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Syntheses and Stereochemistry of Metalloceno Cycloocta-1,5-dienes: [2]Orthocyclo[2](1,2)benchrotrenophane and -ferrocenophane, [2.2](1,2)Ferrocenophane[a]

Stereochemistry of Metallocenes, 41;
Ferrocenederivatives, 62[1]

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The title compounds **2**, **3**, and **4** have been prepared for configurational and conformational studies—mainly in comparison with cyclophanes of related structures, such as [2.2]orthocyclophane (**1**).

Whereas the benchrotreno derivative **2** was accessible in one step from **1** and $Cr(CO)_6$, the ferrocenophanes **3** and **4** were prepared by a stepwise reaction sequence starting with a Wittig reaction: thereby hydroxymethylated ferrocenyl phenyl and diferrocenyl ethylenes were obtained in which (after hydrogenation to the corresponding ethanes) the CH_2OH groups were transformed into acetic acid residues. Subsequent ringclosure and reduction of the cyclic ketones **19** and **33** afforded the desired phanes, of which the diferroceno derivative **4** was obtained as a 3:1 mixture of the *trans* and *cis* isomers **a** and **b**, resp. The configurational assignment was based mainly on the ^{1}H-nmr spectra.

Conformational possibilities especially of **4** are briefly discussed and tentative conformations are assigned to the stereoisomers of **4**.

Synthesen und Stereochemie von Metallocenocycloocta-1,5-dienen: [2]Orthocyclo[2](1,2)benchrotrenophan und -ferrocenophan, [2.2](1,2)Ferrocenophan

Die im Titel genannten Verbindungen **2**, **3** und **4** wurden im Hinblick auf die Untersuchung ihrer Konfiguration und Konformation — vor allem im Vergleich mit Cyclophanen verwandter Struktur, wie [2.2]Orthocyclophan (**1**) — dargestellt.

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Während das Benchrotrenderivat **2** in einem Schritt aus **1** und $Cr(CO)_6$ zugänglich war, wurden die Ferrocenophane **3** und **4** ausgehend von einer Wittigreaktion schrittweise aufgebaut: Dabei erhielt man hydroxymethylierte Ferrocenyl-phenyl- und Diferrocenyl-ethylene, in denen — nach Hydrierung zu den entsprechenden Ethanen — die CH_2OH-Gruppen in Essigsäurereste umgewandelt wurden. Anschließender Ringschluß und Reduktion der cyclischen Ketone **19** und **33** lieferten die gewünschten Phane, von denen das Diferrocenoderivat **4** als 3:1-Mischung der *trans*- und *cis*-Isomeren **a** bzw. **b** erhalten wurde. Die konfigurative Zuordnung erfolgte vor allem auf Grund der ^1H-NMR-Spektren.

Die konformativen Möglichkeiten — vor allem von **4** — werden kurz diskutiert und vorläufige Konformationen für die Stereoisomeren von **4** vorgeschlagen.

Introduction

Phanes* are—because of their topology and mostly rigid molecular structure—attractive objects for configurational and conformational studies.

Stereochemical aspects of [2.2]metacyclophanes have been investigated in some detail in our group[3]; based on this and similar experiences in the metallocene field[4] it seemed of considerable interest to prepare and study related metallocenophanes, especially in the ferrocenophane-series.

According to its molecular geometry ferrocene cannot accomodate two ethylene bridges between two ferrocene units in the 1.3 (or β-) positions such as in [2.2]metacyclophane; the corresponding [2.2](1,2)-ferrocenophane (**4**, structurally related to [2.2]orthocyclophane or dibenzocycloocta-1,5-diene, **1**) however seemed to be—according to molecular models—a promising target for synthetic and stereochemical investigations.

Many ferrocenophanes of the [*m*](1,2)- or [*m*](1,1')-type are known[4] in which one (or more) *intra*molecular bridges link *homo*- or *hetero*anular positions within one ferrocene moiety; however only a few examples of the binuclear representatives have been described, e.g. [*m.n*](1,1')ferrocenophanes in which two ferrocenes are linked in the 1,1'-positions—either directly ([0.0]ferrocenophane)[5] or by C_1-, C_2-, and C_4-bridges, resp.[6a–c].

Of those metallocenophanes topologically related to [2.2]ortho- or metacyclophanes only the mono- and bis-tricarbonylchromium-π-complexes ("benchrotrenes") of the latter have been described. They were obtained by the reaction of [2.2]metacyclophane with $Cr(CO)_6$[7].

This paper deals with the preparations and general stereochemical aspects of three metallocenophanes in which metallocene moieties are

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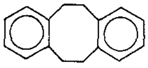
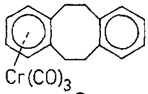
* The nomenclature proposed by *Vögtle* and *Neumann*[2] is used throughout this paper.

anellated to a central cyclooctadiene ring, namely [2]orthocyclo[2](1,2)benchrotrenophane (**2**), [2]orthocyclo[2](1,2)ferrocenophane (**3**) and [2.2](1,2)ferrocenophane(s) (**4**).



1



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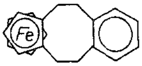
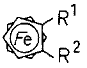


3

a **4** b

Syntheses

For the benchrotrene derivative **2** the obvious synthetic route was the reaction of [2.2]orthocyclophane (**1**)[8] with $Cr(CO)_6$. In contrast to the previously mentioned [2.2]metacyclophane[7] (as well as [2.2]paracyclophane)[7,9] even under drastic conditions (cf. experimental part) only the mono tricarbonylchromium complex **2** was formed in moderate yields. It was fully characterized by nmr and mass spectra.



	R^1	R^2
5	CH_2OH	CH_2OH
6	CH_2OAc	CH_2OAc
7	CH_2CN	CH_2CN
8	CH_2COOH	CH_2COOH
9	CH_3	CHO
10	CH_2OH	CHO

Based on our experiences in the ferrocene field (cf. ref. [4]) and on synthetic routes employed for [2.2]orthocyclophane (**1**)[8] several approaches seemed feasible for preparing the ferrocenophanes **3** and **4**.

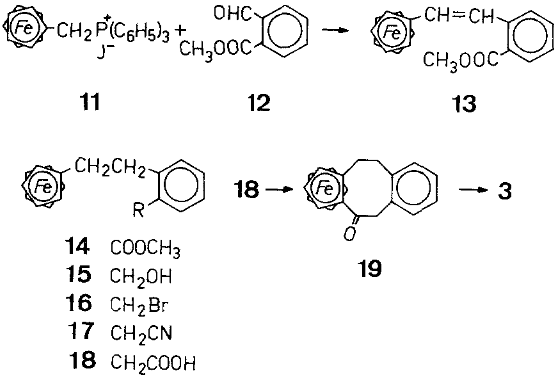
Onestep syntheses such as a direct *Friedel-Crafts* acylation of ferrocene with the hitherto unknown ferrocene-1,2-bisacetic acid (**8**)—prepared from 1,2-bis(hydroxymethyl)ferrocene (**5**)[10] *via* its acetate **6** and the dinitrile **7**—or an attempted reductive coupling of **5** (in analogy to the preparation of 1,2-diferrocenylethane from hydroxymethylferrocene)[11] were unsuccessful.

Similarily unsatisfactory were attempts towards a stepwise synthesis of **4** making use of the reductive coupling of carbonyl compounds with $TiCl_3/LiAlH_4$

which gives excellent results in the benzene series[12]. Although coupling of ferrocene carboxaldehyde by this method gave mainly the expected 1,2-diferrocenyl ethylene (besides some diferrocenylethane) the degree of reduction (and some rearrangement) increases in the series acetyl-, benzoyl- and ferrocenoyl-ferrocene and α-methyl- as well as α-hydroxymethyl-ferrocenealdehyde (**9** and **10**, resp.); the latter (**10**)[10] being a potential starting compound for the synthesis of **4**. Additionally, coupling of *homo*anular disubstituted ferrocenes gives rise to a mixture of meso and racemic forms.

A detailed investigation of these briefly mentioned aspects of the $TiCl_3/LiAlH_4$ coupling reaction in the ferrocene (and metallocene) series is now in progress.

Scheme 1

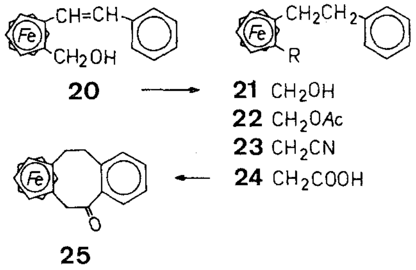


Finally, the following stepwise syntheses of **3** and **4** as outlined in schemes 1-3 were successful:

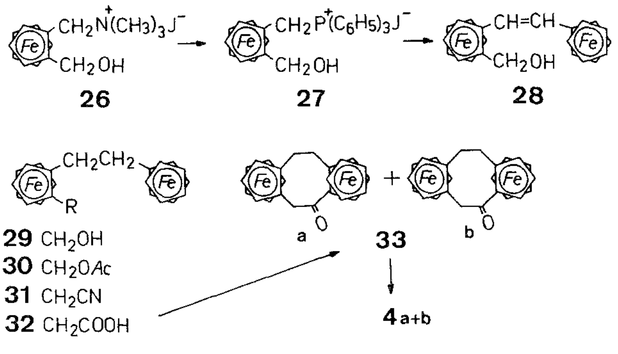
Wittig reaction of the phosphonium salt **11**[13] with methyl o-formylbenzoate **12** gave the ethylene **13**. After hydrogenation of the double bond (**13** → **14**) and thereby introducing the first C_2-bridge CO_2CH_3 was transformed into the acetic acid **18** by standard procedures (*via* the intermediates **15**, **16** and **17**). Usual cyclization of the acid **18** with trifluoroacetic anhydride (cf. ref. [4]) was unsuccessful, since **18** is rather sensitive to trifluoroacetic acid. Ringclosure in the presence of alumina however furnished the desired ketone **19** in 33% yield; the latter could smoothly be reduced with $LiAlH_4/AlCl_3$ to yield the hydrocarbon **3** as a crystalline compound (with 3% overall yield).

A similar reaction sequence—this time starting with a *Wittig* reaction between benzyl triphenylphosphonium iodide and the previously mentioned hydroxymethyl-ferrocenealdehyde **10**[10]—afforded the phenyl ethylenes and ethanes **20** and **21**, resp. which were now substituted in the ferrocene part. In this case CH_2OH was transformed into the nitrile **23** *via* its acetate **22**, since, as we found, acetoxy is a very good leaving group if attached to Fc-CH_2 allowing smooth nucleophilic substitution of OH in Fc-CH_2OH and related compounds—such as the above mentioned preparation of the bis acetic acid **8** from the bis(hydroxymethyl)ferrocene **5**. The final cyclization step (**24** → **25**) however is rather unfavourable compared with the cyclization of the isomeric acetic acid **18** (to give **19**, cf. scheme 1) since the benzene part is much less reactive towards electrophilic substitution as compared with the ferrocene moiety (cf. [4]).

Scheme 2



Scheme 3



From these results the synthetic route to the ferrocenophane **4** seemed obvious: Again the first step was a *Wittig* reaction, this time between the substituted ferrocenylmethylphosphonium salt **27** (easily accessible from the corresponding trimethylammonium salt **26**[10] and triphenylphosphine) and ferrocenealdehyde. [Reaction of this salt **27** with benzaldehyde gave the previously mentioned (hydroxymethylferrocenyl)phenylethylene **20**.]

The further sequence is outlined in scheme 3: It leads *via* the ethylene **28** to the ethane **29**, the acetate **30** and the nitrile **31** to the acetic acid **32**. Cyclization of the latter gave the two diastereomeric ketones **33** (**a** and **b**) (as seen by TLC!); reduction of the mixture with $LiAlH_4/AlCl_3$ furnished the desired hydrocarbon **4** again as a mixture of two isomers **a** and **b** (in a ratio of 3:1, as determined by nmr spectroscopy—*vide infra*). From this mixture the faster moving main product **4 a** could be obtained pure by a rather tedious chromatography on a silicagel column (with hexane:chloroform, 7:1); preparative layer chromatography was unsuccessful since **4** is rather insoluble.

Stereochemistry

The conformational behaviour of eightmembered rings and especially of dibenzocyclooctadiene **1** and its derivatives has been extensively studied[14]. According to X-ray analysis **1** adopts the rigid chair conformation in the solid state whereas in solution a 1:1 equilibrium exists between chair and boat (or twist boat) conformations with a barrier of appr. 10 kcal/mole—as revealed by nmr studies (cf. Fig. 1).

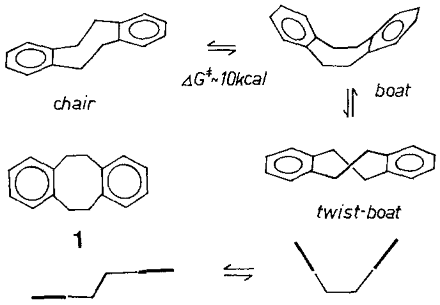


Fig. 1. Conformations of [2.2]orthocyclophane (**1**)

The high symmetry of **1** (D_{2h} for an average planar conformation, C_{2h} and C_{2v}, resp. for chair and boat, D_2 for the twist boat, cf. Fig. 1)[14] is reduced by introduction of metallocene units: C_s for **2** and **3** (Fig. 2), C_s, C_{2h} or C_{2v} for the possible conformations of **4** (Fig. 3). This results in the discrimination of "above" and "below". Consequently, for a bismetalloceno cyclooctadiene (such as **4**) two diastereomers are possible which can be designated as *cis* and *trans*; this is in agreement with the experimental results where for **4** two isomers **a** and **b** in the ratio of 3:1 were obtained (*vide supra*). Of both isomers several conformers are feasible as shown in the schematic representations of Fig. 3. Obviously in each case *one* of the conformers seems to be more favourable because of less steric interactions between the bulky ferrocene residues—as can be deduced from molecular models. These conformers are the *exo-exo-*

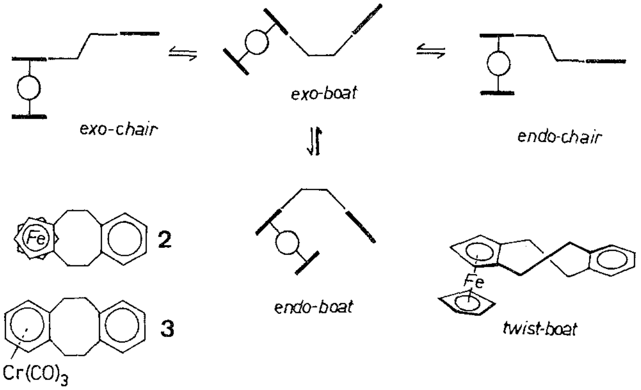


Fig. 2. Possible conformers for [2]orthocyclo[2](1,2)benchrotrenophane (**2**) and -ferrocenophane (**3**)

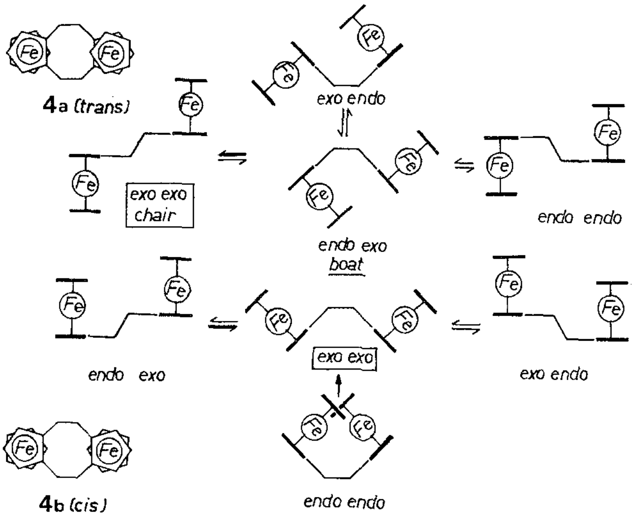


Fig. 3. Possible configurations and conformers for [2.2](1,2)ferrocenophane (**4a** and **b**)

chair for the *trans*-isomer **4a** and the *exo-exo*-boat (or twist boat) for the *cis*-isomer **4b**.

On the basis of model considerations on the cyclization mechanism (**32** → **33**) the *exo-exo*-chair conformation can be tentatively assigned to the main product **a** of **4**.

In the acylation step leading from **32** to **33** there are two possible α-positions for the electrophilic attack (*hetero*anular cyclization, i.e. attack in 1′ can be excluded because of the nmr supported structures of **33** and **4**). For one of them—leading to the *trans*-isomer a—there is in the transition state much less steric interaction between the ferrocene residues than in the other.

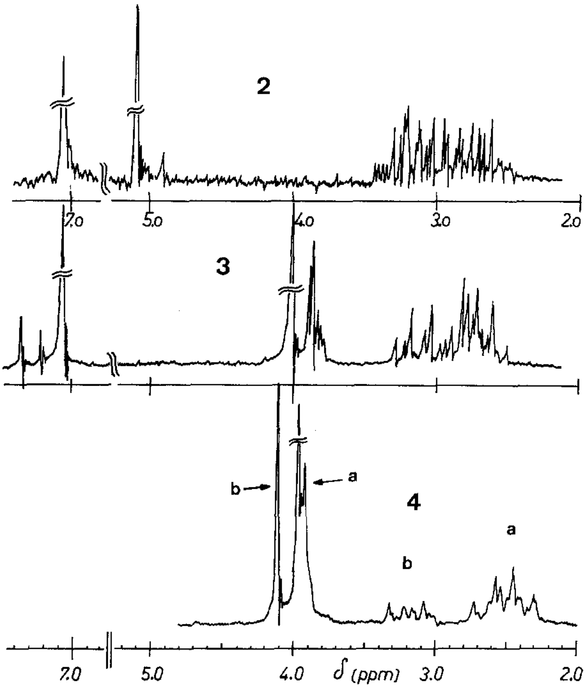


Fig. 4. NMR spectra of the metallocenophanes **2**, **3** and **4** ($CDCl_3$, 100 MHz)

^{1}H-nmr Spectra

This assignment (*trans*-configuration for the main product **a** of **33** and **4**) is strongly supported by the nmr spectra. For the dibenzo derivative **1** there are only two singulets at roomtemperature, namely at 7.0 and 3.05 ppm, corresponding to the benzene and bridge protons[14]. The absorption pattern in the CH_2-region of the metalloceno derivatives **2**, **3** and **4** is much more complex (cf. Fig. 4). In the main isomer **4 a** this multiplet is centered around 2.5 ppm whilst the isomer **4 b** absorbs around 3.15 ppm. (From these signals also the ratio of isomers in the mixture could be deduced.) This is compatible with the rigid *trans*-configuration for **4 a** whereas in the much more flexible *cis*-

isomer (*exo-exo*-boat, cf. Fig. 3) the bridge protons are—in the average—more deshielded by the adjacent ferrocene rings and are therefore shifted downfield. (The same would also be true for the *cis endo-exo*-chair which however seems to be energetically much less favoured, cf. Fig. 3.)

Besides this assignment the ^{1}H-nmr spectra (as well as the mass spectra) support the structures of all compounds mentioned.

Detailed conformational analyses, especially nmr studies (such as temperature dependence, calculations and lanthanide induced shift experiments for the ketones **19** and **33**) are now in progress and will be reported elsewhere. Moreover, X-ray studies shall give information on the conformations of the metallocenophanes in the solid state.

Acknowledgements

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Experimental Part

All reactions were performed under Argon. Compounds **2, 7, 16, 17, 23** and **31** are especially sensitive to light and/or air and should be stored under Ar in a refrigerator.

Instruments, materials: mp: Kofler heatingplate-microscope; temperatures in °C and uncorrected; *ir:* Perkin-Elmer 237 (only main bands are reported); ^{1}H-*nmr:* Varian EM-360 and Varian XL-100 (spectra in $CDCl_3$ with TMS as internal standard; chemical shifts in ppm on the δ-scale; *ms:* Varian MAT CH-7 (only main peaks are reported). *Column-chromatography:* on aluminium oxide 90 (activity grad II-III, Merck) and silicagel 60 (Merck); *preparative layer chromatography:* silicagel HF_{254} (Merck), 0.75 mm; *TLC:* cards, aluminium oxide ALF (Riedel-DeHaen) and silicagel 60 F_{254} (Merck).

[2]Orthocyclo[2](1,2)benchrotrenophane (**2**)

3.0 g (13.6 mmol) of $Cr(CO)_6$ were added to a solution of 0.58 g (2.8 mmol) of **1** (prepared according to[8]) in diglyme (12 ml). After stirring the mixture at 130° for 2 h. the solvent and excess of $Cr(CO)_6$ were removed *in vacuo*. The residue was then dissolved in benzene, the solution washed three times with water, dried ($MgSO_4$) and finally evaporated to dryness. From the yellowish product the desired benchrotrene **2** was isolated by preparative layer chromatography on silicagel in hexane/benzene (1:1) (under Ar, protected from light). Thereby 10 mg (1%) of yellow crystals of mp 185-192° were obtained. *TLC* (alumina; hexane:benzene, 5:1) R_f 0.3.

Variation of the reaction conditions (such as time, temp. or ratio of reactants as well as heating of **1** and $Cr(CO)_6$ in sealed ampoules with or without solvent) gave no better results.

$C_{19}H_{16}CrO_3$ (344.3). Calcd. C 66.28, H 4.68.
Found C 66.47, H 4.84.

nmr (100 MHz): 7.05 (s, 4 H, *Ph*), 5.10 (s, 4 H, benchrotrene-H), 3.50-2.40 (m, 8 H, CH_2); cf. also Fig. 4.

ms (*m/e*): 344 (10, molecular ion), 330 (3), 260 (100, M-3 CO), 246 (29), 193 (9), 191 (6), 52 (94, Cr).

1,2-Bis(acetoxymethyl)ferrocene (**6**)

4 ml of acetic anhydride were added at 0 °C to a solution of 1.23 g (5 mmol) of **5** (prepared according to[10]) in dry pyridine (10 ml). After 24 h. at roomtemp. the solvent and excess of acetic anhydride were removed *in vacuo* and the residue was twice evaporated with dry benzene. Yield 1.65 g (100%). mp (benzene/hexane) 84-85°. *TLC* (alumina; benzene:ethanol, 10:1) showed one spot; R_f 0.8 (starting material: R_f 0.35). $C_{16}H_{18}FeO_4$ (330.2).

nmr (60 MHz): 4.94 (s, 4 H, CH_2), 4.35-4.2 (m, 3 H, *Fc*), 4.15 (s, 5 H, *Fc hetero*), 2.03 (s, 6 H, CH_3).

1,2-Bis(cyanomethyl)ferrocene (**7**)

To a solution of 0.99 g (3 mmol) of **6** in acetonitrile (20 ml) 3.0 g (46 mmol) of KCN in water (30 ml) were added. After refluxing for 1 h. and subsequent cooling the mixture was extracted with ether. Washing of the etherextract with water, drying over $MgSO_4$ and evaporation furnished 0.79 g (100%) of a nearly pure product (a trace of **5** could be detected by *TLC*; column chromatography on alumina in benzene gives a completely pure compound, causes however great losses according to considerable decomposition on the column). For the next step (**8**) the purity of the product is sufficient. mp (ether) 78-81°. *TLC* (alumina; benzene:ethanol, 10:1); R_f 0.73 (yellow spot which quickly turns brown upon exposure to air). $C_{14}H_{12}FeN_2$ (264.1).

nmr (60 MHz): 4.30 (s, 8 H, *Fc*), 3.46 (s, 4 H, CH_2).

Ferrocene-1,2-bisacetic acid (**8**)

A solution of 0.75 g (2.84 mmol) of **7** in ethanol (8 ml) together with 1.5 g KOH in water (15 ml) was refluxed for 6 h. After evaporation *in vacuo*, addition of water (15 ml) and extraction with ether the aqueous phase was acidified with 85% phosphoric acid. The yellow precipitate formed was collected, washed with water and dried *in vacuo*. Yield 0.70 g (82%). The diacid does not melt below 250° but decomposes slowly from 160°. $C_{14}H_{14}FeO_4$ (302.1). Equiv.-weight found 148 (titration). The *dimethylester* ($C_{16}H_{18}FeO_4$; 330.2) was prepared with CH_2N_2 in ether/methanol. mp 67-72°; *TLC* (alumina; benzene:ethanol, 10:1) R_f 0.8.

nmr (60 MHz): 4.30-4.05 (m, 3 H, *Fc*), 4.05 (s, 5 H, *Fc hetero*), 3.67 (s, 6 H, CH_3), 3.37 (s, 4 H, CH_2).

1-Ferrocenyl-2-(2-methoxycarbonylphenyl)ethylene (**13**)

A suspension of 5.29 g (9 mmol) of **11**[13] in dry *THF* (65 ml) was treated with 16 ml of a 1*N* $LiOCH_3$-solution in methanol. After stirring for 5 min. at roomtemp. 3.12 g (19 mmol) of **12** in dry *THF* (45 ml) were added and subsequently the mixture stirred under reflux for 4 h. Cooling and stirring with

1 ml of conc. HCl gave 2.3 g of starting material **11** which was removed by filtration. The filtrate was evaporated to dryness and the residue was dissolved in ether. This solution was washed with water, twice with $NaHSO_3$-solution, twice with K_2CO_3-solution (10%) and finally with water. Then the etherphase was dried ($MgSO_4$), evaporated and the residue subjected to chromatography on alumina with benzene. The first yellow band (0.30 g) was identified by its nmr spectrum as *methylferrocene*. The second orange band gave 1.27 g (41%) of a *cis/trans* mixture (*nmr*!) of the desired ethylene **13** as a viscous red oil. On *TLC* (alumina; benzene) it was *one* spot: R_f 0.70. $C_{20}H_{18}FeO_2$ (346.2).

nmr (60 MHz): 8.0-7.0 (m, *Ph*), 7.3-6.0 (m, probably two *AB*q with $J = 12$ Hz and 16 Hz, resp., CH=), 4.6-4.0 (m, *Fc*) 4.16 and 4.06 (two s, *Fc hetero*), 3.91 and 3.89 (two s, CH_3).

1-Ferrocenyl-2-(2-methoxycarbonylphenyl)ethane (**14**)

1.27 g (3.67 mmol) of **13** were hydrogenated in ethanol (40 ml) for 3 h. at roomtemp. with *Raney*-Ni (*T*-1) as catalyst. Usual workup gave 1.20 g (94%) of **14** which was pure according to *TLC* (alumina; benzene:hexane, 1:1): yellow spot with R_f 0.65 (**13**, R_f 0.4). $C_{20}H_{20}FeO_2$ (348.2).

nmr (60 MHz): 8.0-7.0 (m, 4 H, *Ph*), 4.11 (s, 5 H, *Fc hetero*), 4.07-4.0 (m, 4 H, *Fc*), 3.88 (s, 3 H, CH_3), 3.4-3.0 (m, 2 H, CH_2), 2.8-2.4 (m, 2 H, CH_2).

1-Ferrocenyl-2-(2-hydroxymethylphenyl)ethane (**15**)

A solution of 1.20 g (3.45 mmol) of **14** in 80 ml of dry ether was stirred with an excess of $LiAlH_4$ for 1 h. at roomtemp. The mixture was then poured onto ice, filtrated, the etherphase washed with water, dried and evaporated to give 1.09 g (99%) of a yellow solid. mp (hexane/benzene) 92-94°. $C_{19}H_{20}FeO$ (320.2).

nmr (60 MHz): 7.19 ("s", 4 H, *Ph*), 4.57 (s, 2 H, CH_2O), 4.05 (s, 5 H, *Fc hetero*), 3.98 ("s", 4 H, *Fc*), 3.05-2.35 (m, 4 H, CH_2), 1.56 (s, broad, 1 H, OH).

1-(2-Bromomethylphenyl)-2-ferrocenylethane (**16**)

A solution of **15** (1.09 g, 3.4 mmol) in dry benzene (8 ml) was treated with 0.50 g (6.3 mmol) of dry pyridine and (with cooling) with a solution of PBr_3 (0.46 g, 1.7 mmol) in 3 ml of dry benzene. Instantly a precipitate formed. The mixture was then stirred for 2.5 h., subsequently diluted with ether and water to give two phases and the etherphase separated. It was washed with water, dried and evaporated to yield 1.10 g (84%) of a yellow, viscous oil which—according to *TLC*—was almost pure. $C_{19}H_{19}FeBr$ (383.1). Crude **16** was immediately used for preparing **17**.

1-(2-Cyanomethylphenyl)-2-ferrocenylethane (**17**)

A mixture of 1.10 g (2.87 mmol) of **16** in acetonitrile (20 ml) and 1.5 g (23 mmol) of KCN in water (6 ml) was refluxed under stirring for 3 h. Dilution with water, extraction with ether, washing (water), drying ($MgSO_4$) and finally evaporating of the ethersolution afforded a residue, which was chromatographed on alumina with benzene. From the first band 0.425 g (45%) of the nitrile were obtained; mp 87-90°. The second band (eluted with ether/methanol-mixtures) gave 0.43 g of **15**, identified by *TLC*-comparison. **17**, $C_{20}H_{19}FeN$ (329.2).

nmr (60 MHz): 7.21 (s, 4 H, *Ph*), 4.08 (s, 5 H, *Fc hetero*), 4.05-3.95 (m, 4 H, *Fc*), 3.47 (s, 2 H, CH_2CN), 2.70 ("s", broad, 4 H, CH_2).

1-(2-Carboxymethylphenyl)-2-ferrocenylethane (**18**)

0.425 g (1.29 mmol) of **17** were heated together with 4.3 g KOH in ethylene glycol (45 ml) at 130° for 10 h. under stirring. Dilution with water (45 ml) gave a clear solution which was extracted with ether and then acidified with phosphoric acid (85%). The yellow precipitate was extracted with ether, the etherphase washed with water, dried and evaporated to yield 0.314 g (70%) of the desired acid.

$C_{20}H_{20}FeO_2$ (348.2). Found equiv. weight 353 (titr.).

The *methylester* was prepared with CH_2N_2 in ether. *TLC* (alumina; benzene) R_f 0.7. $C_{21}H_{22}FeO_2$ (362.3).

nmr (60 MHz): 7.20 (s, 4 H, *Ph*), 4.13 (s, 5 H, *Fc hetero*), 4.07 ("s", 4 H, *Fc*), 3.70 (s, 3 H, CH_3), 3.63 (s, 2 H, $COCH_2$), 3.05-2.35 (m, 4 H, CH_2).

1-Oxo-[2]orthocyclo[2](1,2)ferrocenophane (**19**)

To a solution of 290 mg (0.83 mmol) of **18** in dry CH_2Cl_2 (14.5 ml) 4.4 g of alumina (Merck 90, act. gr. II-III) and 2.9 ml of trifluoroacetic anhydride were added and the mixture stirred at roomtemp. for 1 h. Solvent and excess of *TFAA* were then removed *in vacuo* (at roomtemp.) and the adsorbed product extracted with ether. Rapid chromatography of the evaporation-residue on a short alumina column (2 × 1 cm) with benzene furnished 90 mg (33%) of orange crystals, mp 113-116°: one single spot with R_f 0.30 on *TLC* (alumina, benzene). $C_{20}H_{18}FeO$ (330.2).

ir ($CHCl_3$): 1655 cm^{-1} (CO).

nmr (100 MHz): 7.3-7.05 (m, 4 H, *Ph*), 4.78 ("t", 1 H, *Fc*), 4.30 ("d", 2 H, *Fc*), 4.10 (s, 5 H, *Fc hetero*), 4.54 and 3.74 (ABq, $J_{AB} = 12.7$ Hz, 2 H, CH_2CO), 3.6-2.7 (m, 4 H, CH_2).

ms (*m/e*): 330 (100, molecular ion).

[2]Orthocyclo[2](1,2)ferrocenophane (**3**)

a) *From* **19**: To a stirred suspension of 20 mg (0.53 mmol) of $LiAlH_4$ and 60 mg (0.45 mmol) of $AlCl_3$ in 4 ml of dry ether 50 mg (0.15 mmol) of **19** in 8 ml of dry ether were added, whereby the colour of the mixture changed quickly from orange to yellow. After stirring for 30 min. at roomtemp. the mixture was poured onto ice and extracted with ether. Washing of the etherphase with $NaHCO_3$ (in water) and water, drying and evaporation gave 44 mg of a residue which was subjected to chromatography on alumina in benzene to separate **3** from the corresponding *exo*- and *endo*-carbinols, resp., which were formed as byproducts. Yield: 37 mg (77%) of yellow crystals; mp (hexane): 125-127°. *TLC* (silicagel, hexane) R_f 0.11 and 0.70, (in benzene:$CHCl_3$, 1:1), resp.

b) *From* **25**: Hydrogenation of 10 mg (0.03 mmol) of **25** in methanol with Pd/C (10%) as catalyst at 5 atm. for 1 h. gave 6 mg of a crude product which was purified by preparative layerchromatography (silicagel, benzene; R_f 0.6). Yield: 1 mg (10%) of **3** which was identified by *TLC*-comparison with a sample prepared according to method a) and by its mass spectrum.

$C_{20}H_{20}Fe$ (316.2). Calc. C 75.96, H 6.37.
Found C 75.73, H 6.55.

nmr (100 MHz): 7.07 (s, 4 H, *Ph*), 4.01 (s, 5 H, *Fc hetero*), 3.90-3.75 (m, 3 H, *Fc*), 3.40-2.40 (m, 8 H, CH_2). (Cf. also Fig. 4).

ms (*m/e*): 316 (100, molecular ion), 302 (7), 301 (5), 252 (10), 251 (50), 250 (15), 249 (14), 248 (6), 121 (23), 91 (17).

1-(2-Hydroxymethylferrocenyl)-2-phenylethylene (**20**)

In the *Wittig*-reaction between the phosphonium salt **27** and benzaldehyde either lithium ethoxide or *n*-butyl lithium were employed as bases with equally good success. The separation from byproducts was performed after the next (hydrogenation) step (**20** → **21**, *vide infra*).

a) Li*OEt-method*: A stirred suspension of 8.4 g (13.6 mmol) of **27** in 100 ml of dry *THF* was treated with 40 ml (40 mmol) of a 1N-Li*OEt*-solution in ethanol. After 5 min. 2.23 g (21 mmol) of benzaldehyde were added in 10 ml of dry *THF*. Stirring at roomtemp. was continued for another 2 h. After evaporation of *THF* the residue was dissolved in ether and the etherphase washed with water, dried and evaporated. Finally excess of benzaldehyde was removed by evaporation at 0.1 Torr and 50-60° (bathtemp.) to give 5.27 g of a crude product. *TLC* (alumina; benzene:ethanol, 20:1) showed **20** as an orange spot (R_f 0.54) besides a yellow spot (R_f 0.43), partly covered by a large spot of triphenylphosphine oxide.

b) *Bu*-Li-*method*: When 6 ml of a 1N-*Bu*Li solution in hexane (13.5 mmol) were added to a stirred suspension of 3.8 g (6.15 mmol) of **27** in dry *THF* (110 ml) at 0° the colour changed rapidly from yellow to red and the mixture became homogeneous. After 5 min. a solution of 0.95 g (9 mmol) of benzaldehyde in 20 ml of dry *THF* was added and stirring continued for 20 min. at 0° and additional 20 min. at roomtemp. whereby the colour changed from red to orange. Some triphenylphosphine oxide was removed by filtration, the filtrate evaporated to dryness *in vacuo*, the residue dissolved in benzene and the solution washed with water, dried and evaported. Again the excess of benzaldehyde was removed (cf. method a) and the residue purified by chromatography on alumina in benzene. The first band eluted gave 0.04 g of the *aldehyde* corresponding to **20**; this aldehyde was identified by *nmr*- and *TLC*-comparison with a sample prepared from **20** by oxidation with active MnO_2 in $CHCl_3$. From the second band 1.49 g of impure **20** (contaminated with some triphenylphosphine oxide, as shown by *TLC*) were obtained. A pure sample (for the *nmr* spectrum) was isolated from the first fraction of the justmentioned second band. For *TLC vide supra*. $C_{19}H_{18}FeO$ (318.2).

nmr (60 MHz): 7.5-7.1 (m, 5 H, *Ph*), 6.95 and 6.75 (*AB*q, $J = 16$ Hz, 2 H, CH), 4.57 (s, 2 H, CH_2), 4.55-4.10 (m, 3 H, *Fc*), 4.08 (s, 5 H, *Fc hetero*), 1.58 (s, broad, 1 H, OH).

1-(2-Hydroxymethylferrocenyl)-2-phenylethane (**21**)

a) 5.27 g (16.5 mmol) of crude **20** (obtained by the Li*OEt* method) were hydrogenated in ethanol (100 ml) at 1 atm H_2 with *Raney*-Ni (W2) as a catalyst. Usual workup and chromatography of the product on alumina with benzene gave 2 bands:

1. 1.6 g of **21** (37% overall yield based on **27**). *TLC* (alumina, benzene:ethanol, 20:1) R_f 0.6 (single yellow spot). Viscous oil.
2. 2.8 g of the above mentioned byproduct together with triphenyl phosphine oxide. Extraction with cold hexane furnished 1.5 g of a pure compound (*TLC*!) identified by its *nmr* spectrum as *α-(hydroxymethyl)methylferrocene*.

b) 1.49 g of crude **20** (obtained by the *Bu*-Li method) were hydrogenated as described under a) to give 0.69 g (34% overall yield based on **27**) of **21**. $C_{19}H_{20}FeO$ (320.2).

nmr (60 MHz): 7.17 ("s", 5 H, *Ph*), 4.25-3.95 (m, 5 H, *Fc* and CH_2O), 4.06 (s, 5 H, *Fc hetero*), 2.72 (s, 4 H, CH_2), 1.17 (s, broad, 1 H, OH).

1-(2-Acetoxymethylferrocenyl)-2-phenylethane (**22**)

Acetylation of 1.6 g (5 mmol) of **21** was performed in dry pyridine (15 ml) with 3 ml of acetic anhydride at 0°. After 16 h. at roomtemp. the mixture was evaporated *in vacuo* and the residue 3 times evaporated with dry benzene to yield 1.78 g (98%) of a pure oily product. *TLC* (alumina; benzene:ethanol, 20:1) R_f 0.8. $C_{21}H_{22}FeO_2$ (362.3).

1-(2-Cyanomethylferrocenyl)-2-phenylethane (**23**)

A solution of 1.78 g (4.9 mmol) of **22** in acetonitrile (35 ml) was refluxed with a solution of 2.0 g (30.8 mmol) of KCN in water (20 ml). After 90 min. and subsequent cooling the mixture was extracted with ether, the etherphase washed with water, dried and evaporated to give 1.61 g (100%) of a yellow oil. *TLC* (alumina, benzene:ethanol, 20:1) R_f 0.75 (the yellow spot turns quickly brown upon exposure to air). $C_{20}H_{19}FeN$ (329.2).

nmr (60 MHz): 7.35-6.95 (m, 5 H, *Ph*), 4.20-3.95 (m, 3 H, *Fc*), 4.09 (s, 5 H, *Fc hetero*), 3.02 and 2.78 (*AB*q, 2 H, $J = 18$ Hz, CH_2CN), 2.8-2.6 (m, 4 H, CH_2).

1-(2-Carboxymethylferrocenyl)-2-phenylethane (**24**)

A solution of **23** (1.61 g, 4.9 mmol) in ethanol (30 ml) was refluxed for 10 h. with a solution of 3.0 g (54 mmol) of KOH in 20 ml of water. Evaporation, addition of water, extraction with ether and acidification of the aqueous phase with phosphoric acid (85%) gave a deposit which was dissolved in ether, washed with water, dried and evaporated. Yield: 1.38 g (81%) of the oily acid.

$C_{20}H_{20}FeO_2$ (348.2). Found equiv. weight 343 (titr.).

The *methylester* was prepared with CH_2N_2 in ether. Oil. *TLC* (alumina; benzene:ethanol, 20:1) R_f 0.85. $C_{21}H_{22}FeO_2$ (362.2).

nmr (60 MHz): 7.20 (s, 5 H, *Ph*), 4.3-3.9 (m, 3 H, *Fc*), 4.03 (s, 5 H, *Fc hetero*), 3.67 (s, 3 H, CH_3), 3.32 (s, 3 H, CH_2CO), 2.73 ("s", 4 H, CH_2).

2-Oxo-[2]orthocyclo[2](1,2)ferrocenophane (**25**)

The acidchloride was prepared by stirring 0.35 g (1 mmol) of **24** in 5 ml of dry benzene with 0.14 g (1 mmol) of PCl_3 and a trace of dry pyridine for 90 min. at 70-80°. Decanting and evaporation of the solution with dry benzene (3 times) afforded 0.36 g (98%) of the oily chloride. For the cyclization a solution of 165 mg (0.45 mmol) of this chloride in CH_2Cl_2 (60 ml) was added during 5 h. to a stirred suspension of 600 mg (4.5 mmol) of $AlCl_3$ in 45 ml of CH_2Cl_2. The mixture was then poured onto ice, a trace of ascorbic acid added and (because of poor phase separation) the solvent removed *in vacuo*. Extraction of the residue with ether and usual workup gave 70 mg of a crude product which was purified by preparative layer chromatography (silicagel; benzene:ethanol, 20:1; R_f 0.6) but partly decomposed during this process (to form a violet product). Yield: 10 mg (7%) of a yellow oil. $C_{20}H_{18}FeO$ (330.2).

Variation of the conditions (rate of addition, amount of solvent and ratio of the reactants) gave no better results.

ir ($CHCl_3$): 1730 cm^{-1} (CO; the relatively high wave number for the CO-band is possibly due to a nonplanar benzene-CO-conformation).

nmr (60 MHz): 7.2-7.1 ("s", 4 H, *Ph*), 4.2-3.9 (m, 3 H, *Fc*), 4.0 (s, 5 H, *Fc hetero*), 3.3 ("s", 2 H, CH_2CO), 2.7 ("s", broad, 4 H, CH_2).

Triphenyl[2-(hydroxymethyl)ferrocenylmethyl]phosphonium iodide (**27**)

A mixture of 16.0 g (61 mmol) of triphenylphosphine and 12.5 g (30 mmol) of **26** (prepared according to [10]) in 400 ml of ethanol was refluxed for 16 h. Concentration *in vacuo* to about 150 ml and addition of ether afforded a crystalline product which was collected on a filter, washed with ether, dried and recrystallized from ethanol to give 15.8 g (85%) of the salt which did not melt below 300°.

$C_{30}H_{28}FeIOP$ (618.3). Calc. C 58.28, H 4.56.
Found C 58.01, H 4.30.

1-Ferrocenyl-2-(2-hydroxymethylferrocenyl)ethylene (**28**)

In this case LiO*Et* proved to be superior to *Bu*-Li in the *Wittig* reaction between **27** and ferrocenecarboxaldehyde, since *Bu*-Li gave rise to many byproducts. (Cf. however the preparation of **20**.) A stirred suspension of **27** (6.18 g, 10 mmol) in dry *THF* (100 ml) was treated with 30 ml of a 1N-LiO*Et*-solution (in ethanol) and after 5 min. 1.93 g (9 mmol) of ferrocenecarboxaldehyde were added. Stirring was then continued under reflux for 2 h., the solvent was evaporated *in vacuo*, water was added and the mixture extracted with ether. *TLC* (alumina; benzene: ethanol, 20:1) of the ether solution showed three spots: R_f 0.6 (orange, **28**), R_f 0.8 (violet; *aldehyde* corresponding to **28**) and R_f 0.45 (yellow, covered partly by triphenylphosphine oxide, cf. **20** and **21**). To reduce the aldehyde, the washed and dried ethersolution was stirred for 5 min. with $LiAlH_4$ until the violet spot had vanished. Water was then added, the precipitate formed removed by filtration, the etherphase dried and evaporated to give 6.9 g of a crude product. From a small sample the desired **28** was isolated by preparative layer chromatography (silicagel, benzene) as organe crystals; mp 142-144°. $C_{23}H_{22}Fe_2O$ (426.1).

nmr (100 MHz): 6.50 (s, 2 H, CH), 4.6-4.05 (m, 9 H, *Fc* and CH_2), 4.12 (s, 10 H, *Fc hetero*), 1.58 (s, broad, 1 H, OH).

ms (*m/e*): 426 (3, molecular ion).

Separation of byproducts from the main batch proved to be more convenient after the hydrogenation step (**28** → **29**, *vide infra*).

1-Ferrocenyl-2-(2-hydroxymethylferrocenyl)ethane (**29**)

Hydrogenation of crude **28** (6.9 g) was performed in 50 ml of ethanol at 1 atm H_2 with *Raney*-Ni (W2) for 2 h. Usual workup and chromatography on alumina (40 × 4 cm) with benzene gave 2.1 g of pure **29** (54% overall yield based on *Fc*-CHO) moving with the first band. Yellow crystals; mp 121-123° (ether). *TLC* (alumina, benzene: ethanol, 20:1) R_f 0.65. $C_{23}H_{24}Fe_2O$ (418.1).

nmr (60 MHz): 4.3-3.8 (m, 9 H, *Fc* and CH_2O), 4.07 (s, 10 H, *Fc hetero*), 2.51 (s, 4 H, CH_2), 1.23 (s, broad, 1 H, OH).

ms (*m/e*): 428 (92, molecular ion).

1-(2-Acetoxymethylferrocenyl)-2-ferrocenylethane (**30**)

Acetylation of 2.1 g (4.9 mmol) of **29** was performed in dry pyridine (15 ml) with 3 ml of acetic anhydride at 0°. After 16 h. at roomtemp. solvent and excess of acetic anhydride were removed *in vacuo* and the residue evaporated 3 times with dry benzene to give 2.3 g (100%) of a yellow oil. *TLC* (alumina; benzene:ethanol, 20:1) R_f 0.77. $C_{25}H_{26}Fe_2O_2$ (470.2).

1-(2-Cyanomethylferrocenyl)-2-ferrocenylethane (**31**)

Substitution of acetoxy by cyano was performed as described for **23**. Thereby from 2.3 g (4.9 mmol) of **30** (in 50 ml of acetonitrile with 2.0 g KCN in 20 ml of water) 2.13 g (100%) of **31** were obtained. Yellow oil. *TLC* (alumina; benzene:ethanol, 20:1) R_f 0.75 (yellow, turns brown upon exposure to air). $C_{24}H_{23}Fe_2N$ (437.2).

nmr (60 MHz): 4.2-3.9 (m, 7 H, *Fc*), 4.10 (s, 5 H, *Fc hetero*), 3.05 and 3.01 (internal lines of an *AB*q, external lines are not discernible; estimated shifts: 3.10 and 2.96: 2 H, CH_2CN), 2.6-2.3 (m, 4 H, CH_2).

1-(2-Carboxymethylferrocenyl)-2-ferrocenylethane (**32**)

A mixture of 2.11 g (4.83 mmol) of **31** in 30 ml of *n*-butanol and 3.0 g (54 mmol) of KOH in 6 ml of water was stirred under reflux for 17 h. The butanolic phase was decanted from the colourless aqueous layer and evaporated *in vacuo*. The residue was digested and extracted with boiling ether (extract 1). The remaining residue was then shaken with aqueous phosphoric acid and ether. This etherextract was washed (water), dried ($MgSO_4$) and evaporated to give 1.40 g (64%) of the acid **32** which was pure according *TLC* of its methylester prepared with CH_2N_2 (*vide infra*). Extract 1 was washed with dilute phosphoric acid to remove residual butanol and then treated with 2N-NaOH. The sodium salt of **32** deposited as a dark red oil from which the ether and aqueous phases were decanted. This salt gave (by treating with phosphoric acid and ether and usual workup) another 0.39 g (18%) of **32** contaminated with dark byproducts. For purification it was converted into its *methylester* (with CH_2N_2 in ether) and the latter chromatographed on a short alumina column in benzene. Yield 0.25g. *TLC* (alumina; benzene:ethanol, 20:1) R_f 0.8. $C_{25}H_{26}Fe_2O_2$ (470.2).

nmr (60 MHz): 4.25-3.90 (m, 7 H, *Fc*), 4.06 (s, 5 H, *Fc hetero*), 4.02 (s, 5 H, *Fc hetero*), 3.66 (s, 3 H, OCH_3), 3.30 (s, 2 H, CH_2CO), 2.49 (s, 4 H, CH_2).

Hydrolysis of this ester (0.25 g in 25 ml of methanol, refluxing for 30 min. with 0.3 g of KOH in 3 ml of H_2O) gave 0.22 g of the pure acid. Total yield of **32**: 1.62 g (74%).

$C_{24}H_{24}Fe_2O_2$ (456.2). Found equiv. weight 448 (titr.).

1-Oxo-[2.2](1,2)ferrocenophane (**33**)

To a solution of 0.69 g (1.5 mmol) of **32** in dry CH_2Cl_2 (35 ml) 10 g of alumina (Merck 90, activity II-III) and 7 ml of trifluoroacetic anhydride were added and the mixture stirred for 1 h. at roomtemp. Solvent and excess of *TFAA* were then removed *in vacuo* (at 20°) and the product adsorbed on alumina extracted with ether. This solution was concentrated *in vacuo* to about 10 ml and rapidly chromatographed on a short column of alumina (15 g). Evaporation of the eluate *in vacuo* yielded 0.41 g (62%) of orange crystals, dec. around 195°. *TLC* (alumina; benzene) R_f 0.3 (the orange spot turns quickly violet upon exposure to air); (silicagel; benzene:$CHCl_3$, 3:1) two orange spots: After three runs "R_f" 0.45 (**33 a**) and 0.40 (**33 b**), besides some violet products formed during chromatography. 200 mg of the mixture were subjected to preparative layer chromatography (silicagel; benzene:$CHCl_3$, 3:1) whereby only **33a** was obtained pure. Yield: 90 mg. $C_{24}H_{22}Fe_2O$ (438.1).

ir ($CHCl_3$): 1655 cm^{-1} (CO).

nmr (100 MHz): 5.15-5.05 (m, 1 H, *Fc*), 4.55-4.40 (m, 2 H, *Fc*), 4.15 (s, 5 H, *Fc hetero*), 3.99 (s, 3 H, *Fc*), 3.71 (s, 5 H, *Fc hetero*), 4.03 and 3.32 (*AB*q, $J = 13.8$ Hz, 2 H, CH_2CO), 3.35-2.60 (m, 4 H, CH_2).

ms (*m/e*): 438 (99, molecular ion).

[2.2](1,2)Ferrocenophane (**4**)

To a stirred suspension of 80 mg (2.1 mmol) of $LiAlH_4$ and 240 mg (1.8 mmol) of $AlCl_3$ in dry ether (15 ml) 200 mg (0.46 mmol) of **33** (**a** and **b**) were added in 35 ml of dry ether, whereby the colour quickly changed from orange to yellow. Stirring was continued for 30 min at roomtemp., then the mixture was poured onto ice and extracted with ether and CH_2Cl_2. These extracts were washed with aqueous $NaHCO_3$-solution and water, dried and evaporated to yield 170 mg of crude product. This was subjected to chromatography on silicagel in benzene:$CHCl_3$, 1:1, to separate the hydrocarbon (fast moving) from some (*endo-* and *exo-*)carbinols formed during the reduction. **4** (150 mg, 77%; yellow crystals) did not melt below 300° but darkened from 230°. *TLC* (alumina; benzene) R_f 0.77; (silicagel; hexane:$CHCl_3$, 10:1) two yellow spots: R_f 0.42 (**4a**) and 0.37 (**4b**). For separation 100 mg of **4** were dissolved in $CHCl_3$ (15 ml), 10 g of silicagel were added and the solvent was carefully removed *in vacuo*. This sample was then placed on top of a silicagel column (30 × 3 cm) and eluted with hexane:$CHCl_3$, 7:1. A complete separation of **4a** and **4b** could not be achieved, but the very first band afforded 50 mg of pure **4a** (*TLC*!). It could be sublimed at 0.001 Torr and 160-190° (bath temp.).

$C_{24}H_{24}Fe_2$ (424.2). Calcd. C 67.96, H 5.70.
Found C 68.22, H 5.98.

nmr (100 MHz): 4.1-3.85 (m, 6 H, *Fc*), 3.93 (s, 10 H, *Fc hetero*), 2.80-2.20 (m, 8 H, CH_2).

In the *nmr*-spectrum (100 MHz) of the original mixture of **4a** and **b** the following additional peaks were observed: 4.1 (s, *Fc*), 3.9 (s, *Fc*), 3.4-2.9 (m, CH_2). The ratio **a**:**b** was determined as 3:1 by integration of the CH_2 (bridge) proton signals (cf. Fig. 4).

ms (*m/e*) of the mixture: 424 (100, molecular ion), 359 (42), 238 (40), 212 (32), 121 (69).

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