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Synthesis of 'three-petal' carbocyclic systems based on *s-cis*-diferrocenyltrienes

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Abstract

Acid-catalyzed intramolecular, homoannular alkylation of one of the ferrocenyl substituents in spirocyclodimers derived from 1,3-bis(ferrocenylmethylidene)-2-methylidene-cyclohexane, -cycloheptane, and 3,5-bis(ferrocenylmethylidene)-4-methylidene-*N*-methylpiperidine results in a fused system with a 'three-petal' moiety in the center. The structure of 1-ferrocenyl-3,11-bis(ferrocenylmethylidene)-2,3,4,5,6,6b,10,10a,11,12,13,14-dodecahydro-1*H*-benzo[*d*](ferroceno[*a*])phenanthrene was established by X-ray diffraction analysis. © 2002 Published by Elsevier Science B.V.

Keywords: *s-cis*-Diferrocenyltrienes; Homoannular alkylation; Spirocyclodimers; Fragmentation; X-ray diffraction analysis; Ferrocene

1. Introduction

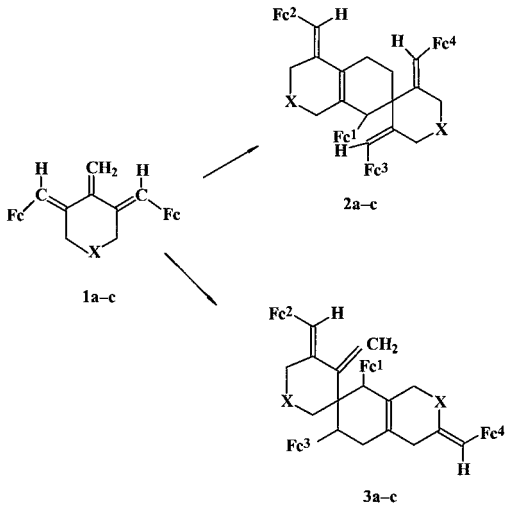
Previously, we have reported on the synthesis and some chemical properties of exocyclic cross-conjugated diferrocenyltrienes **1a–c** [1–4] (Scheme 1). It was shown that thermally induced and cationic cyclodimerizations of these trienes result in spirocyclodimers **2a–c** and **3a–c**, respectively.

Their structures were established based on the ^{1}H- and ^{13}C-NMR spectra. However, we failed to prepare crystals suitable for X-ray diffraction analysis from either of the cyclodimers.

In the present work, we continued our investigations into the chemical behavior of the spiranes **2a–c** and **3a–c**. It is known that cycloaddition of 1,3-diferrocenylallylic [5] and 1,3-diarylallylic [6] cations to 1,3-diferrocenylbuta-1,3-dienes is often accompanied by homoannular alkylation of one of the ferrocenyl substituents, resulting in fused carbocyclic products of type **4** (Scheme 2).

These reactions occur with high regio- and stereoselectivity and result in the preferential formation of one diastereomer of compound **4**.

In our opinion, the ferrocenyl (Fc^{1}) and methylidene ($Fc^{3}CH$=, CH_2=) fragments of the spirocyclodimers **2a–**



Hereinafter, X = CH_2 (a), $(CH_2)_2$ (b), and NMe (c)
Fc = $C_5H_5FeC_5H_4$

Scheme 1.

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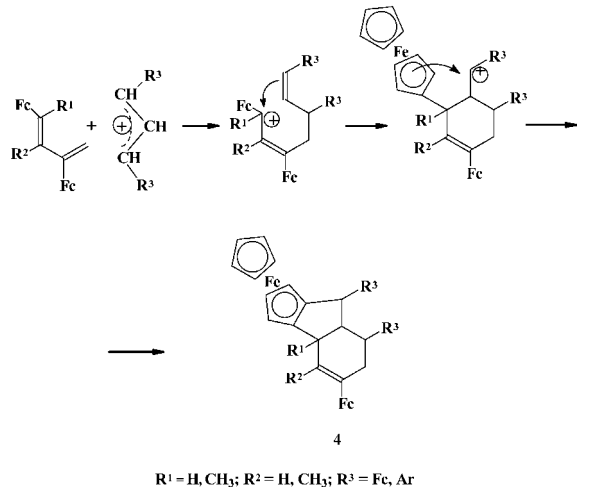

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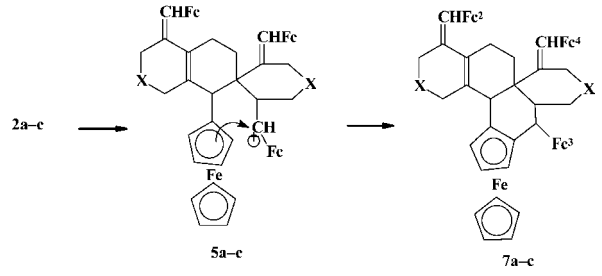
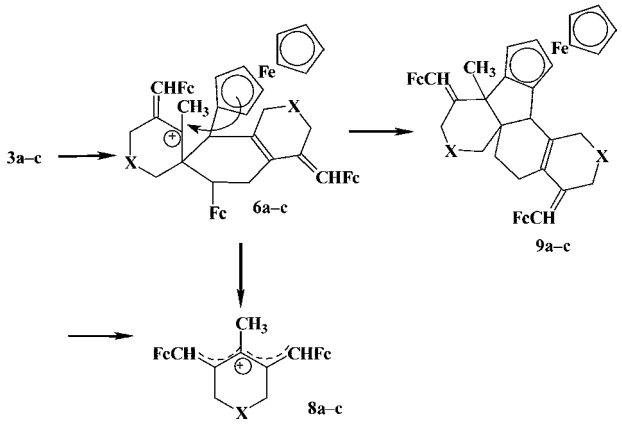
$R^1 = H, CH_3$; $R^2 = H, CH_3$; $R^3 = Fc, Ar$

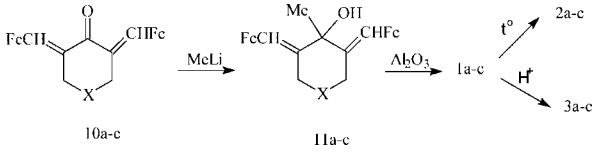
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

c and **3a**–**c** are in spatial proximity. Protonation of these methylidene groups may result in stable ferrocenylcarbenium ions (**5a**–**c**) and allylic cations (**6a**–**c**) [7,8]. The former can undergo homoannular alkylation of the ferrocenyl (Fc^1) fragment, eventually leading to new fused cyclic compounds with an interesting 'three-petal' ring system with one central quaternary carbon atom, presumably with the structures **7a**–**c** (Scheme 3).

Possible transformations of the cations **6a**–**c** appear to be more ambiguous. One can anticipate their fragmentation as well as intramolecular alkylation, resulting in methyl(diferrocenyl)dienyl cations (**8a**–**c**) and polycyclic products (**9a**–**c**), respectively (Scheme 4).

In order to check whether the above suggestion is correct, we examined the pathways of transformations of spirocyclodimers **2a**–**c** and **3a**–**c** induced by acetic acid and trifluoroacetic acid and tetrafluoroboric acid etherate.

2. Results and discussion

The initial cyclodimers were prepared by dehydration of the corresponding tertiary alcohols [1–4] (Scheme 5).

We demonstrated that acetic acid (a weak acid) did not affect compounds **2a**–**c** and **3a**–**c** even upon prolonged reflux. On the other hand, treatment of the dimers **2a**–**c** with CF_3COOH or HBF_4 etherate resulted in the intramolecular alkylation products **7a**–**c** in 35–50% yields.

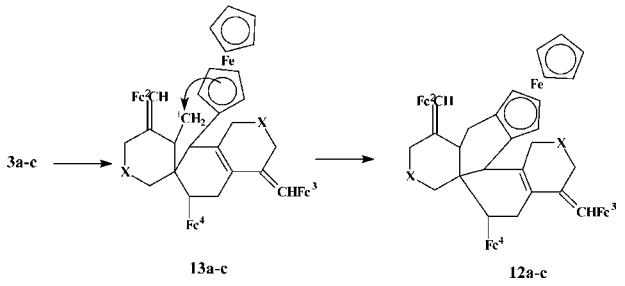
The structures of compounds **7a**–**c** were established on the basis of the following data. Their ^{1}H-NMR spectra contain (i) four singlets of protons of four ferrocene C_5H_5 groups and multiplets of 15 protons of four substituted ferrocene cyclopentadiene rings; (ii) a one-proton singlet of the Fc^1CH group; (iii) a one-proton doublet of the Fc^3CH fragment; (iv) a multiplet of a methine proton of the $CHCH_2$ group; (v) two singlets of the olefinic protons (Fc^2CH=, Fc^4CH=); and (vi) a definite number of multiplets of the methylene protons in accordance with the particular structure, i.e. eight, ten, and six for compounds **7a**, **7b**, and **7c**, respectively. The spin–spin coupling constants of the aliphatic protons correspond to the proposed structures.

This was also confirmed by data from ^{13}C-NMR spectra. Thus, the presence of five signals for ferrocene carbon atoms bearing no protons, together with signals for four unsubstituted C_5H_5 rings, points unambiguously to one 1,2-disubstituted ferrocene group. The presence of a signal for the C(spiro) atom, three signals for the methine groups, and two signals for the olefinic carbon atoms corroborate the structures of compounds **7a**–**c**. The number of signals for the quaternary carbon atoms and carbon atoms of the CH_2 and CH_3 groups in compounds **7a**–**c** and the respective chemical shifts correspond completely to their structures.

The dimers **3a**–**c**, unlike spirocyclodimers **2a**–**c**, react in a different manner with CF_3COOH and HBF_4 etherate.

The reaction with CF_3COOH proceeds regio- and stereospecifically, giving rise to compounds **12a**–**c** (^{1}H- and ^{13}C-NMR spectroscopic evidence) rather than to the expected *C*-methyl derivatives **9a**–**c**.

The main characteristics of their ^{1}H-NMR spectra are as follows: no *C*-CH_3 singlet was present, while the spectra of each contained, inter alia, a singlet and two triplets of the methine protons, two singlets of the olefinic protons, four singlets of the C_5H_5 groups and a multiplet for 15 signals of substituted ferrocene Cp rings, and two doublets of the aliphatic methylene groups. The following signals were present in the ^{13}C-NMR spectra: five signals for the C(Fc)$_{ipso}$, four signals for the carbon atoms of the ferrocene C_5H_5 groups and 15 signals for the carbon atoms of substituted Cp rings, a signal for one C(spiro) atom and four signals for C= atoms bearing no protons, two signals for the FcCH= groups, and three signals for the methine carbon atoms. The number of signals for the methylene groups was eight (**12a**), ten (**12b**), and six (**12c**). The spectrum of **12c** also contained two signals for the *N*-CH_3 groups. These spectroscopic data altogether agree with the structures of compounds **12a**–**c** (Scheme 6).



Scheme 6.

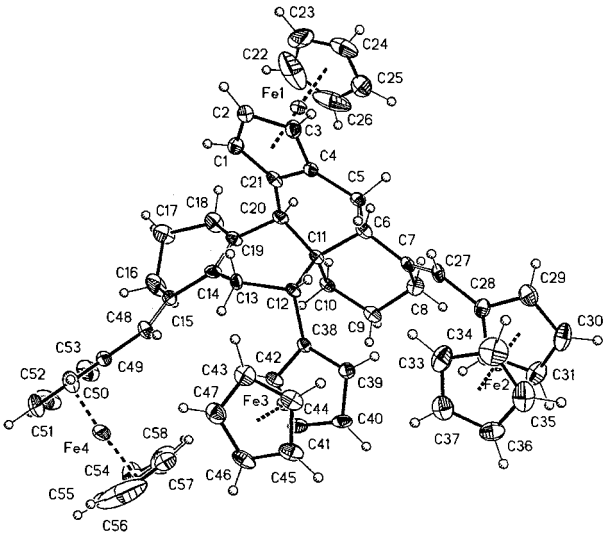


Fig. 1. Crystal structure of **12a**.

Table 1
Selected bond lengths r (Å) and bond angles ω (°) for **12a**

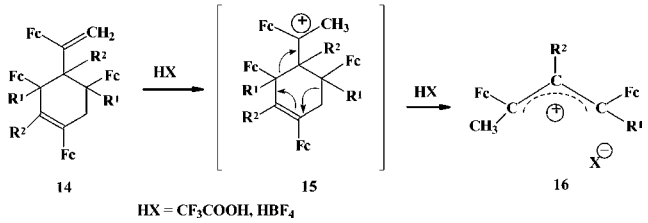
Bond lengths			
C(4)–C(21)	1.434(13)	C(14)–C(13)	1.517(11)
C(4)–C(5)	1.502(11)	C(13)–C(12)	1.562(11)
C(5)–C(6)	1.523(12)	C(12)–C(11)	1.585(10)
C(6)–C(11)	1.575(11)	C(11)–C(10)	1.558(11)
C(11)–C(20)	1.564(11)	C(10)–C(9)	1.538(13)
C(20)–C(21)	1.498(13)	C(8)–C(9)	1.526(13)
C(20)–C(19)	1.506(12)	C(8)–C(7)	1.512(12)
C(19)–C(14)	1.326(12)	C(6)–C(7)	1.526(12)
Bond angles			
C(10)–C(11)–C(6)	108.8(7)	C(21)–C(20)–C(11)	111.4(7)
C(10)–C(11)–C(20)	106.0(6)	C(38)–C(12)–C(11)	115.1(7)
C(20)–C(11)–C(6)	106.4(6)	C(19)–C(20)–C(11)	110.4(6)
C(10)–C(11)–C(12)	113.8(6)	C(9)–C(10)–C(11)	116.9(7)
C(6)–C(11)–C(12)	112.6(6)	C(5)–C(6)–C(11)	113.3(7)
C(20)–C(11)–C(12)	108.7(6)	C(7)–C(6)–C(11)	112.1(7)
C(13)–C(12)–C(11)	113.2(6)	C(21)–C(4)–C(5)	122.1(8)
C(5)–C(6)–C(11)	113.3(7)	C(4)–C(21)–C(20)	123.1(8)

The spatial structure of single crystals of 1-ferrocenyl - 3,11 - bis(ferrocenylmethylidene) - 2,3,4,5,6,6b,10,10a,11,12,13,14 - dodecahydro - 1*H* - benzo[*d*](ferroceno-[*a*])phenanthrene (compound **12a**) prepared by crystallization from chloroform was determined by X-ray diffraction analysis (Fig. 1). The principal geometrical parameters of this molecule with a 'three-petal' system of fused six-membered rings and a quaternary carbon atom C(11) are listed in Table 1. The bond lengths C(11)–C(6) (1.575 Å), C(11)–C(10) (1.558 Å), C(11)–C(12) (1.585 Å), and C(11)–C(20) (1.564 Å) are somewhat larger than the standard values [9]. On the other hand, the C–C and C–N bond lengths in the carbo- and hetero-cycles, as well as the Fe–C and C–C bond lengths, and the geometrical parameters in the ferrocene fragments are close to the standard values [9].

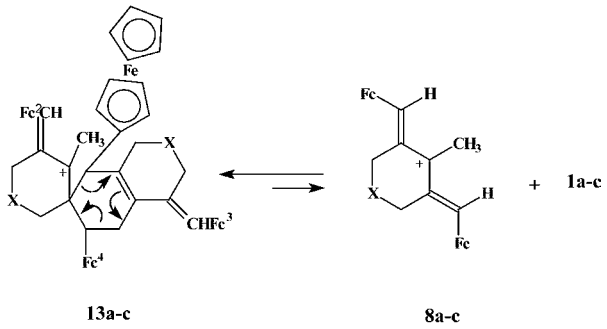
Undoubtedly, the formation of compounds **12a**–**c** is due to the intramolecular, homoannular alkylation of the ferrocenyl substituent Fc^1 by the primary carbocationic centers resulting from the protonation of the intermediates **13a**–**c** (Scheme 6). This type of anti-Markownikoff protonation of a conjugated methylidene group in cationic cyclodimerization products of conjugated dienes and trienes is rather unusual and is observed for the first time.

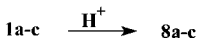
Previously, we have studied the protonation of ferrocenyl-substituted monocyclic diterpenes **14** representing cationic cyclodimerization products of diferrocenyl-1,3-dienes (Scheme 7) [10–14]. This involved the initial formation of ferrocenyl(methyl)carbocations **15**, which was followed by cleavage of the ferrocenylditerpene molecule, resulting in two molecules of more stable salts of ferrocenylallyl cations **16** [15,16].

No intramolecular alkylation products of the ferrocenyl substituents in positions 3 and 5 of the cyclohexene ring were observed, apparently due to the fast fragmentation of the dimeric cations **15**.

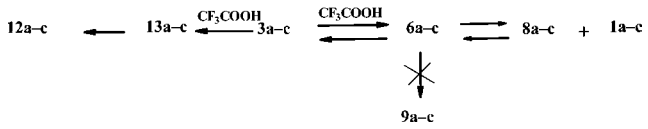


Scheme 7.





Scheme 8.



Scheme 9.

The spirocyclodimers **3a**–**c** comprise methylidene groups, which makes them similar to the diferrocenyl-1,3-diene monocyclic dimers **14**. One might expect that their protonation would result in the preferential formation of ferrocenyl(methyl)allyl cations **6a**–**c**. The fact that the dimers **3a**–**c** gave no fragmentation products upon treatment with CF_3COOH differentiates them from the cyclodimers **14**. This may be due to slower cleavage of the spirocarbocations **6a**–**c** into the cationic (**8a**–**c**) and triene (**1a**–**c**) components (Scheme 8).

This retardation of the cleavage process may be accounted for by the nearly identical stabilities of the allylic (**6a**–**c**) and dienyl (**8a**–**c**) cations [4,8,9].

As a consequence, conditions are provided for the minor, unstable primary carbocations **13a**–**c** to alkylate the spatially proximal ferrocenyl substituent Fc^1, resulting in compounds **12a**–**c**, thereby shifting the reaction equilibrium (Scheme 9).

The steric factors of the conformational character seem to favor the formation of the alkylation products **12a**–**c** with an additional six-membered ring and prevent the formation of a five-membered fragment (compounds **9a**–**c**).

Complete fragmentation of compounds **12a**–**c** can apparently be achieved, provided the ferrocenyl(methyl)dienyl cations **8a**–**c** are taken away from the reaction mixtures as insoluble salts, which would shift the equilibrium toward monomeric products. In fact, this could be effected by employing HBF_4 etherate as the protonating agent. One molecule of each of the dimers **12a**–**c** produced two molecules of tetrafluoroborates of the cations **8a**–**c**, insoluble in dry ether in nearly quantitative yields. Their structures were confirmed by data from elemental analysis and ^{1}H-NMR spectra. The latter are in full agreement with those of the corresponding salts prepared earlier [1–4] from 2,6-bis(ferrocenylmethylidene)-1-methylcyclohexanol (**11a**), 2,7-bis(ferrocenylmethylidene)-1-methylcycloheptanol (**11b**), and 3,5-bis(ferrocenylmethylidene)-1,4-dimethylpiperidin-4-ol (**11c**).

The high diastereoselectivity of the formation of compounds **7a**–**c** and **12a**–**c** in the reaction studied is especially worth noting. Despite the presence of several chiral centers and chiral 1,2-Fc fragments, these compounds were isolated as single diastereomers. This may be probably accounted for by the configurational features of the starting spirocyclodimers **2a**–**c** and **3a**–**c**, where no steric hindrances exist for them to adopt conformations most favorable for intramolecular cyclization of the cations **5a**–**c** and **13a**–**c**.

3. Experimental

^{1}H- and ^{13}C-NMR spectra were recorded in a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ with Me_4Si as the internal standard. ^{1}H-NMR spectra of tetrafluoroborates **8a**–**c** were obtained for solutions in CD_2Cl_2. Column chromatography was carried out on Al_2O_3 (Brockmann activity III). TLC was performed on plates with a fixed silica gel layer. All reactions were carried out in a flow of dry nitrogen.

The following reagents were from Aldrich: ferrocenecarbaldehyde, 99%; cyclohexanone, 99%; 1-methyl-4-piperidone, 97%; trifluoroacetic acid, 99%; methyllithium, 1.4 M solution in Et_2O; anhydrous pyridine, 99.8%; phosphorus oxychloride, 99.999%. Tetrafluoroboric acid etherate, 50–52%, was purchased from Alfa AESAR.

Diethyl ether was dried with $CaCl_2$ and then distilled from sodium diphenyl ketyl. Dichloromethane was washed with concentrated sulfuric acid, water, 5% aqueous NaOH, and water again, dried with calcined K_2CO_3, and distilled over 4 Å molecular sieves.

The unit cell parameters and the X-ray diffraction intensities were recorded in a Siemens P4/PC diffractometer. The crystallographic data, parameters of the X-ray diffraction experiment, and refinements are listed

in Table 2. The structure of compound **12a** was solved by the direct method and refined by the least-squares method in a full-matrix anisotropic approximation for the non-hydrogen atoms.

3.1. 2,6-Bis(ferrocenylmethylidene)cyclohexanone **10a** and 3,5-bis(ferrocenylmethylidene)-1-methyl-4-piperidone **10c**

These were prepared by a standard procedure by condensation of ferrocenecarbaldehyde with cyclohexanone [1] and 1-methyl-4-piperidone [4], respectively, in aqueous-ethanolic alkali. The isolation and purification of the chalcones was carried out by column chromatography in 3:1 hexane–chloroform solvent mixture.

3.2. 2,7-Bis(ferrocenylmethylidene)cycloheptanone **10b**

Chalcone **10b** was prepared by refluxing ferrocenecarbaldehyde with cycloheptanone in toluene in the presence of Bu^{t}OK [2,3].

3.3. Alcohols **11a–c**

These were synthesized from the corresponding chalcones **10a–c** and methyllithium [1–4]. Compound **11a**, yield 72%, m.p. 156–157 °C [1]; compound **11b**, yield 73%, m.p. 167–168 °C [2]; compound **11c**, yield 71%, m.p. 184–185 °C [4].

Table 2
Crystal data and structure refinement parameters for **12a**

Empirical formula	$C_{58}H_{56}Fe_4$
Formula weight	976.43
Temperature (K)	293
Wavelength (Å) (Mo–K_α radiation)	0.71073
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions	
a (Å)	7.1480(1)
b (Å)	28.028(3)
c (Å)	22.445(2)
α (°)	90.0
β (°)	98.48
γ (°)	90.0
V (Å^3)	4447.6(9)
Z	4
ρ_{calc} (g cm^{-3})	1.458
Absorption coefficient (mm^{-1})	1.319
F(000)	2032
Monochromator	Graphite
θ Scanning range (°)	1.50–25.00
Total number of reflections	7901
Number of independent reflections	7283
R_{int}	0.0669
Number of refinable parameters	570
Goodness-of-fit on F^2	1.022 (full-matrix least-squares refinement on F^2)
Residual electron density (e Å^{-3}), ρ_{min}/ρ_{max}	−0.467/0.446

3.4. Ferrocenyltrienes **1a–c**

These were obtained by dehydration of the alcohols **11a–c**, respectively, using Al_2O_3 (Brockmann activity II) as described earlier [2]. The trienes were purified by chromatography on alumina in hexane.

Triene **1a**, yield 35%, m.p. 126–127 °C [2]; triene **1b**, yield 61%, m.p. 148–149 °C [2]; triene **1c**, yield 60%, m.p. 201–202 °C [4].

3.5. Spirocyclodimers **2a–c**

These were prepared by boiling the benzene solutions of the trienes (**1a–c**) for 2–7 h. Compound **2a**, yield 74%, m.p. 237–239 °C [2]; compound **2b**, yield 68%, m.p. 258–260 °C [2]; compound **2c**, yield 47%, m.p. ca. 287 °C (dec.) [4].

3.6. Dehydration of the alcohols **11a–c** with $POCl_3$ in pyridine

$POCl_3$ (1 ml) was added dropwise at 5–10 °C to a stirred solution of the alcohols **11a–c** (3 mmol) in dry pyridine (100 ml). Stirring was continued for 4 h at ~20 °C and then water (200 ml) was added. The reaction products were extracted with benzene (3 × 50 ml) and the combined extracts were repeatedly washed with water. The solvent was evaporated in vacuo and the residue was chromatographed on Al_2O_3 (hexane–benzene, 3:1) to obtain compounds **3a** (42%), m.p. 262–263 °C [2], **3b** (28%), m.p. 254–256 °C [3], and **3c** (63%), m.p. 270 °C (dec.) [4].

3.7. The action of trifluoroacetic acid on cyclodimers **2a–c**

Compounds **1a–c** (1 mmol) were dissolved in benzene (50 ml), trifluoroacetic acid (20 ml) was added, and mixtures were refluxed for 48 h. Following addition of water (50 ml), the organic layers were separated, washed repeatedly with water, and concentrated in vacuo. Compounds **7a–c** were isolated from the residues by preparative TLC (hexane–benzene, 2:1).

Compound **7a**, yield 0.31 g (63%), $R_f = 0.54$; compound **7b**; yield 0.34 g (66%), $R_f = 0.58$; compound **7c**, yield 0.30 g (61%), $R_f = 0.44$.

11-Ferrocenyl-4,7-bis(ferrocenylmethylene)-2,3,4,5,6,7,8,9,10,10a,11,14b-dodecahydro-1*H*-benzo[*d*](ferroceno[*a*])phenanthrene **7a**: m.p. 272–273 °C, ^{1}H-NMR:

δ 1.64 (2H, m, CH_2), 1.84–1.99 (4H, m, $2CH_2$), 2.10–2.31 (4H, m, $2CH_2$), 2.42 (2H, m, CH_2), 2.58–2.74 (4H, m, $2CH_2$), 3.34 (1H, m, CH, $J = 6.2$, 7.0 Hz), 4.01 (1H, s, CH), 4.14 (1H, d, CH, $J = 6.2$ Hz), 4.03 (5H, s, C_5H_5); 4.10 (5H, s, C_5H_5), 4.18 (5H, s, C_5H_5), 4.22 (5H, s, C_5H_5), 3.89 (2H, m), 4.06 (1H, m); 4.15 (2H, m), 4.20 (4H, m), 4.25 (3H, m), 4.31 (1H, m), 4.36 (2H, m) ($3C_5H_4$, $1C_5H_3$); 6.02 (1H, s, CH=); 6.24 (1H, m, CH=). ^{13}C-NMR: δ 20.58, 21.63, 22.84, 23.38, 25.04, 27.94, 29.93, 34.41 ($8CH_2$); 43.18 (CH); 52.49 (C_{spiro}); 61.24, 66.31 (2 Fc–CH); 65.61, 65.98, 66.19, 66.87, 67.12, 68.52, 68.91, 69.09, 69.18, 70.21, 70.25, 70.63, 70.90, 71.81, 72.13 ($3C_5H_4$, $1C_5H_3$); 68.12, 68.35, 69.00, 70.11 ($4C_5H_5$); 82.71, 83.54, 84.61, 84.99, 88.75 ($5C_{ipso}$Fc); 121.14, 123.28 (2CH=); 126.19, 129.82, 134.17, 138.12 (4C). Anal. Calc. for $C_{58}H_{56}Fe_4$,: C, 71.34; H, 5.78; Fe, 22.88. Found: C, 71.18; H, 5.96; Fe, 23.06%.

13-Ferrocenyl-5,8-bis(ferrocenylmethylene)-2,3,4,5,6,7,8,9,10,11,12,12a,13,16b-tetradecahydro-1*H*-dicyclohepta[2,3-*h*, 2,3-*h*]-ferroceno[*a*])naphthalene **7b**: m.p. 287–288 °C, ^{1}H-NMR: δ 1.15 (4H, m, CH_2), 1.45 (4H, m, CH_2), 1.68 (2H, m, CH_2), 1.74 (2H, m, CH_2), 1.86 (2H, m, CH_2), 2.14 (2H, m, CH_2), 2.36(2H, m, CH_2), 2.65 (2H,m, CH_2), 3.08 (1H, m, CH, $J = 5.8$, 6.4 Hz), 3.98 (1H, s, CH), 4.14 (1H, d, CH, $J = 5.8$ Hz), 4.06 (5H, s, C_5H_5), 4.12 (5H, s, C_5H_5), 4.19 (5H, s, C_5H_5), 4.24 (5H, s, C_5H_5); 3.85 (2H, m), 4.08 (2H, m), 4.13 (1H, m), 4.20 (2H, m), 4.28 (2H, m), 4.32 (3H, m), 4.34 (1H, m), 4.39 (2H, m) ($3C_5H_4$, $1C_5H_3$); 6.11 (1H, s, CH=), 6.32 (1H, s, CH=). ^{13}C-NMR: δ 21.09, 21.78, 32.31, 32.63, 42.79, 44.95 ($6CH_2$); 47.81 (CH); 54.23 (C_{spiro}); 62.93, 66.48 (2Fc–CH); 67.12, 67.28, 67.54, 67.84, 67.98, 68.55, 68.78, 68.99, 69.06, 69.14, 69.37, 69.33, 69.92, 70.17, 71.36 ($3C_5H_4$, $1C_5H_3$); 68.51, 68.63, 69.08, 69.21 ($4C_5H_5$); 81.12, 81.28, 82.34, 82.63, 88.91 ($5C_{ipso}$Fc); 121.97, 123.19 (2CH=); 126.93, 129.01, 130.84, 138.93 (4C). Anal. Calc. for $C_{60}H_{60}Fe_4$: C, 71.74; H, 6.02; Fe, 22.24. Found: C, 71.92; H, 5.87; Fe, 22.39%.

11-Ferrocenyl-4,7-bis(ferrocenylmethylene)-2,9-dimethyl-2,3,4,5,6,7,8,9,10,10a,11,14b-dodecahydro-1*H*-ferroceno[*g*]-(isoquinolino[8,9-*i*])isoquinoline **7c**: m.p. 347–351 °C, ^{1}H-NMR: δ 1.92 (3H, s, CH_3), 2.28 (3H, s, CH_3), 2.12 (2H, m, CH_2), 2.31 (2H, m, CH_2), 2.83 (2H, d, CH_2, $J = 13.8$ Hz), 3.09 (2H, d, CH_2, $J = 15.0$ Hz), 3.27 (2H, d, CH_2, $J = 13.8$ Hz), 3.42 (2H, d, CH_2, $J = 15.0$ Hz), 3.58 (1H, m, CH), 3.74 (1H, d, CH, $J = 6.1$ Hz), 3.95 (1H, s, CH), 4.11 (5H, s, C_5H_5), 4.14 (5H, s, C_5H_5), 4.23 (5H, s, C_5H_5), 4.27 (5H, s, C_5H_5); 4.08 (2H, m), 4.16 (2H, m), 4.18 (2H, m), 4.21 (3H, m), 4.34 (2H, m), 4.32 (1H, m), 4.39 (1H, m), 4.45 (2H, m) ($3C_5H_4$, $1C_5H_3$); 6.05 (1H, s, CH=), 6.29 (1H, s, CH=). ^{13}C-NMR: δ 21.09, 21.78, 32.31, 32.64, 42.79, 44.95 ($6CH_2$); 27.53, 34.01 ($2CH_3$); 47.81 (CH); 54.22 (C_{spiro}); 62.93, 65.43 (2 Fc–CH); 67.12, 67.23, 67.54, 67.84, 67.96, 68.02, 68.31, 68.42, 68.56, 68.73, 69.27, 69.31, 69.94, 70.18, 72.35 ($3C_5H_4$, $1C_5H_3$); 68.51, 68.63, 69.08, 69.19 ($4C_5H_5$); 81.12, 81.28, 81.36, 82.63, 87.91 ($5C_{ipso}$Fc); 121.97, 123.18 (2CH=); 126.93, 127.08, 130.84, 138.01 (4C). Anal. Calc. for $C_{58}H_{58}Fe_4N_2$: C, 69.21; H, 5.81; Fe, 22.20; N, 2.78. Found: C, 69.40; H, 5.67; Fe, 22.39; N, 2.63%.

3.8. The action of HBF_4 etherate on the cyclodimers **2a–c**

Tetrafluoroboric acid etherate (2 ml) was added dropwise, with stirring, to a solution of each of compounds **2a–c** (1 mmol) in dry CH_2Cl_2 (50 ml) and the mixtures were stirred for 5 h at ~20 °C. Then, water (50 ml) was added, the organic layers were separated, washed with 5% aqueous $NaHCO_3$ and water, and dried with $CaCl_2$. Following evaporation of the solvent in vacuo, the residues were subjected to TLC on SiO_2 (hexane–benzene, 2:1) to yield compounds **7a** (0.26 g, 62%), $R_{\_f} = 0.53$; **7b** (0.26 g, 60%), $R_f = 0.57$; and **7c** (0.30 g, 60%), $R_f = 0.44$.

3.9. The action of trifluoroacetic acid on the cyclodimers **3a–c**

Trifluoroacetic acid (10 ml) was added, with stirring, to a solution of each of compounds **3a–c** (1 mmol) in dry CH_2Cl_2 (100 ml) and mixtures were stirred for 72 h at ~20 °C. Then, they were washed with water and 5% aqueous $NaHCO_3$ and dried with $CaCl_2$. Following evaporation of the solvent in vacuo, the residues were subjected to TLC on SiO_2 (hexane–benzene, 2:1) to yield compounds **12a** (0.21 g, 42%), $R_f = 0.50$; **12b** (0.23 g, 45%), $R_f = 0.52$; and **12c** (0.18 g, 35%), $R_f = 0.42$.

1-Ferrocenyl-3,11-bis(ferrocenylmethylene)-2,3,4,5,6,6b,10,10a,11,12,13,14-dodecahydro-1*H*-benzo[*d*](ferroceno[*a*])phenanthrene **12a**: m.p. 259–261 °C, ^{1}H-NMR: δ 1.49 (2H, m, CH_2), 1.73–1.88 (4H, m, $2CH_2$), 2.06 (2H, m, CH_2), 2.25 (2H, m, CH_2), 2.52 (2H, m, CH_2), 2.78 (2H, d, CH_2, $J = 7.2$ Hz), 2.87 (2H, d, CH_2, $J = 6.7$ Hz), 3.98 (1H, t, CH, $J = 6.7$ Hz), 4.05 (1H, t, CH, $J = 7.2$ Hz), 4.12 (1H, s, CH), 4.06 (5H, s, C_5H_5); 4.09 (5H, s, C_5H_5), 4.10 (5H, s, C_5H_5), 4.12 (5H, s, C_5H_5), 3.95 (1H, m), 4.00 (1H, m); 4.13 (3H, m), 4.15 (4H, m), 4.18 (3H, m), 4.21 (2H, m), 4.33 (2H, m) ($3C_5H_4$, $1C_5H_3$); 5.45 (1H, s, CH=); 6.18 (1H, m, CH=). ^{13}C-NMR: δ 20.97, 22.65, 23.25, 28.12, 30.32, 31.57, 32.37, 41.51 ($8CH_2$); 45.13 (CH); 55.36 (C_{spiro}); 64.78, 65.06 (2Fc–CH); 65.64, 66.96, 67.05, 67.52, 67.85, 68.14, 68.33, 68.82, 68.91, 69.02, 69.28, 69.56, 69.69, 70.19, 72.39 ($3C_5H_4$, $1C_5H_3$); 68.28, 68.77, 69.07, 69.94 ($4C_5H_5$); 83.65, 84.40, 85.37, 87.57, 92.78 ($5C_{ipso}$Fc); 118.14, 118.20 (2CH=); 127.95, 135.30, 135.68, 139.31 (4C). Anal. Calc. for $C_{58}H_{56}Fe_4$: C, 71.34; H, 5.78; Fe, 22.88. Found: C, 71.45; H, 5.68; Fe, 23.03%.

1-Ferrocenyl-3,12-bis(ferrocenylmethylene)-2,3,4,5,6,7,7b,11,11a,12,13,14,15,16-tetradecahydro-1*H*-dicyclo-

hepta[2,3-*d*; 2,3-*h*](ferroceno[*a*])naphthalene **12b**: m.p. 307–308 °C, ^{1}H-NMR: δ 1.04 (4H, m, CH_2), 1.25 (2H, m, CH_2), 1.77 (2H, m, CH_2), 1.92 (2H, m, CH_2), 2.00 (4H, m, $2CH_2$), 2.29 (2H, m, CH_2), 2.65 (2H, d, CH_2, $J = 6.6$ Hz), 2.77 (2H, d, CH_2, $J = 7.2$ Hz), 4.01 (1H, t, CH, $J = 7.2$ Hz), 3.98 (1H, s, CH), 4.08 (1H, t, CH, $J = 6.6$ Hz), 4.11 (1H, s, CH), 4.12 (5H, s, C_5H_5), 4.15 (5H, s, C_5H_5), 4.17 (5H, s, C_5H_5), 4.20 (5H, s, C_5H_5); 4.05 (2H, m), 4.13 (1H, m), 4.15 (2H, m), 4.23 (2H, m), 4.27 (2H, m), 4.29 (2H, m), 4.36 (1H, m), 4.42 (1H, m), 4.46 (1H, m), 4.50 (1H, m) ($3C_5H_4$, $1C_5H_3$); 5.91 (1H, s, CH=), 6.25 (1H, s, CH=). ^{13}C-NMR: δ 19.95, 20.89, 25.91, 26.38, 26.77, 29.31, 29.66, 30.83, 34.29, 36.80 ($10CH_2$); 41.72 (CH); 55.32 (C_{spiro}); 64.91, 65.89 (2Fc–CH); 66.53, 67.08, 67.48, 67.59, 67.75, 68.33, 68.61, 68.65, 68.77, 68.83, 68.94, 69.40, 69.52, 69.74, 69.76 ($3C_5H_4$, $1C_5H_3$); 68.51, 68.90, 69.04, 69.10 ($4C_5H_5$); 82.78, 83.26, 85.38, 92.63, 93.10 ($5C_{ipso}$Fc); 121.12, 121.90 (2CH=); 127.21, 132.31, 137.47, 138.29 (4C). Anal. Calc. for $C_{60}H_{60}Fe_4$: C, 71.74; H, 6.02; Fe, 22.24. Found: C, 71.89; H, 6.21; Fe, 22.09%.

16 - Ferrocenyl - 4,10 - bis(ferrocenylmethylene) - 2,8-dimethyl-2,3,4,5,6,7,8,9,10,10a,11,14b-dodecahydro-1*H*-ferroceno[*g*](isoquinolino[7,8-*i*])isoquinoline **12c**: m.p. 347–351 °C, ^{1}H-NMR: δ 1.94 (3H, s, CH_3), 2.31 (3H, s, CH_3), 2.46 (2H, d, CH_2, $J = 6.3$), 2.56 (2H, d, CH_2, $J = 5.7$), 2.87 (2H, d, CH_2, $J = 14.4$ Hz), 3.19 (2H, d, CH_2, $J = 15.0$ Hz), 3.32 (2H, d, CH_2, $J = 14.4$ Hz), 3.48 (2H, d, CH_2, $J = 15.0$ Hz), 3.12 (1H, t, CH, $J = 6.3$), 3.92 (1H, t, CH, $J = 5.7$ Hz), 4.00 (1H, s, CH), 4.09 (5H, s, C_5H_5), 4.15 (5H, s, C_5H_5), 4.20 (5H, s, C_5H_5), 4.26 (5H, s, C_5H_5); 4.05 (2H, m), 4.12 (2H, m), 4.14 (2H, m), 4.17 (4H, m), 4.22 (2H, m), 4.26 (2H, m), 4.33 (1H, m) ($3C_5H_4$, $1C_5H_3$); 5.71 (1H, s, CH=), 6.28 (1H, s, CH=). ^{13}C-NMR: δ 22.27, 22.49, 24.53, 31.20, 32.04 2 ($6CH_2$); 28.01, 37.61 ($2CH_3$); 53.61 (CH); 55.61 (C_{spiro}); 65.54, 66.02 (2Fc–CH); 67.03, 67.10, 67.15, 67.43, 67.45, 67.60, 67.85, 68.10, 68.12, 68.56, 68.72, 68.88, 68.95, 69.50, 69.62 ($3C_5H_4$, $1C_5H_3$); 68.49, 68.61, 68.78, 69.06 ($4C_5H_5$); 79.02, 80.10, 82.18, 83.50, 92.09 ($5C_{ipso}$Fc); 122.01, 124.33 (2CH=); 127.35, 133.52, 134.23, 137.03 (4C). Anal. Calc. for $C_{58}H_{58}Fe_4N_2$: C, 69.21; H, 5.81; Fe, 22.20; N, 2.78. Found: C, 69.12; H, 5.73; Fe, 22.37; N, 2.96%.

*3.10. Fragmentation of the spirocyclodimers **3a–c***

Tetrafluoroboric acid etherate (3 ml) was added dropwise, with stirring, in an atmosphere of dry nitrogen, to a solution of each of compounds **3a–c** (1 mmol) in dry ether (100 ml) and the mixtures were stirred for 1 h at ~20 °C. Black precipitates were filtered off, washed with several portions of dry ether, and dried in vacuo.

Tetrafluoroborate **8a** (black powder, yield 0.51 g (88%)) decomposes at ~230 °C [1]. ^{1}H-NMR (CD_2Cl_2): δ 2.13 (3H, s, CH_3), 2.71 (2H, t, CH_2, $J = 6.2$ Hz), 3.49 (4H, m, CH_2, $J = 6.2$), 5.31 (5H, s, C_5H_5), 5.32 (5H, s, C_5H_5), 5.10 (4H, s, C_5H_4), 5.50 (4H, s, C_5H_4), 8.33 (2H, s, CH=). Anal. Calc. for $C_{29}H_{29}BF_4Fe_2$: C, 60.46; H, 5.07; F, 13.20; Fe, 19.39. Found: C, 60.31; H, 5.29; F, 13.32; Fe, 19.23%.

Tetrafluoroborate **8b** (black powder, yield 0.54 g (90%)) decomposes at ~320 °C [3]. ^{1}H-NMR (CD_2Cl_2): δ 2.18 (3H, s, CH_3), 1.93 (4H, m, CH_2), 2.89 (4H, m, CH_2), 4.65 (10H, s, C_5H_5), 5.26 (4H, m, C_5H_4), 5.72 (4H, m, C_5H_4), 8.25 (2H, s, CH=). Anal. Calc. for $C_{30}H_{31}BF_4Fe_2$: C, 61.06; H, 5.30; F, 12.88; Fe 18.93. Found: C, 60.89; H, 5.44; F, 13.04; Fe, 19.07%.

Bistetrafluoroborate **8c** (black powder, yield 0.52 g (89%)) decomposes at ~320 °C [4]. ^{1}H-NMR (CD_2Cl_2): δ 2.42 (3H, s, CH_3), 3.45 (3H, s, CH_3), 3.89 (4H, m, CH_2), 5.18 (10H, s, C_5H_5), 4.93 (2H, m, C_5H_4), 5.31 (2H, m, C_5H_4), 6.23 (2H, m, C_5H_4), 6.26 (2H, m, C_5H_4), 7.58 (2H, s, CH=). Anal. Calc. for $C_{29}H_{31}B_2F_8Fe_2N$: C, 51.30; H, 4.60; Fe, 16.45; N, 2.06. Found: C, 51.09; H, 4.75; Fe, 16.54; N, 2.12%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 169746 for compound **12a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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