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XXXI *. *N,N*-DIMETHYLAMINOMETHYLATION OF BIFERROCENE AND CONVERSIONS OF THE PRODUCTS INTO SEVERAL BIFERROCENE DERIVATIVES

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Summary

Five (*N,N*-dimethylaminomethyl)biferrocenes (II—VI) have been isolated from the product given by the Mannich reaction of biferrocene with bis-(*N,N*-dimethylamino)methane and phosphoric acid. Several 1′- and 1′,1‴-substituted biferrocene derivatives have been synthesized by some transformation reaction of 1′- and 1′,1‴-bis(*N,N*-dimethylaminomethyl)biferrocenes (II and IV).

A number of ferrocene derivatives has already been synthesized by various transformations of (*N,N*-dimethylaminomethyl)biferrocenes [2], which were prepared by Mannich reaction of ferrocene. Especially, regiospecific lithiation of (*N,N*-dimethylaminomethyl)ferrocene at the *ortho* position provided valuable methods for syntheses [3] and information on the stereochemistry [4] of ferrocene derivatives. On the other hand, there has been no report on the direct dimethylaminomethylation of biferrocene, in spite of the importance of the resulting products as intermediary compounds of many biferrocene derivatives. All (*N,N*-dimethylaminomethyl)biferrocenes already described [5—7], which are derivatives substituted only on the fulvalene moiety (rings A and C **), were prepared by coupling of 2-lithio(*N,N*-dimethylaminomethyl)ferrocene. Substitution reactions of biferrocene already reported are acetylation [8], formyla-

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[*] For part XXX, see ref. 1.

[**] Rings A, B, C and D of biferrocene are named as shown in Fig. 1. The numbering system of biferrocene follows that given in ref. 10.

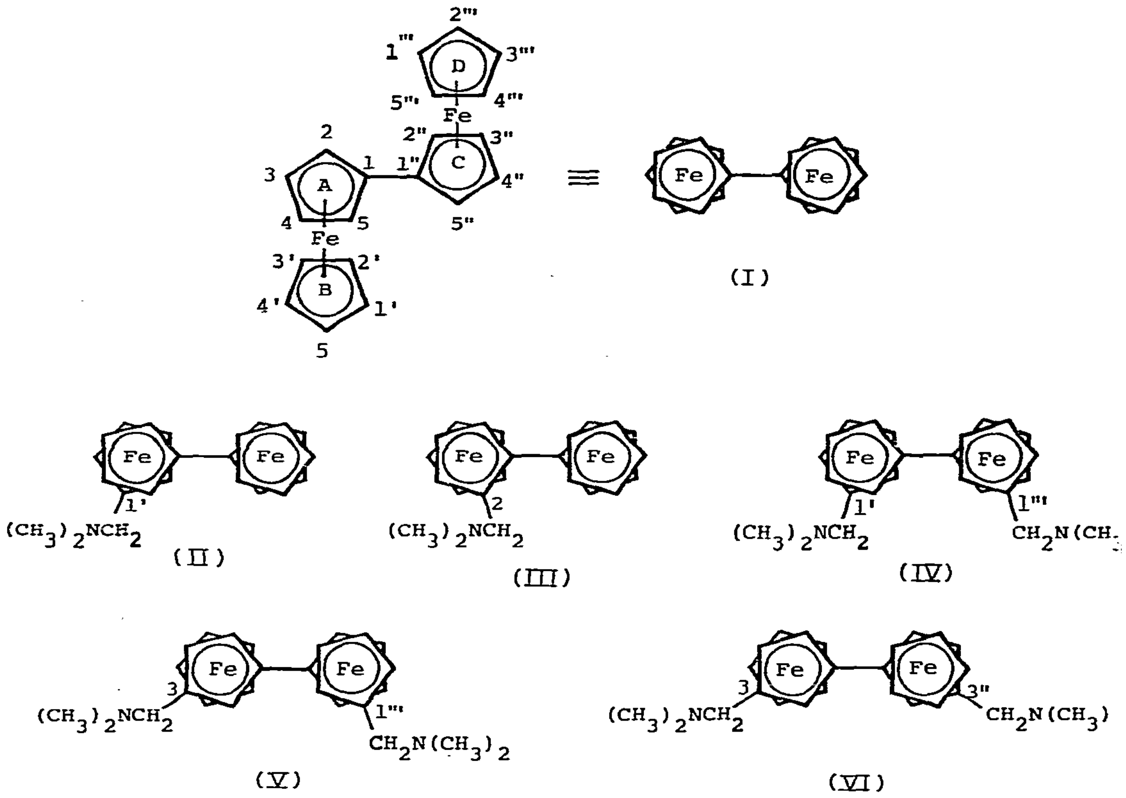

Fig. 1. Structures of biferrocenes I—VI.

tion [9] and benzoylation [10]. *N,N*-Dimethylaminomethylation of biferrocene and the isolation of five substituted biferrocenes (II—VI) are reported in this paper. Conversions of the products into some biferrocene derivatives are also described.

Results and discussion

N,N-Dimethylaminomethylation of biferrocene

N,N-Dimethylaminomethylation of biferrocene (I) was carried out under the modified conditions described by Lindsay and Houser [11] for the preparation of (*N,N*-dimethylaminomethyl)ferrocenes. Repeated column chromatography over deactivated alumina separated the products into five (dimethylaminomethyl)biferrocenes and several unknown products. Commercial activated alumina could not be used in the chromatographic separation because of strong absorption of the amines. Their high-resolution mass spectra indicated that two of them were monosubstituted biferrocenes and that three were disubstituted derivatives.

Purification of II, a monosubstituted biferrocene, was achieved by recrystallization of its hydrogen chloride salt. The PMR spectrum of the free base II (see

TABLE 1

PMR SPECTRAL DATA FOR (*N,N*-DIMETHYLAMINOMETHYL)BIFERROCENES IN $CDCl_3$ (CHEMICAL SHIFTS δ ppm, *J* VALUES: Hz)

Compound	$—N(CH_3)_2$	$—CH_2—$	A and C ring protons	B and D ring protons
I	—	—	4.16, 4.35(each 4H, AA'XX')	4.00(10H, s)
II	2.07(6H, s)	3.01(2H, s)	4.08, 4.24(each 2H, AA'XX') 4.13, 4.30(each 2H, AA'XX')	3.95(9H, s)
III	2.17(6H, s)	3.07, 3.59(2H, AB, *J* = 12.9)	4.12(1H, t, *J* = 2.5, 4-H) 4.18(3H, m) 4.42(2H, m) 4.66(1H, m, 5-H)	3.99(5H, s) 4.06(5H, s)
IV	2.09(12H, s)	3.02(4H, s)	4.13, 4.26(8H, AA'XX')	3.93(8H, s)
V	2.06(6H, s) 2.23(6H, s)	2.97, 3.00(2H, AB, *J* = 13) 3.26, 3.30(2H, AB, *J* = 13)	4.12, 4.25(4H, AA'XX') 4.19(1H, dd, *J* = 1.3, 2.6, 4-H) 4.30(1H, dd, *J* = 1.3, 2.6, 5-H) 4.40(1H, t, *J* = 1.3, 2-H)	3.91(4H, s) 3.93(5H, s)
VI	2.20(12H, s)	3.21, 3.30(4H, AB, *J* = 12.7)	4.16(2H, dd, *J* = 1.3, 2.6, 4— & 4″ — H) 4.29(2H, dd, *J* = 1.3, 2.6, 5— & 5″ — H) 4.39(2H, t, *J* = 1.3, 2— & 2″ — H)	3.91(10H, s)

Table 1) confirmed its 1'-substituted structure from the appearance of two sets of AA'XX' signals assigned to fulvalene moiety (rings A and C). The last part of the third band eluted with benzene was repeatedly chromatographed and recrystallized to yield the other monosubstituted (dimethylaminomethyl)biferrocene (III). In the PMR spectrum of compound III, one of ring proton signals appeared as a triplet with a *J* value of 2.5 Hz *; the presence of a 1,2-substituted ring was indicated. The chemical shift difference (0.52 ppm) between the nonequivalent methylene protons was larger than those of the 3- and 3″-substituted derivatives (V, 0.03 and 0.04 ppm; VI, 0.09 ppm) described below. The PMR behavior indicated that the compound had a methylene group in the 2-position where substitution caused steric hindrance. Therefore, the monosubstituted compound III was identified as 2-(*N,N*-dimethylaminoethyl)biferrocene.

The disubstituted compound (VI) yielded from the band eluted with benzene/ethyl acetate (10/1) showed the PMR spectrum of a biferrocene substituted at the symmetric positions of the fulvalene moiety; a singlet of methyl protons (12 H), a singlet of unsubstituted Cp-ring protons (10 H) and an AB quartet of methylene protons (4 H) appeared in the spectrum. The signals of the fulvalene moiety consisted of a triplet with a *J* value of 1.3 Hz [12] and two double doublets. Furthermore, the melting point of the compound (171—173°C) was different from those of 2,2″- and 2,5″-bis(*N,N*-dimethylaminomethyl)biferrocenes (103—105.5°C and 203—205.5°C, respectively) synthesized by coupling of (*N,N*-dimethylaminomethyl)ferrocene-2-boric acid [5,6].

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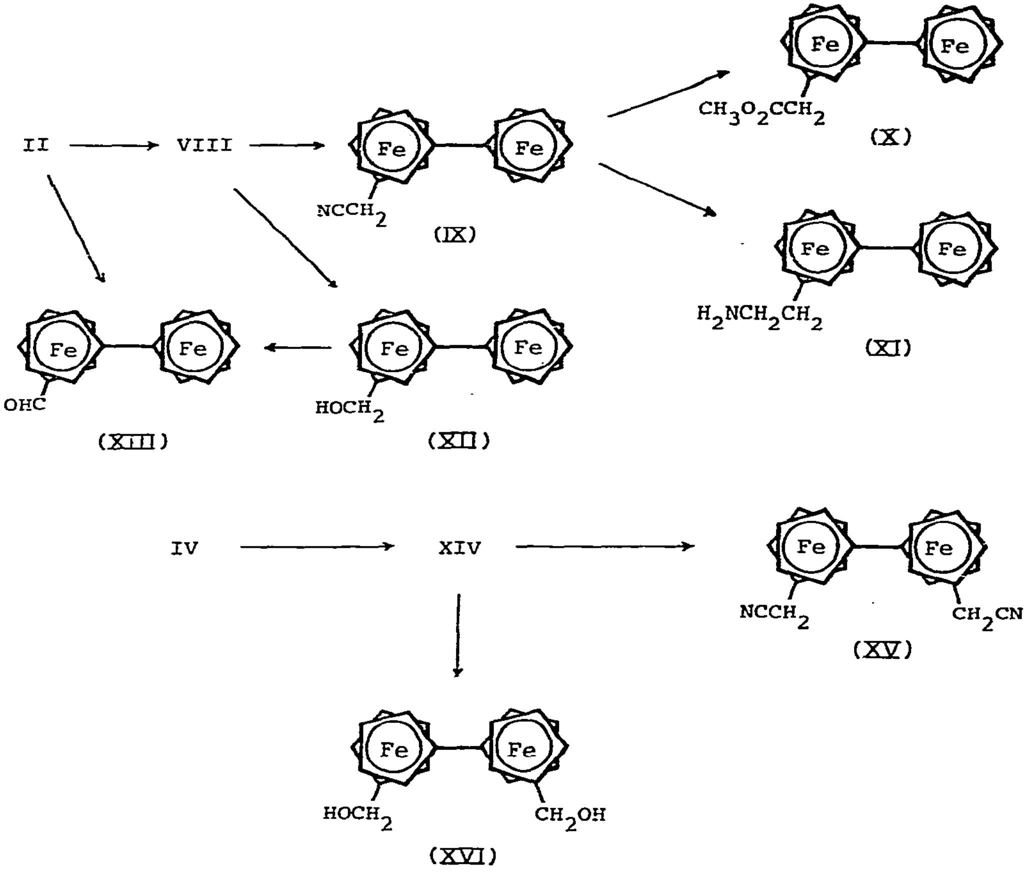
* Coupling constants of 2.5 and 1.3 Hz of the cyclopentadienyl (Cp) ring correspond to those between *ortho* protons and between *meta* protons, respectively [12].

SCHEME 1

TRANSFORMATIONS OF 1'- AND 1',1'''-BIS(*N*,*N*-DIMETHYLAMINOMETHYL)BIFERROCENES (II AND IV)



Accordingly, the symmetrically substituted compound VI was identified as 3,3''- and/or 3,4''-bis(*N*,*N*-dimethylaminomethyl)biferrocene *.

The PMR spectrum of the disubstituted compound IV from the following band showed a simple pattern, in which methylene, substituted Cp-ring and fulvalene moiety-ring protons appeared as a singlet at δ 3.02 ppm, a singlet at δ 3.93 ppm and an AA'XX' system at δ 4.13 and 4.26 ppm, respectively. Thus, the diamine IV was evidently 1'-1'''-bis(*N*,*N*-dimethylaminomethyl)biferrocene.

An asymmetric disubstituted biferrocene (V) was obtained from the band eluted after that of IV. Its PMR spectrum showed two singlets of methyl groups, two AB system signals of methylene protons and two singlets (5 H and 4 H) of the Cp ring protons. The ring protons of the fulvalene moiety appeared as one set of AA'XX' system signals, two double doublets and a triplet with a *J* value of 1.3 Hz. Appearance of a triplet with the *meta* coupling constant indi-

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* There was no evidence to determine whether VI was the 3,3''- or 3,4''-disubstituted compound (meso form and racemic form, respectively).

cated that the fulvalene moiety was substituted at the 3-position with a dimethylaminomethyl group. Thus, it was confirmed that the diamine V was 3,1‴-disubstituted biferrocene. The structures of the five *N,N*-dimethylaminomethyl derivatives of biferrocene assigned above were supported by their mass spectral fragmentation [13]. Further dimethylaminomethylation of 1′-substituted biferrocene II gave bis(*N,N*-dimethylaminomethyl)biferrocenes IV and V, and other unknown products.

Formation of several other substituted compounds in addition to the biferrocene derivatives isolated in this study should also be possible. Some of them were obtained, but purification and spectral measurements were difficult because of the small amounts and contamination with compounds of similar polarity.

Some transformation reactions of (N,N-dimethylaminomethyl)biferrocenes

Some biferrocene derivatives were prepared from 1′- and 1′,1‴-substituted biferrocenes (II and IV), which had been obtained in comparatively large quantities by the dimethylaminomethylation, as shown in Scheme 1. The oxidation product (XIII) of alcohol XII with MnO_2 was identical in melting point with the 1′-formylbiferrocene given by the Vilsmeier formylation of biferrocene [8]. Direct oxidation [7] of (dimethylaminomethyl)biferrocene (II) with activated MnO_2 also gave formylbiferrocene (XIII). Since chromatographic separation of aldehyde compounds is usually easier than that of aminomethyl derivatives, isolation of other formyl derivatives was attempted by direct oxidation of the crude reaction product from the dimethylaminomethylation, followed by chromatography. However, the expected products were not obtained.

Experimental

All melting points are uncorrected. Wako activated alumina (300 mesh), Kanto-kagaku silica gel (100 mesh) and Mallinckrodt silicic acid (100 mesh) were used for column chromatography. Deactivated alumina, used in the separation of (*N,N*-dimethylaminomethyl)biferrocenes, was prepared by washing the Wako activated alumina with aq. HCl, aq. Na_2CO_3 and then ion-exchanged water, followed by heating at ca. 200°C for five minutes. IR spectra were measured Hitachi-Perkin-Elmer model 225 or Hitachi model 215 grating infrared spectrometers, employing KBr disks. PMR spectra were measured on JEOL JNM-4H-100 or JEOL JNM-FX-100 spectrometers at 100 MHz at room temperature in $CDCl_3$ with TMS as an internal standard. Mass spectra were obtained with a Hitachi RMU-7M double-focussing mass spectrometer at 70 eV ionizing energy by the direct insertion method. Numbers in parentheses in the mass spectral data indicate the relative intensities of the peaks compared to the intensity of the base peak. High-resolution mass spectra were analysed on a Hitachi datalyser system 002.

Biferrocene (m.p. 236—237°C) [14] and bis(*N,N*-dimethylamino)methane (b.p. 81—84°C) [11] used in this work were prepared according to the procedures previously reported.

N,N-Dimethylaminomethylation of biferrocene (I)

According to the modified procedure described by Lindsay and Houser [11] in the reaction of ferrocene, biferrocene (I, 1.00 g, 2.70 mmol) was added to a stirred mixture of bis(*N,N*-dimethylamino)methane (1.00 g, 9.80 mmol), paraformaldehyde (0.50 g) and phosphoric acid (0.50 g) in acetic acid (40 ml). The resulting suspension was heated at 85—95°C under an N_2 atmosphere for 5 h. The reaction mixture was poured into ice-water and then made alkaline by addition of aq. NaOH. The mixture was extracted with CH_2Cl_2, and the extracts was washed with water and dried over $CaCl_2$. The residual dark brown oil given by evaporation of the solution was column-chromatographed over deactivated alumina. The recovered biferrocene (16%) was first eluted with benzene. The second band eluted with benzene yielded 1′-(*N,N*-dimethylaminomethyl)biferrocene (II) (442 mg, 38%), which was contaminated with the immediately subsequently eluted compound (III). Since the contaminant could not be removed by repeated chromatography and recrystallization, purification of compound II was carried out according to the following procedure. Dry hydrogen chloride gas was bubbled to an ether solution of the contaminated compound II, and the resulting precipitated hydrogen chloride salt was filtered off. The salt was reprecipitated from its methanol solution by adding ether dropwise to give a yellow powder, m.p. 150—153°C (dec.). The free amine was liberated from an aqueous solution of the salt by addition of aq. NaOH. On recrystallization of the amine II from hexane, orange-yellow needles, m.p. 105.5—107°C, were obtained. (Found: C, 64.35; H, 5.97; N, 3.25; M^+, 427.0671. $C_{23}H_{25}NFe_2$ calcd.: C, 64.67; H, 5.90; N, 3.27%; mol. wt., 427.0684.) IR spectrum (cm^{-1}): 2940 and 2775 [ν(CH)]. Mass spectrum (*m/z*): 427 (100, M^+), 383 (21, $[M - N(CH_3)_2]^+$), 305 (56, $[FeC_5H_4C_5H_4FeC_5H_5]^+$), 304 (60, $[FeC_5H_4C_5H_4FeC_5H_4]^+$).

The last part of the third band eluted with benzene was rechromatographed and then recrystallized from ethanol to give orange-yellow prisms, m.p. 112—114°C, of 2-(*N,N*-dimethylaminomethyl)biferrocene (III) (20 mg, 1.7%). (Found: M^+, 427.0704. $C_{23}H_{25}NFe_2$ calcd.: mol. wt., 427.0684). IR spectrum (cm^{-1}): 2940 and 2775 [ν(CH)]. Mass spectrum (*m/z*): 427 (100, M^+), 383 (27, $[M - N(CH_3)_2]^+$), 318 (57, $[M - N(CH_3)_2 - C_5H_5]^+$), 305 (34, $[FeC_5H_4C_5H_4FeC_5H_5]^+$), 304 (8.0, $[FeC_5H_4C_5H_4FeC_5H_4]^+$), 262 (31, $[C_5H_4C_5H_4FeC_6H_6]^+$).

The fourth band, eluted with benzene/ethyl acetate (10/1), yielded 1′,1‴-bis(*N,N*-dimethylaminomethyl)biferrocene (IV) (199 mg, 15%), which was recrystallized from ethyl acetate to give orange-yellow needles, m.p. 106—107°C. (Found: C, 64.49; H, 6.88; N, 5.65; M^+, 484.1288. $C_{26}H_{32}N_2Fe_2$ calcd.: C, 64.49; H, 6.66; N, 5.79%, mol. wt., 484.1262.) IR spectrum (cm^{-1}): 2940 and 2775 [ν(CH)]. Mass spectrum (*m/z*): 484 (86, M^+), 426 (29, $[M - CH_2N(CH_3)_2]^+$), 396 (12, $[M - 2\ N(CH_3)_2]^+$), 395 (18, $[M - 2\ N(CH_3)_2 - H]^+$), 318 (100, $[FeC_5H_4C_5H_4FeC_6H_4]^+$), 305 (12, $[FeC_5H_4C_5H_4FeC_5H_5]^+$), 304 (13, $[FeC_5H_4C_5H_4FeC_5H_4]^+$).

The compound obtained from elution with benzene/ethyl acetate (10/1) after elution of the band of IV was 3,1‴-bis(*N,N*-dimethylaminomethyl)biferrocene (V) (89 mg, 6.8%), which was recrystallized from hexane to give orange-yellow prisms, m.p. 81—84°C. (Found: M^+, 484.1235. $C_{26}H_{32}N_2Fe_2$ calcd., mol. wt., 484.1262.) IR spectrum (cm^{-1}): 2940 and 2775 [ν(CH)]. Mass spectrum (*m*/*z*): 484 (100, M^+), 396 (47, $[M - 2\ N(CH_3)_2]^+$), 318 (51, $[M - 2\ N(CH_3)_2 - C_6H_6]^+$).

In the other run for the dimethylaminomethylation, 3,3″-bis(*N*,*N*-dimethylaminomethyl)biferrocene (VI) (2.1%) was isolated from the band eluted after monosubstituted biferrocene III. The crude compound VI was recrystallized from hexane to give orange-yellow prisms, m.p. 171—173°C. (Found: M^+, 484.1246. $C_{26}H_{32}N_2Fe_2$ calcd.: mol. wt., 484.1262.) IR spectrum (cm^{-1}): 2960 and 2775 [ν(CH)]. Mass spectrum (*m*/*z*): 484 (100, M^+), 440 (23, $[M - N(CH_3)_2]^+$), 375 (20, $[M - N(CH_3)_2 - C_5H_5]^+$), 373 (20, $[M - HN(CH_3)_2 - C_5H_6]^+$), 332 (34, $[M - N(CH_3)_2 - CH_2NCH_3 - C_5H_5]^+$), 319 (22, $[M - N(CH_3)_2 - FeC_5H_5]^+$), 275 (30, $[C_6H_5C_6H_5FeC_5H_5]^+$).

N,N-Dimethylaminomethylation of 1′-(N,N-dimethylaminomethyl)biferrocene (II)

Further dimethylaminomethylation of II was carried out according to the same procedure as the reaction of biferrocene. 1′-(*N*,*N*-Dimethylaminomethyl)biferrocene (II) (0.94 g, 2.2 mmol) was added to a solution of bis(*N*,*N*-dimethylamino)methane (0.98 g, 9.6 mmol), paraformaldehyde (0.50 g) and phosphoric acid (0.50 g) in acetic acid (40 ml). Column chromatography of the reaction product over deactivated alumina yielded the recovered II (94 mg, 10%), 1′,1‴-bis(*N*,*N*-dimethylaminomethyl)biferrocene (IV) (294 mg, 28%) and 3,1‴-bis(*N*,*N*-dimethylaminomethyl)biferrocene (V) (53 mg, 5.0%).

Methiodides (VIII and XIV) of 1′- and 1′,1‴-bis(N,N-dimethylaminomethyl)biferrocenes (II and IV)

A methanol solution (20 ml) of methyl iodide (560 mg) was added to a stirred solution of 1′-(*N*,*N*-dimethylaminomethyl)biferrocene (II) (534 mg) in methanol (20 ml). The solution was refluxed for 30 min and cooled to room temperature, and then ether was added to the solution. The methiodide VIII (579 mg, 83%) obtained by filtration of the mixture was recrystallized from water to give a brown-yellow powder, m.p. 172—175°C (dec.).

According to the same procedure, dimethiodide XIV (2.1 g, 66%), m.p. 198—200°C (dec.), was prepared from the compound IV (2.0 g) and methyl iodide (4.0 g).

1′-(Cyanomethyl)biferrocene (IX)

Methiodide VIII (200 mg) was added to a solution of KCN (220 mg) in water (10 ml). The reaction mixture was heated at 80—100°C for 2 h under an N_2 atmosphere. The reaction product was extracted with benzene, and the organic extracts were washed with water, dried over Na_2SO_4 and evaporated. The residue was column-chromatographed over alumina to give 1′-(cyanomethyl)biferrocene (IX) (74 mg, 51%), from the band eluted with benzene. On recrystallization from hexane/ethyl acetate, reddish brown granules, m.p. 121—123°C, were obtained. (Found: C, 64.06; H, 4.69; N, 3.16; M^+, 409.0210. $C_{22}H_{19}NFe_2$ calcd.: C, 64.59; H, 4.68; N, 3.42%; mol. wt., 409.0214.) IR spectrum (cm^{-1}): 2915 [ν(CH)], 2245 [ν(C≡N)]. PMR spectrum (δ): 3.07 (2 H, s, $>CH_2$), 3.99 (5 H, s, D ring-H), 4.02 (4 H, m, B ring-H), 4.24 and 4.39 ppm (each 4 H, AA′XX′ systems, A and C ring-H). Mass spectrum (*m*/*z*): 409 (100, M^+), 344

(12, $[M - C_5H_5]^+$), 305 (12, $[FeC_5H_4C_5H_4FeC_5H_5]^+$), 304 (9.0, $[FeC_5H_4C_5H_4FeC_5H_4]^+$), 266 (46, $[FeC_5H_4C_5H_4FeCN]^+$), 262 (39, $[C_5H_4C_5H_4FeC_6H_6]^+$).

1′-(Methoxycarbonylmethyl)biferrocene (X)

A solution of 1′-(cyanomethyl)biferrocene (IX) (103 mg) in 20% aq. KOH (10 ml) and ethanol (10 ml) was refluxed for 5 h. The reaction mixture was poured into 200 ml of water, and the water solution was washed with ether. A trace of the recovered nitrile (IX) was found from the ether extract. The water layer was made acidic with phosphoric acid, and extracted with ether. After the extracts had been washed once with water an ether solution of CH_2N_2 was added to the extracts. The solution was dried over Na_2SO_4 and evaporated, and the residue was purified by column chromatography over alumina. The band eluted with benzene/ethyl acetate (10/1) yielded 1′-(methoxycarbonylmethyl)-biferrocene (X) (36 mg, 33%), which was recrystallized from hexane to give yellow flakes, m.p. 130—132°C. (Found: C, 62.63; H, 5.09; M^+, 442.0288. $C_{23}H_{22}O_2Fe_2$ calcd.: C, 62.48; H, 5.01%; mol. wt., 442.0316). IR spectrum (cm^{-1}): 1725 [ν(C=O)]. PMR spectrum (δ): 3.34 (2 H, s, $\geq CH_2$), 3.73 (3 H, s, $-CH_3$), 3.94 (4 H, s, B ring-H) 3.99 (5 H, s, D ring-H), 4.16—4.43 ppm (8 H, m, A and C ring-H). Mass spectrum (m/z): 442 (100, M^+), 383 (6.0, $[M - CO_2CH_3]^+$), 377 (7.0, $[M - C_5H_5]^+$), 319 (14, $[M - C_5H_5 - CO_2CH_2]^+$), 317 (12, $[FeC_5H_4C_5H_4FeC_6H_5]^+$).

1′-(2-Aminomethyl)biferrocene (XI)

To a stirred suspension of $LiAlH_4$ (57 mg) in ether (3 ml) a solution of 1′-(cyanomethyl)biferrocene (IX) (84 mg) in ether (5 ml) was added dropwise. After refluxing for 1 h, wet ether was added to the reaction mixture. The organic product was extracted with ether/benzene, and the extracts were dried over Na_2SO_4 and evaporated. Recrystallization of the residual solid (83 mg, 93%) gave yellowish brown granules, m.p. 77—80°C, of 1′-(2-aminomethyl)biferrocene (XI). (Found: M^+, 413.0526. $C_{22}H_{23}NFe_2$ calcd.: mol. wt., 413.0527.) IR spectrum (cm^{-1}): 3420 and 3362 [ν(NH)]. PMR spectrum (δ): 1.35 (2 H, bs, $-NH_2$), 2.23 and 2.67 (each 2 H, an A_2B_2 system, $\geq CH_2$), 3.90 and 3.98 (each 2 H, an AA′XX′ system, B ring-H), 3.96 (5 H, s, D ring-H), 4.15, 4.26 and 4.32 ppm (4 H, 2 H, and 2 H, respectively, m, A and C ring-H). Mass spectrum (m/z): 413 (100, M^+), 383 (30, $[M - CH_2NH_2]^+$), 305 (50, $[FeC_5H_4C_5H_4FeC_5H_5]^+$), 304 (18, $[FeC_5H_4C_5H_4FeC_5H_4]^+$).

1′-(Hydroxymethyl)biferrocene (XII)

A mixture of methiodide VIII (367 mg) and 10% aq. NaOH (10 ml) was heated at 90—100°C for 2 h. The reaction product was neutralized with aq. HCl, and then extracted with benzene. The extracts were washed with water, dried over Na_2SO_4, and evaporated. The residue was column-chromatographed over alumina with ethyl acetate to yield 1′-(hydroxymethyl)biferrocene (XII) (110 mg, 42%), which was recrystallized from benzene/hexane to give orange-yellow prisms, m.p. 126—127°C. (Found: M^+, 400.0198. $C_{21}H_{20}OFe_2$ calcd.: mol. wt., 400.0210.) IR spectrum (cm^{-1}): 3350 and 3390 [ν(OH)]. PMR spectrum (δ): 3.97 (5 H, s, D ring-H), 3.96 and 4.02 (each 2 H, m, B ring-H), 3.99 (2 H, s, $\geq CH_2$), 4.11 (1 H, bs, -OH), 4.18 and 4.35 ppm (each 4 H, AA′XX′ systems, A and C ring-H). Mass spectrum (*m/z*): 400 (73, M^+), 304 (100, $[FeC_5H_4C_5H_4FeC_5H_4]^+$), 262 (56, $[C_5H_4C_5H_4FeC_6H_6]^+$).

Oxidation of 1′-(N,N-dimethylaminomethyl)biferrocene (II) and 1′-(hydroxymethyl)biferrocene (XII)

1′-(*N,N*-Dimethylaminomethyl)biferrocene (II) (40 mg) and activated MnO_2 (500 mg) in benzene (5 ml) were refluxed for 24 h. MnO_2 was filtered off, and the filtrate was evaporated. The residue was column-chromatographed over silica gel. The band eluted with benzene/ethyl acetate (50/1) yielded 1′-formylbiferrocene (XIII) (11 mg, 29%), m.p. 170—172°C (lit. [8], m.p. 170—171°C).

Oxidation of 1′-(hydroxymethyl)biferrocene (XII) (24 mg) with activated MnO_2 (300 mg) in benzene (5 ml) by refluxing for 2 h gave also 1′-formylbiferrocene (XIII) (16 mg, 67%).

1′,1‴-Bis(cyanomethyl)biferrocene (XV)

1′,1‴-Bis(*N,N*-dimethylaminomethyl)biferrocene dimethiodide (XIV) (200 mg) was added to aq. KCN (600 mg) in water (10 ml) under an N_2 atmosphere. The mixture was heated at 80—100°C for 2.5 h, and then was extracted with benzene. The extracts were washed with water, dried over Na_2SO_4 and evaporated. The residue was column-chromatographed over silica gel with benzene to yield 1′,1‴-bis(cyanomethyl)biferrocene (XV) (48 mg, 41%), which was recrystallized from hexane/ethyl acetate to give yellowish brown needles, m.p. 152—154°C. (Found: M^+, 448.0318. $C_{24}H_{20}N_2Fe_2$ calcd.: mol. wt., 448.0323.) IR spectrum (cm^{-1}): 2930 [ν(CH)], 2260 [ν(C≡N)]. PMR spectrum (δ): 3.30 (4 H, s, $\gtrless CH_2$), 4.01 (8 H, m, B and D ring-H), 4.28 and 4.44 ppm (each 4 H, AA′XX′ systems, A and C ring-H). Mass spectrum (*m/z*): 448 (99, M^+), 344 (59, $[M - C_5H_4CH_2CN]^+$), 266 (100, $[FeC_5H_4C_5H_4FeCN]^+$).

1′,1‴-Bis(hydroxymethyl)biferrocene (XVI)

A mixture of 1′,1‴-bis(*N,N*-dimethylaminomethyl)biferrocene dimethiodide (XIV) (100 mg), 5% aq. KOH (25 ml) and benzene (20 ml) was heated at 90—100°C for 4 h. The organic layer was phase-separated, washed with water, dried over Na_2SO_4 and evaporated. The residue was column-chromatographed over alumina to separate into two bands eluted with ethyl acetate/ethanol (10/1). The second yellow band yielded 1′,1‴-bis(hydroxymethyl)biferrocene (XVI) (10 mg, 18%), which was recrystallized from benzene to give orange-yellow needles, m.p. 157.5—159°C. (Found: M^+, 430.0310. $C_{22}H_{22}O_2Fe_2$ calcd.: mol. wt., 430.0316.) IR spectrum (cm^{-1}): 3300 [ν(OH)]. PMR spectrum (δ): 1.25 (2 H, t, -OH), 4.03 (8 H, m, B and D ring-H), 4.08 (4 H, d, $\gtrless CH_2$), 4.23 and 4.37 ppm (8 H, AA′XX′ systems, A and C ring-H). Mass spectrum (*m/z*): 430 (52, M^+), 304 (100, $[FeC_5H_4C_5H_4FeC_5H_4]^+$), 256 (30, $[FeC_5H_4C_5H_4FeO]^+$).

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