Monatshefte für Chemie 121, 945–953 (1990)

Monatshefte für Chemie
Chemical Monthly

Ferrocene Derivatives, Part 70: Syntheses and Stereochemistry of Chiral 1,1′-Biferrocenyls**
(Stereochemistry of Metallocenes, Part 55 [1])

P. Krajnik[1], **Ch. Kratky**[2], **K. Schlögl**[1,*], and **M. Widhalm**[1]

[1] Institut für Organische Chemie, Universität Wien, A-1090 Wien, Österreich
[2] Institut für Physikalische Chemie, Universität Graz, A-8010 Graz, Österreich

Summary. 2,2′-Disubstituted 1,1′-biferrocenyls have been prepared by coupling of appropriate ferrocene derivatives. The stereochemistry of the diastereoisomers obtained thereby is discussed on the basis of n.m.r.-spectroscopy and in two cases (**2a, b**) from X-ray structure analyses. Chiroptical properties of optically active 1,1′-biferrocenyls – obtained from (+)(*R*)-1-ferrocenyl-N,N-dimethylaminoethane – are reported. Attempts to prepare 2,2′,5,5′-tetrasubstituted biferrocenyls failed.

Keywords. X-ray structure; Torsional isomerism; Absolute chiralities.

Synthese und Stereochemie chiraler 1,1′-Biferrocenyle. 70. Mitt. über Ferrocenderivate [1]

Zusammenfassung. 2,2′-Disubstituierte 1,1′-Biferrocenyle wurden durch Kupplung entsprechender Ferrocenderivate dargestellt. Die Stereochemie der dabei erhaltenen Diastereomeren wird aufgrund der NMR-Spektren und in zwei Fällen (**2a, b**) der röntgenographischen Kristallstruktur-Daten diskutiert. Chiroptische Eigenschaften von optisch aktiven Biferrocenylen – erhalten aus (+)(*R*)-1-Ferrocenyl-N,N-dimethylaminoethan – wurden bestimmt. Versuche, 2,2′,5,5′-tetrasubstituierte Biferrocenyle darzustellen, schlugen fehl.

Introduction

Compounds combining the elements of planar and axial chirality are of considerable interest both for theoretical and practical reasons. Thus, e.g., tricarbonylchromium-complexes of biphenyls [2] as well as chiral 2,2′-bisannulenyls [3] have been studied in some detail, but so far little is known about chiral biferrocenyls. The synthesis of 2,2′-bis(dimethylaminomethyl)-1,1′-biferrocenyl had furnished the expected mixture of two diastereoisomers, each of them comprising two chiral ferrocene moities [4]. If these have the same chirality the result is a racemic compound which may be separated into the optically stable enantiomers by conventional methods (cf. [4a]). The other diastereomer consists of two "ferrocene halfes" of opposite chiralities and may be designated as "*meso*-form". The latter can only give rise to

---

** Dedicated to Prof. Dr. Edwin Hengge on the occasion of his 60th birthday

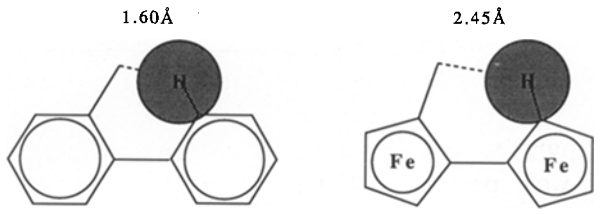
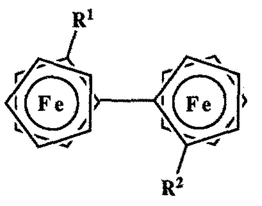
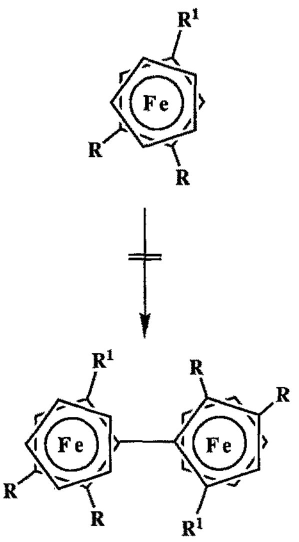


Fig. 1. Schematic representation of the steric situation in 2,2′-disubstituted biphenyls and biferrocenyls

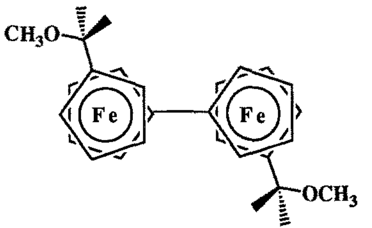


	R^1	R^2
1	$CH_2N(CH_3)_2$	
2	$CH(CH_3)N(CH_3)_2$	
3	$CH(CH_3)N(CH_3)_2$	$CH(CH_3)N(CH_3)_3I$
4	$C(CH_3)_2N(CH_3)_2$	
5	$CH(CH_3)N(CH_3)_2$	$CH(CH_3)OCH_3$
6	$CH(CH_3)OCH_3$	
7	$C(CH_3)_2OCH_3$	



$R^1 = CH_2N(CH_3)_2$

	R
9	CH_3
10	$-(CH_2)_4-$



8

enantiomers (via its torsional = axial chirality) if a sufficient restriction of the torsion around the *Fc-Fc* axis is introduced by appropriate substituents.

In the present paper we want to discuss the steric requirements which might lead to the occurrence of torsional isomeric biferrocenyls, and report on some synthetic efforts to achieve this goal.

Substituted biferrocenyls have been prepared by copper acetate [5], cobalt chloride [4] or bis[triphenylphosphine]dichloronickel [6] assisted homocoupling reactions of appropriate lithioferrocenes. As expected for 2,2′-bis(N,N-dimethylaminomethyl)-1,1′-biferrocenyl (**1**) no coalescence could be observed in its ^{1}H-n.m.r. spectrum indicating the presence of torsional isomers. This is not surprising when considering a simplified geometric model: Fig. 1 gives a schematic representation of the steric situation in 2,2'-disubstituted biphenyls and biferrocenyls; especially for the latter ones it is evident from this figure that only (very) large substituents, or more efficient *four* substituents in positions 2,2', 5, and 5', will lead to a significant increase in the rotational barrier.

For appropriately substituted bipyrryls, which seemed to be suitable model compounds, force field calculations were performed [7] to obtain approximate rotational barriers for substituted biferrocenyls. They resulted in 14.3 ± 2 kcal (60 ± 8 kJ) for 4,4'-di *tert*-butyl-3,3'-bipyrryl and 30.8 ± 3 kcal (129 ± 13 kJ) for 2,2',4,4'-tetramethyl-3,3'-bipyrryl. In the former case this should give rise to the corresponding coalescence phenomens in the ^{1}H-n.m.r.-spectrum, while in the latter the occurrence of (isolable) atropic isomers may be expected. This assumption is supported by the fact that for 1,1',3,3'-tetramethyl-2,2'-bipyrryl a considerable optical stability was observed. Its rotational barrier was found to be high enough for optical resolution by conventional methods [8].

For these reasons and considering the aspects of their synthetic accessibility the compounds **2**, **4**, **6**, **7**, **9**, and **10** have been choosen as promising candidates for our studies.

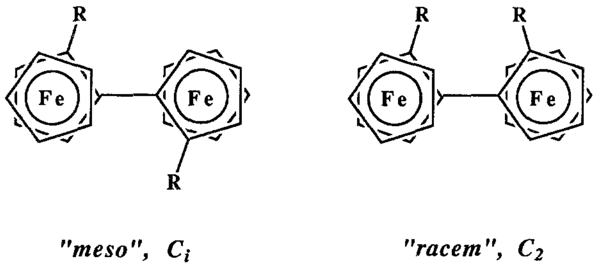
Results and Discussion

The biferrocenyl **2** in analogy to **1** was accessible by a homocoupling reaction of 1-ferrocenyl-N,N-dimethylaminoethane via *o*-lithiation and subsequent treatment with $CoCl_2$ [4]. Besides some starting material two coupling products **2 a** and **b** were isolated (in a ratio of 1 : 3) by chromatography on alumina; one (**2 a**) with C_1-symmetry and the second one (**2 b**) having higher symmetry as unambiguously deduced from their ^{1}H-n.m.r. spectra.

According to expectations such a coupling should lead to a racemate (with C_2-symmetry) and an achiral diastereoisomer ("*meso*-former" with C_i-symmetry), provided there were no stable rotamers at r.t.

By temperature depending ^{1}H-n.m.r. spectroscopy (between −100 and +100 °C) of both **2 a** and **b**, no coalescence or decoalescence could be dedected. Consequently there is no restricted rotation around the biferrocenyl bond in the temperature range studied.

X-ray structure determination of both diastereoisomers revealed that **2 b** was the expected *meso*-form (having C_i-symmetry), whereas the second isomer was, rather surprisingly, the heterocoupling product between the major and the minor product of the preceeding *o*-lithiation in such a manner that in the ferrocene halfes



"*meso*", C_i

"*racem*", C_2
(only one enantiomer shown)

Fig. 2. Chirality of 2,2'-substituted 1,1'-biferrocenyls

Table 1. Fractional atomic coordinates [$\times 10^4$] and isotropic temperature coefficients [$Å^2 \times 10^4$] for the crystal structure of **2 a**. Estimated standard deviations (in unit of the last significant digit) in paranthesis. The isotropic temperature factor has the form $T = \exp\{-[\pi^2 U_{iso}(\sin^2\Theta/\lambda^2)]\}$. The equivalent isotropic temperature coefficient was calculated as one third of the trace of the orthogonalized u_{13}-matrix

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
FE (1)	0 (0)	0 (0)	0 (0)	192 (7)
FE (2)	3 461 (2)	5 926 (1)	2 159 (1)	209 (8)
C (1)	2 140 (9)	−1 300 (6)	888 (7)	205 (26)
C (2)	2 348 (10)	15 (7)	2 033 (7)	218 (28)
C (3)	2 642 (10)	1 282 (6)	1 492 (7)	267 (29)
C (4)	2 738 (10)	747 (7)	123 (10)	332 (37)
C (5)	2 422 (10)	−815 (7)	−298 (8)	256 (32)
C (6)	−2 551 (12)	−1 385 (10)	−786 (13)	575 (56)
C (7)	−2 645 (13)	−200 (11)	338 (14)	543 (63)
C (8)	−2 433 (13)	1 122 (11)	− 166 (16)	589 (66)
C (9)	−2 073 (13)	811 (11)	−1 465 (13)	607 (58)
C (10)	−2 150 (14)	−839 (11)	−1 891 (12)	600 (55)
C (11)	2 589 (12)	76 (8)	3 641 (8)	301 (36)
C (12)	4 170 (19)	1 183 (14)	4 899 (19)	986 (96)
N (1)	732 (17)	193 (8)	3 901 (12)	655 (73)
C (13)	−222 (18)	1 664 (10)	3 715 (14)	590 (79)
C (14)	1 056 (26)	−101 (15)	5 571 (20)	844 (136)
C (15)	1 676 (9)	−2 844 (7)	931 (7)	218 (27)
C (16)	2 054 (10)	−4 169 (6)	63 (7)	218 (28)
C (17)	1 309 (10)	−5 386 (7)	496 (8)	288 (32)
C (18)	597 (12)	−4 872 (8)	1 654 (11)	438 (45)
C (19)	836 (10)	−3 251 (7)	1 925 (8)	264 (33)
C (20)	6 065 (12)	−2 709 (10)	3 435 (12)	498 (50)
C (21)	6 435 (12)	−3 949 (11)	2 580 (11)	457 (51)
C (22)	5 752 (12)	−5 278 (10)	2 877 (12)	509 (54)
C (23)	5 065 (15)	−4 852 (10)	4 024 (10)	509 (52)
C (24)	5 284 (15)	−3 276 (10)	4 398 (10)	546 (51)
C (25)	2 915 (11)	−4 275 (8)	−1 211 (10)	342 (39)
N (2)	1 380 (14)	−4 032 (8)	−2 478 (7)	446 (46)
C (26)	3 732 (15)	−5 732 (9)	−1 501 (10)	435 (55)
C (27)	−590 (21)	−5 174 (14)	−2 780 (17)	1 162 (103)
C (28)	2 447 (32)	−3 898 (13)	−3 397 (17)	1 161 (174)

of **2 a** the metallocene chiralities are opposite, whereas the centro chiralities at the α-carbon (side chain) are identical (Fig. 3)[1].

The crystal structure of **2 a** shows that both five-membered rings are remarkably twisted around the 1,1′-bond by about 20°, whereas the *meso*-form **2 b** – as expected – adopts a perfect coplanar structure (which is enforced by the space group symmetry).

---

[1] It should be noted that in **2** we are dealing with compound(s) containing three elements of chirality, namely ferrocene-, axial (= torsional)- and centro chirality (in the side chains)

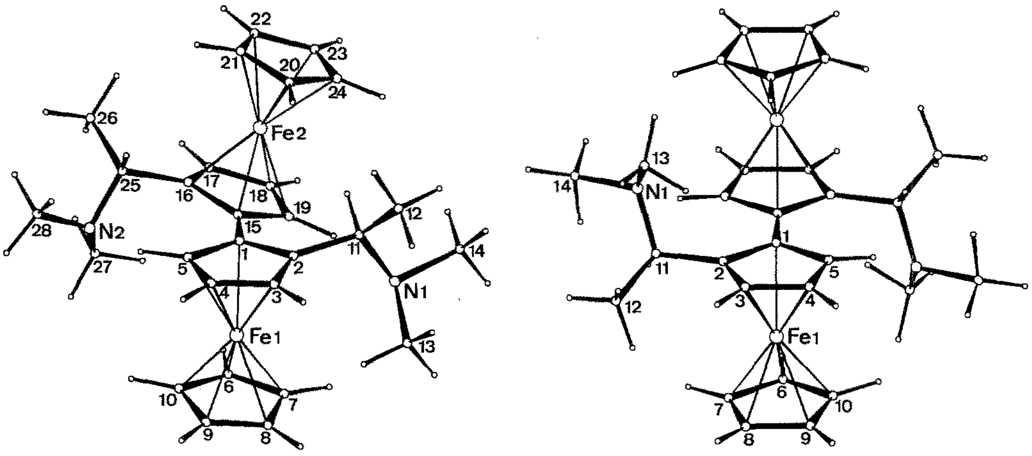


Fig. 3. Crystal structures of **2a** (left) and **2b** (right)

Table 2. Fractional atomic coordinates [× 10^4] and isotropic temperature coefficients [$\text{Å}^2 \times 10^4$] for the crystal structure of **2b**

Atom	x/a	y/b	z/c	U_{iso}
FE (1)	1 672 (1)	−1 824 (1)	1 133 (1)	336 (3)
C (1)	−226 (4)	−792 (3)	28 (3)	290 (18)
C (2)	−45 (5)	−2 101 (3)	−969 (3)	321 (19)
C (3)	676 (5)	3 372 (4)	479 (4)	390 (22)
C (4)	−1 175 (5)	−2 877 (4)	811 (4)	401 (23)
C (5)	−889 (5)	−1 300 (4)	1 130 (4)	352 (21)
C (6)	4 244 (6)	−200 (5)	2 187 (6)	604 (30)
C (7)	4 538 (6)	−1 389 (6)	1 194 (6)	601 (31)
C (8)	4 016 (6)	−2 719 (5)	1 619 (6)	657 (34)
C (9)	3 400 (7)	−2 342 (6)	2 877 (6)	686 (36)
C (10)	3 535 (7)	−785 (6)	3 218 (5)	681 (34)
C (11)	581 (6)	−2 210 (4)	−2 341 (4)	448 (25)
C (12)	1 372 (8)	−3 605 (5)	−2 705 (5)	657 (36)
N (1)	−1 004 (6)	−2 106 (4)	−3 567 (4)	595 (26)
C (13)	2 813 (9)	3 316 (6)	4 016 (6)	848 (41)
C (14)	367 (11)	1 952 (7)	4 859 (6)	967 (55)

It is yet unknown whether **2a** adopts the same twisted conformation in solution as in the crystal, but its high optical rotation ($[\alpha]_D$ − 486° in ethanol) and its pronounced CD-effects (see below) are in favour of an inherently *chiral* biarylchromophor caused by the steric influence of two chiral centers with equal chiralities, rather than an *achiral* biaryl chromophor, chirally disturbed by adjacent asymmetric centers.

Attempts to prepare the dimethyl derivative **4** from **2** by introducing a second methyl group at each α-carbon failed. Neither the oxidation with MnO_2 [9] and subsequent addition of methyllithium, nor the reaction of the methiodide (only the *mono*-methiodide **3** could be obtained) of **2** with methylmagnesiumbromide [10] led to higher substituted products. Also the reaction of **2** with CH_3ONa/CH_3OH did not result in the symmetrical product **6**, but gave the unsymmetrical aminoether **5**.

Therefore the coupling of appropriately substituted ferrocenes was performed. Coupling of 1-ferrocenyl methoxyethane afforded the desired biferrocenyl **6** as a mixture of *racem*- and *meso*-form (ratio 2 : 3) separable by column chromatography.

Neither of these compounds (**5, 6**) exhibit a rotational barrier sufficient for the occurrence of rotamers. Coupling of 2-ferrocenyl 2-methoxypropane [11] gave only the achiral (*meso*-) diastereoisomer of **7** and compound **8**, resulting from heteroanular coupling, indicating that the transition state in this reaction obviously is very sensitive to steric interactions.

2a was accessible also in optically active form by coupling of optically pure (+)-1-ferrocenyl-N,N-dimethylaminoethane of known absolute chirality (*R*). The sole product of the coupling reaction was laevorotatory. Subsequently (−)-$(R)_c(R)_c(R)_m(S)_m$-**2a**[2] was transformed into (−)-**5**. The chiroptical properties are reported in the experimental part.

Finally the coupling of 1,3-disubstituted ferrocenes was investigated, for which only a moderate steric repulsion during the coupling reaction should be expected. Moreover, the introduction of an additional substituent in 5- and 5′-positions of the resulting biferrocenyl should decrease their mobility. For practical reasons appropriately 1,3,4-trisubstituted ferrocenes [1, 12] were choosen as starting compounds which obviously can form only *one* single Li-intermediate. However, under several reaction conditions no coupling products **9** (and **10** resp.) could be detected; only starting material was recovered, although the Li intermediate seemed to have been formed, since significant color changes were observed at this stage.

Our results lead to the assumption that the relatively low rotational barrier around the 1,1′-biferrocenyl bond could be sufficiently increased (if at all) by rather spacefilling substituents. Such substituents, however, decrease dramatically the reactivity in coupling reactions.

A different approach to achieve the desired goal, i.e. to obtain torsional isomeric biferrocenyls, may be a "total synthesis" of compounds such as **9** or **10**. Studies towards this aim are now being planned.

Experimental Part

Melting points: Kofler-melting point apparatus, uncorrected; ^{1}H-n.m.r.: Bruker WM 250 in $CDCl_3$ with tetramethylsilane as internal standard; MS: Varian MAT-CH7; CD-spectra: Jobin Yvon Dichrograph Mark III; optical rotations: Perkin Elmer polarimeter 241 at 20 °C (thermostated).

For the syntheses of 3,4-dimethyl-1-(N,N-dimethylaminomethyl)-ferrocene and 3,4-tetramethylene-1-(N,N-dimethylaminomethyl)-ferrocene see Ref. [1].

2,2′-Bis-[1-(N,N-dimethylamino)-ethyl]-1,1′-biferrocenyl (**2a** *and* **2b**)

A solution of 5.14 g (20 mmol) of 1-ferrocenyl-N,N-dimethylethylamine in 100 ml of dry ether under Ar was treated with 18.8 ml (30 mmol) of a 1.6 molar solution of *n-Bu*Li (in hexane). After stirring for 6 h the mixture was cooled to −78 °C and 4 g (30 mmol) of carefully dried $CoCl_2$ was added in one portion. The suspension was slowly warmed up to r.t. in the course of which the color changed

---

[2] *c*: centro chirality; *m*: metallocene chirality (see Ref. [2])

to green-black. The reaction was quenched by addition of water and 1 *N* NaOH and the insoluble material separated by filtration over celite. After separation of the organic layer, the aquous layer was extracted with three 50 ml portions of ether. The combined extracts were dried over $MgSO_4$ and concentrated to a small volume (5–10 ml). Crystallisation of a mixture of **2a** and **2b** was introduced by adding a few seeding crystals. From the mother liquor 3.82 g of nearly pure starting material could be recovered which was pure enough for further coupling reactions. The crystalized mixture of products was separated by chromatography on Al_2O_3: Elution with petroleum ether/triethylamine (99.8 : 0.2) yielded 200 mg (3.9%) of **2a**. Even repeated recrystallisation from *n*-hexane did not furnish a sharp melting point: 172–196 °C. ^{1}H-n.m.r. ($CDCl_3$): $\delta = 1.18$ (d, 3 H, $CHCH_3$), 1.42 (d, 3 H, $CHCH_3$), 2.19 [s, 6 H, $N(CH_3)_2$], 2.62 [s, 6 H, $N(CH_3)_2$], 3.78 (q, 1 H, $CHCH_3$, $J(CHCH_3) = 7.4$ Hz, 4.00 (s, 5 H, *Fc*-**H**), 4.06 (s, 5 H, *Fc*-**H**), 4.09 (m, 3 H, *Fc*-**H**), 4.23 (m, 4 H, *Fc*-**H**, $CHCH_3$). MS: *m*/e (%): 512 (6), 467 (6), 452 (12), 438 (7), 423 (14).

Elution with ethanol/ether/triethylamine (49.9 : 49.9 : 0.2) afforded 645 mg (13%) of **2b** which was recrystallized from ethylacetate; m.p.: 206–207 °C. ^{1}H-n.m.r. ($CDCl_3$): $\delta = 1.48$ (d, 6 H, $CHCH_3$), 2.16 [s, 12 H, $N(CH_3)_2$], 4.05 (s, 10 H, *Fc*-**H**), 4.19 (m, 6 H, *Fc*-**H**), 4.37 (q, 2 H, $CHCH_3$, $J(CHCH_3) = 7.4$ Hz). MS: identical with **2a** (see above).

(−)-2,2'-Bis-[1-(N,N-dimethylamino)-ethyl]-1,1'-biferrocenyl [(−)-**2a**]

(+)-(*R*)-1-ferrocenyl-N,N-dimethylethylamine [13] was coupled to (−)-**2a** as described for the racemate. $[\alpha]_D^{20} - 486°$ (*Et*OH, $c = 0.2$). CD [*Et*OH, $\lambda(\Delta\varepsilon)$]: 468 (2.07), 420 − 370 (0), 285 (−6.76), 266 (−4.53), 223 (−71.7).

Crystal Structure of **2a**

Orange-red crystals were obtained from benzene/ethanol: $C_{28}H_{36}N_2Fe_2$, (512.30); space group **P1**. Cell constants obtained by least-squares to the setting anlges of 16 reflections with $4 \leqslant 2\Theta \leqslant 14°$: $a = 7.202$ (7), $b = 9.282$ (9), $c = 9.920$ (12) Å, $\alpha = 102.13$ (8), $\beta = 109.92$ (9), $\gamma = 92.17$ (8)°, $V = 605.2$ (7) Å^3 (at 92 K) and $a = 7.246$ (4), $b = 9.392$ (5), $c = 9.987$ (7) Å, $\alpha = 101.77$ (5), $\beta = 109.95$ (5), $\gamma = 91.79$ (4)°, $V = 621.7$ (5) Å^3 (at r.t.); $Z = 1$, d_{calc} (r.t.) = 1.368 gcm^{-3}, d_{obs}(r.t.) = 1.376 gcm^{-3} (flotation method, CsCl in H_2O); data were collected on a STOE 4-circle diffractometer with MoK_α-radiation ($\lambda = 0.71069$ Å, graphite monochromator) at 92 (1) K for all independent reflections with $4 \leqslant 2\Theta \leqslant 80°$ (4 ocatants: $-13 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 16$, $0 \leqslant l \leqslant 17$); 3 standard reflections ([2 0 −4], [−3 0 0], [0 3 2]) were measured every 100 reflections; their maximum fluctuation was 8%; 8 051 observed, 7 629 unique and 4 368 significant [$F > 4\sigma(F)$] reflections. Structure solution with direct methods, least square refinement of anisotropic atomic displacement parameters for all non-hydrogen atoms; H atoms were included at calculated positions, an isotropic temperature factor was refined for each H atom. Empirical absorption correction [14], no extinction correction; $R = 0.064$ (unit weights) for 322 parameters and 4 368 observations. A final difference Fourier synthesis showed features up to 1.3 e/Å^3; Computer programs are listed in [15].

Crystal structure of **2b**

Conditions analogous to the crystal structure determination of **2a**: $C_{28}H_{36}N_2Fe_2$, (512.30); space group **P$\bar{1}$**, cell constants from 18 reflections with $9 \leqslant 2\Theta \leqslant 16°$: $a = 7.311$ (4), $b = 9.441$ (4), $c = 9.758$ (6) Å, $\alpha = 102.60$ (4), $\beta = 105.42$ (5), $\gamma = 101.06$ (4)°, $V = 610.9$ (5) Å^3; $Z = 1$, $d_{calc} = 1.392$ gcm^{-3}. Data were collected at 298 (2) K for all independent reflections with $4 \leqslant 2\Theta \leqslant 50°$ (4 octants: $-8 \leqslant h \leqslant 8$, $-11 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 11$); 3 standard reflections ([0 2 0], [1 3 −1], [2 0 −3]) showed maximum fluctuations of 6%: 2 362 observed, 2 156 unique and 1 754 significant [$F > 4\sigma(F)$] reflections. Anisotropic temperature coefficients for all non-hydrogen atoms; aliphatic H atoms were included at observed positions and refined with isotropic temperature coefficients. Empirical absorption correction [14], no extinction correction; $R = 0.0373$ (unit weights) for 187 parameters and 1 862 observations. Features up to 1.3 e/Å^3 in a final difference Fourier synthesis.

mono-Methiodide of **2 a** (**3**)

To a solution of 1.28 g (2.5 mmol) of **2 a** in 10 ml of methanol 1.56 ml (25 mmol) of methyliodide were added and the mixture was warmed to 50 °C for 10 min. After cooling to r.t. the salt was precipitated by addition of ether, washed with *n*-hexane and dried in vacuo. Yield: 1.51 g (92%) of **3**; m.p.: 175–180 °C (dec.). $C_{29}H_{39}Fe_2IN_2$, (653.92).

2-[1-(N,N-Dimethylamino)-ethyl]-2′-(1-methoxyethyl)-1,1′-biferrocenyl (**5**)

50 mg (0.76 mmol) of **3** were added to a solution of 100 mg (2.5 mmol) NaOH in 10 ml of absolute methanol and the solution was refluxed under Ar for 18 h. Methanol was removed in vacuo, then water was added and the mixture extracted with ether, the extract dried over $MgSO_4$ and evaporated to give 35 mg (92%) of **5**; m.p.: 113–114 °C. $C_{27}H_{33}Fe_2NO$ (499.26).

^{1}H-n.m.r. ($CDCl_3$): $\delta = 1.19$ (d, 3 H, $CHCH_3$), 1.69 (d, 3 H, $CHCH_3$), 2.59 [s, 6 H, $N(CH_3)_2$], 3.38 (s, 3 H, OCH_3), 3.98 (s, 5 H, *Fc*-**H**), 4.00 (s, 5 H, *Fc*-**H**), 4.15 (m, 8 H, *Fc*-**H**, $CHCH_3$). MS *m*/e (%): 499 (100), 484 (15), 467 (26), 454 (16), 423 (10).

(−)-2-[1-(N,N-Dimethylamino)-ethyl]-2′-(1-methoxyethyl)-1,1′-biferrocenyl [(−)-**5**]

From (−)-**2 a** on treatment with methanolic NaOH as described for the racemate, (−)-**5** was obtained exhibiting ^{1}H-n.m.r. and mass spectra identical with those of racemic **5**. $[\alpha]_D^{20} - 286°$ (CH_2Cl_2, $c = 1.2$). CD (CH_2Cl_2), $\lambda(\Delta\varepsilon)$: 452 (1.91), 339 (−6.53), 322 (−5.37), 302 (−8.78), 272 (0.1), 255 (−2.54), 239 (1.66), 223 (−45.3), 208 (−56.6).

2,2′-Bis-(1-methoxyethyl)-1,1′-biferrocenyl (**6 a**, **6 b**)

To a solution of 1 g (4.1 mmol) of 1-methoxyethyl ferrocene in 20 ml of dry ether under Ar, 3.9 ml (6.24 mmol) of a 1.6 molar *n-Bu*Li solution in hexane were added dropwise. After stirring for 12 h at r.t. the mixture was cooled to −78 °C and 819 mg (6.24 mmol) of dry $CoCl_2$ were added. The mixture was stirred for 15 h, during which time the temperature was gradually raised to r.t. The work up was the same as described for **2** and the crude product was separated on Al_2O_3 in *n*-hexane yielding the following fractions: the first band contained 159 mg (16%) of racemic **6 a**. $C_{26}H_{30}Fe_2O_2$ (486.22).

^{1}H-n.m.r. ($CDCl_3$): $\delta = 1.65$ (d, 6 H, $CHCH_3$), 3.24 (s, 6 H, OCH_3), 4.02 (s, 10 H, *Fc*-**H**), 4.21–4.35 (m, 8 H, *Fc*-**H**, $CHCH_3$). MS: *m*/e (%): 486 (33), 454 (15), 422 (26), 344 (28), 304 (18). The second band gave 241 mg (24%) of the achiral *meso* form **6 b**; ^{1}H-n.m.r. ($CDCl_3$): $\delta = 1.82$ (d, 6 H, $CHCH_3$), 3.35 (s, 6 H, OCH_3), 4.06 (s, 10 H, *Fc*-**H**), 4.28–4.50 (m, 8 H, *Fc*-**H**, $CHCH_3$). MS identical with **6 a** (see above). Finally 579 mg (58%) of starting material could be recovered from the third band.

2,2′-Bis-[1-methoxy-1-methyl-ethyl]-1,1′-biferrocenyl (**7**) *and 1,1′-Bis-[1-methoxy-1-methyl-ethyl]-1″,1‴-biferrocenyl* (**8**)

0.96 g (3.72 mmol) of 2-methoxy-2-propylferrocene were coupled under the same conditions as given for **6 a** and **6 b**. The crude reaction mixture was separated by column chromatography on Al_2O_3 in *n*-hexane (fractions 1–3) followed by *n*-hexane/ethylacetate (95 : 5) (fraction 4); the two first bands contained 162 mg (19%) of 2-propenylferrocene and 33 mg (3%) of starting material, followed by fraction 3 with 87 mg (9%) of **7**; m.p.: 116–117 °C.

$C_{28}H_{34}Fe_2O_2$ (514.29). ^{1}H-n.m.r. ($CDCl_3$): $\delta = 1.51$ (s, 6 H, CH_3), 1.58 (s, 6 H, CH_3), 2.90 (s, 6 H, OCH_3), 3.96 (m. 8 H, *Fc*-**H**), 4.13 (t, 4 H, *Fc*-**H**), 4.30 (d, 4 H, *Fc*-**H**). MS *m*/e (%): 514 (11), 482 (9), 450 (100), 344 (30), 304 (23). Fraction 4 afforded 207 mg (22%) of **8**; m.p.: 88–89 °C. $C_{28}H_{34}Fe_2O_2$ (514.29). ^{1}H-n.m.r. ($CDCl_3$): $\delta = 1.50$ (s, 6 H, CH_3), 1.58 (s, 6 H, CH_3), 2.90 (s, 6 H, OCH_3), 3.96 (s, 10 H, *Fc*-**H**), 4.10–4.30 (m, 6 H, *Fc*-**H**). MS identical to that of **7** (see above).

Acknowledgements

We are grateful to Dr. W. Weissensteiner for performing the force field calculations, to Mr. H. Bieler for recording the mass spectra and to Mr. K. Gruber and B. Weigl for their help in the structure determination of **2a**.

References

[1] Ferrocene Derivatives, Part 69: Krajnik P., Schlögl K., Widhalm M. (1990) Monatsh. Chem. **121**: 413; Stereochemistry of Metallocenes, Part 54: Schlögl K., Werner A., Widhalm M. (1986) Monatsh. Chem. **117**: 1423

[2] Schlögl K. (1986) J. Organomet. Chem. **300**: 219

[3] See e.g.: Meyer A., Schlögl K., Keller W., Kratky Ch. (1989) Monatsh. Chem. **120**: 453

[4] Booth D. J., Marr G., Rockett B. W. (1971) J. Organomet. Chem. **32**: 227

[4a] Schlögl K., Walser M. (1969) Monatsh. Chem. **100**: 1515

[5] Marr G., Moore R. E., Rockett B. W. (1969) Tetrahedron **25**: 3477

[6] Iyoda M., Sakatani M., Miyazaki T., Oda M. (1984) Chem. Lett.: 2005

[7] Allinger N. L. (1987) Quantum Chemistry Program Exchange, No. MM2 (87). Indiana University, Bloomington, IN 47405, USA

[8] Webb J. L. A., Threlkeld R. R. (1953) J. Org. Chem. **18**: 1406; Webb J. L. A. (1953) J. Org. Chem. **18**: 1413

[9] Peet J. H. J., Rockett B. W. (1974) J. Organomet. Chem. **67**: 407

[10] Ustynyuk Yu. A., Nesmeyanov A. N. (1963) Izv. Akad. Nauk. SSSR, Ser. Khim. **11**: 1977

[11] Ustynyuk Yu. A., Nesmeyanov A. N. (1963) Izv. Akad. Nauk. SSSR, Ser. Khim. **11**: 1972

[12] Schmitt G., Özman S. (1976) Chem. Ztg. **100** (3): 143

[13] Maquarding D., Klusacek H., Gokel G., Hoffmann P., Ugi I. (1970) J. Am. Chem. Soc. **92**: 5389

[14] Walker N., Stuart D. (1983) Acta Cryst. **A39**: 158

[15] Sheldrick G. M. (1976) SHELX 76, A Program for Crystal Structure Determination. Univ. of Cambridge, England; Motherwell S. (1976) PLUTO, A Program for Plotting Molecular and Crystal Structures. Cambridge Crystallographic Data Centre, England; Sheldrick, G. M. (1986) Programm SHELXS-86. Universität Göttingen

Received May 31, 1990. Accepted June 14, 1990