA) in THF was prepared according to the usual way. To the LDA reagent was added dropwise a solution of α-oxo[4]ferrocenophane in THF at −40 °C under an argon atmosphere. The mixture was stirred at the same temperature for 20 min, and then ethyl formate was added all at once at −30—−40 °C. After stirring at room temperature for 1 h, the reaction mixture was quenched with saturated aq NH_4Cl and the product was extracted with benzene. The combined extracts were washed with saturated aq NaCl and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was treated in the same manner as that in method (a).

General Procedure of Diazotization. To a solution of β-formyl-α-oxo[4]ferrocenophane and excess diethylamine in dichloromethane cooled in an ice bath was added dropwise *p*-toluenesulfonyl (tosyl) azide (ca. 2 mol equiv to the substrate). The solution was stirred in the same ice bath for 15 min, and was then warmed up to room temperature followed by being stirred for 1 h. After 5% KOH was added, the mixture was stirred for 15 min and extracted with dichloromethane. The combined extracts were washed with water and dried over Na_2SO_4. The residue yielded by evaporation of the solvent in vacuo was rapidly eluted through a short column of silica gel with benzene/ethyl acetate (5/1) to remove any unknown highly polar compounds. Since the diazoferrocenophanes were usually unstable, the crude product was immediately used in the following photochemical reaction without further purification.

General Procedure of Wolff Rearrangement. A solution of diazoferrocenophane in absolute ethanol was placed in a flask equipped with a 100-W high-pressure mercury lamp (Ushio electric Inc., UM-102 type) through quartz for internal irradiation, and a stream of argon gas was bubbled through the solution for 30 min. The solution was irradiated for 15—18 h at room temperature. The solvent was evaporated in vacuo, and the residue was column-chromatographed on silica gel with benzene eluent.

β-Formyl-α-oxo[4]ferrocenophane (4). Formylation of α-oxo[4]ferrocenophane (**3**)[19] (300 mg, 1.2 mmol) using LDA (2.5 mmol), HMPA (0.22 ml, 1.3 mmol), ethyl

formate (0.28 ml, 3.5 mmol), and THF (20 ml) was carried out according to method (b) in the general procedure. The first band eluted with benzene/ethyl acetate (40/1) in the column chromatography of the product on silica gel yielded an unknown yellow oil. The second band with benzene/ethyl acetate (20/1) yielded **4** (164 mg, 49%), which was recrystallized from hexane/ethyl acetate to give yellow flakes; mp 107—108 °C. IR (KBr) 1740 and 1650 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$), an equilibrium mixture of keto and enol forms in a 10/1 ratio; keto form, δ=2.29 and 2.45 (1H and 3H, each m, CH_2), 3.58 (1H, m, COC<u>H</u>CHO), 3.92, 4.10, 4.15, 4.24, 4.56, 4.64, 4.70 and 4.81 (each 1H, m, Cp-H), 9.91 (1H, d, J=2.1 Hz, CHO); enol form, δ=2.68 and 2.96 (2H and 1H, each m, CH_2), 4.03, 4.15, 4.41 and 4.53 (each 2H, m, Cp-H), 8.37 (1H, d, J=5.6 Hz, =C<u>H</u>OH), 15.65 (1H, d, J=5.6 Hz, enolic OH); the signal assignments were confirmed by COSY. ^{13}C NMR (125 MHz, $CDCl_3$), keto form, δ=24.43 and 30.43 (CH_2), 61.53 (CO<u>C</u>HCHO), 68.83, 69.27, 69.95, 70.80, 71.50, 72.29, 74.60 and 75.29 (unsubstd. Cp-C), 78.46 and 89.56 (substd. Cp-C), 199.73 (C=O), 205.78 (CHO); enol form, 21.79 and 39.30 (CH_2), 69.31, 70.86 and 75.83 (unsubstd. Cp-C), 198.75 (C=O), the substd. Cp-C and 6- and 7-C of the bridge were not found, possibly, due to their weak intensities. MS m/z (rel intensity) 282 (100, M^+), 254 (80, $[M-CO]^+$).

Found: M^+ m/z 282.0316. Calcd for $C_{15}H_{14}O_2Fe$: M, 282.0342.

The starting material (88 mg, 29%) was recovered from the third band.

α-Ethoxycarbonyl[3]ferrocenophane (6). Diazotization of **4** (200 mg, 0.71 mmol) was carried out according to the general procedure using diethylamine (0.3 ml, 2.9 mmol), tosyl azide (200 mg, 1.0 mmol) and dichloromethane (10 ml). The diazo ketone structure of the crude product (**5**) was confirmed by IR spectrometry. IR (KBr) 2150 (azide) and 1600 (C=O) cm^{-1}.

The crude diazo ketone (**5**) was dissolved in ethanol (40 ml) and the solution was irradiated for 17 h. The product was column-chromatographed on alumina with benzene eluent to yield **6** (93 mg, 44% from **4**), which was recrystallized from hexane to give yellow plates; mp 65—66 °C. IR (KBr) 1725 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.23 (3H, t, J=7.2 Hz, CH_3), 1.76, 2.17, 2.37 and 2.47 (each 1H, m, CH_2 of bridge), 2.78 (1H, dd, J=2.7, 11.8 Hz, 6-H), 4.00, 4.04, 4.06, 4.10, 4.11 and 4.28 (1H, 1H, 1H, 1H, 3H and 1H, each m, Cp-H), 4.14 (2H, m, C<u>H</u>$_2$CH$_3$); MS m/z (rel intensity) 298 (100, M^+), 270 (42, $[M-CO]^+$), 225 (41, $[M-COOC_2H_5]^+$).

Found: C, 65.66; H, 6.81%, M^+ m/z 298.0648. Calcd for $C_{16}H_{18}O_2Fe$: C, 65.45; H, 6.89%; M, 298.0655.

α- Ethoxycarbonyl[3][4](1, 3)ferrocenophane (8). Bridge contraction of α-oxo[4][4](1,3)ferrocenophane (**7**)[20] (250 mg) was carried out according to the general procedure via formylation with NaH and ethyl formate to give a mixture of epimeric **8** (31 mg, 11% from **7**) as a yellow oil. IR (neat) 1740 and 1730 (C=O) cm^{-1}. ^{1}H NMR (100 MHz, $CDCl_3$) δ=1.22 and 1.23 (3H, each t, J=7.5 Hz, CH_3), 1.40—2.77 (12H, m, CH_2 of bridge), 3.76—4.35 (9H, m, Cp-H, 10-H and OC<u>H</u>$_2$CH$_3$); MS m/z (rel intensity) 352 (100, M^+), 324 (15, $[M-CO]^+$), 279 (23, $[M-CO_2C_2H_5]^+$).

α-Ethoxycarbonyl[3][4$_2$](1,2,4)ferrocenophane (10). Bridge contraction of α-oxo[4][4$_2$](1, 2, 4)ferrocenophane (**9**)[21] (250 mg) was carried out according to the general procedure via formylation with NaH and ethyl formate to give a mixture of epimeric **10** (29 mg, 10% from **9**) as a yellow oil. IR (neat) 1730 (C=O) cm^{-1}. ^{1}H NMR (100 MHz, $CDCl_3$) δ=1.22 and 1.29 (3H, each t, J=7.5 Hz, CH_3), 1.42—2.98 (20H, m, CH_2 of bridge), 3.76—4.40 (7H, m, Cp-H, 10-H and OC<u>H</u>$_2$CH$_3$); MS m/z (rel intensity) 406 (100, M^+), 378 (9, $[M-CO]^+$).

α-Ethoxycarbonyl[3][3$_2$](1,2,4)ferrocenophane (12). Bridge contraction of α- oxo[4][3$_2$](1, 2, 4)ferrocenophane (**11**)[13] (274 mg) was carried out according to the general procedure via formylation with NaH and ethyl formate to give a mixture of epimeric **12** (77 mg, 25% from **11**) as a yellow oil. IR (neat) 1730 (C=O) cm^{-1}. ^{1}H NMR (100 MHz, $CDCl_3$) δ=1.23 (3H, t, J=7.5 Hz, CH_3), 1.40—2.84 (16H, m, CH_2 of bridge), 3.68—3.91 (5H, m, Cp-H and 6-H), 4.10 and 4.11 (2H, each q, J=7.5 Hz, OC<u>H</u>$_2$CH$_3$); MS m/z (rel intensity) 378 (100, M^+), 350 (6, $[M-CO]^+$).

α-Oxo[4][3$_3$](1,2,3,4)ferrocenophane (13). To a solution of [4][3$_3$](1,2,3,4)ferrocenophane (**2**)[10,11] (400 mg, 1.1 mmol) in benzene (100 ml) was added activated manganese dioxide (500 mg); the suspension was stirred at 80 °C for 5 h. After the mixture was filtered, the filtrate was washed with saturated of $NaHSO_3$ and then with water, and dried over Na_2SO_4. The solvent was evaporated in vacuo, and the residue was column-chromatographed on silica gel. The first band yielded 50 mg (13%) of the recovered starting material (**2**). The second and fourth bands were unknown compounds. The fifth band eluted with benzene/ethyl acetate (40/1) yielded 220 mg (53%) of **13**, which was recrystallized from ethyl acetate to give yellow prisms; mp 180 °C (decomp). IR (KBr) 1645 (C=O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.53, 1.66, 1.78, 1.82—2.17, 2.23, 2.37 and 2.72 (2H, 2H, 1H, 13H, 3H, 2H and 1H, each m, CH_2), 3.86 (1H, s, 5′-H of Cp), 4.24 (1H, s, 5-H of Cp); ^{13}C NMR (125 MHz, $CDCl_3$) δ=17.98, 18.10, 18.21, 18.29, 19.08, 20.71, 20.76, 28.65, 35.61, 35.80, 36.82 and 39.19 (CH_2), 70.55 and 77.13 (unsubstd. Cp-C), 81.35, 85.50, 86.10, 86.55, 88.82, 90.67, 91.26 and 93.93 (substd. Cp-C), 203.30 (CO); MS m/z (rel intensity) 374 (100, M^+), 346 (11, $[M-COC_2H_4]^+$).

Found: C, 73.85; H, 6.97%, M^+ m/z 374.1323. Calcd for $C_{23}H_{26}OFe$: C, 73.80; H, 7.00%; M, 374.1331.

β-Formyl-α-oxo[4][3$_3$](1,2,3,4)ferrocenophane (14). Formylation of **13** (220 mg, 0.59 mmol) was carried out according to method (b) in the general procedure using LDA (1.50 mmol), HMPA (0.20 ml, 1.2 mmol), ethyl formate (0.21 ml, 1.6 mmol) and THF (40 ml). The product was column-chromatographed on silica gel to give three bands. The second band eluted with benzene/ethyl acetate (20/1) yielded 54 mg (23%) of **14** as yellow crystals. IR (KBr) 1740 and 1650 (C=O) cm^{-1}; MS m/z (rel intensity) 402 (100, M^+), 374 (30, $[M-CO]^+$). The ^{1}H NMR spectrum (500 MHz, $CDCl_3$) showed that the compound was an equilibrium mixture of keto and enol forms in a 1/4 ratio, which was estimated from the relative intensities of the proton signals (keto form, δ=9.78, d, J=3.7 Hz, CHO; enol form, δ=15.84, d, J=4.1 Hz, enolic OH, or δ=8.65, d, J=4.1 Hz, vinyl H). The other signals could not be assigned due to overlapping each other.

The band eluted with benzene/ethyl acetate (20/1) yielded the recovered starting material (97 mg, 44%).

The keto aldehyde (**14**) was used for the following diazo-

tization without further purification.

Bridge Contraction of 14. (1) Ketone (**13**) (200 mg, 0.54 mmol) was formylated with NaH (30 mg, 1.3 mmol) and ethyl formate (110 mg, 1.5 mmol) followed by diazotization with tosyl azide (250 mg, 1.3 mmol), according to the general procedure, to yield diazo compound (**15**) [IR (KBr) 2130 (azide) and 1600 (C=O) cm^{-1}], which was dissolved in ethanol and was irradiated. The crude product was column-chromatographed on silica gel to give many products. The band eluted with benzene/ethyl acetate (40/1) yielded α-oxo[3][3_3]ferrocenophane (**20**) (16 mg, 8.3% from **13**), which was recrystallized from ethyl acetate to give yellow prisms; mp 205—206 °C. IR (KBr) 1665 (C=O) cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ=1.20—2.45, 2.78 and 3.20 (19H, 2H and 1H, each m, CH_2), 4.39 and 4.54 (each s, Cp-H); ^{13}C NMR (25 MHz, $CDCl_3$) δ=17.94 (2C), 18.03, 18.81, 20.71, 20.86, 29.68, 36.89 (2C), 39.87 and 50.30 (CH_2), 73.64 and 75.49 (unsubstd. Cp-C), 76.32, 86.66, 87.09, 88.02, 88.26, 89.14, 90.07 and 92.16 (substd. Cp-C); MS *m/z* (rel intensity) 360 (100, M^+), 332 (8, $[M-CO]^+$).

Found: M^+ *m/z* 360.1192. Calcd for $C_{22}H_{24}OFe$: M, 360.1175.

(2) Ketone (**13**) (560 mg, 1.5 mmol) was formylated with LDA (3.8 mmol), HMPA (0.50 ml, 2.9 mmol) and ethyl formate (0.51 ml, 6.3 mmol), followed by diazotization with tosyl azide (150 mg, 0.76 mmol) according to the general procedure to yield diazo compound. The crude diazo ketone (**15**) in ethanol was irradiated for 17 h, and the product was column-chromatographed on silica gel. The first, second and third bands eluted with benzene were unknown yellow oily compounds. The fourth band with benzene/ethyl acetate (20/1) yielded α, β-dioxo[4][3_3](1,2,3,4)ferrocenophane (**19**) (32 mg, 6% from **13**), which was recrystallized from ethyl acetate to give yellow needles; mp>300°C. IR (KBr) 1700 and 1640 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.42, 1.54, 1.69, 1.77, 1.83, 1.98, 2.05, 2.17, 2.51, 2.66 and 2.13 (2H, 1H, 1H, 1H, 3H, 3H, 3H, 3H, 2H, 2H, and 1H, each m, CH_2), 4.01 and 4.23 (each 1H, s, Cp-H); MS *m/z* (rel intensity) 388 (50, M^+), 360 (100, $[M-CO]^+$).

Found: M^+ *m/z* 388.1125. Calcd for $C_{23}H_{24}O_2Fe$: M, 388.1125.

[3_4](1,2,3,4)Ferrocenophane (1). A solution of keton (**20**) (12 mg) in benzene (3 ml) was added to a suspension of $LiAlH_4$ (20 mg) and $AlCl_3$ (40 mg) in ether (5 ml). The reaction mixture was stirred at room temperature for 3 h. Saturated aq NH_4Cl was added to the mixture and the hydrolyzate was extracted with benzene. The combined extracts were washed with saturated aq NaCl and dried over Na_2SO_4. The solvent was evaporated in vacuo, and the column chromatographic purification of the residue on alumina gave **1** (8 mg, 75%), which was recrystallized from ethyl acetate to give pale yellow prisms; mp 175—177 °C. Since the compound **1** was somewhat unstable in solvent, the crystals which could be available for elemental analysis were not given. ^{1}H NMR (100 MHz, $CDCl_3$) δ=1.40—2.20 (24H, m, CH_2), 3.71 (2H, s, Cp-H); ^{13}C NMR (25 MHz, $CDCl_3$) δ=18.43, 21.30, 37.38 and 40.02 (CH_2), 71.43 (unsubstd. Cp-C), 85.36 and 88.51 (substd. Cp-C); MS *m/z* (rel intensity) 346 (100, M^+).

Found: M^+ *m/z* 346.1392. Calcd for $C_{22}H_{26}OFe$: M, 346.1382.

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