3,5-Bis(ferrocenylmethylene)-1-methyl-4-methylenepiperidine. Synthesis and some chemical properties

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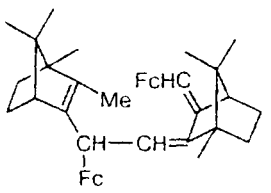
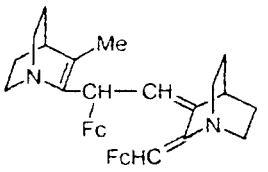
3,5-Bis(ferrocenylmethylene)-1-methyl-4-methylenepiperidine, a diferrocenyltriene with a fixed *s*-cisoid conformation of the exocyclic double bonds, was synthesized. On heating, this compound cyclodimerizes according to the [4+2]-cycloaddition scheme; it forms Diels—Alder adducts with azodicarboxylic and maleic acid *N*-phenylimides. The compound easily cyclodimerizes in the presence of acids by a proton cyclodimerization mechanism to give a spiro cyclodimer. The triene also adds a 3,5-bis(ferrocenylmethylene)-1,4-dimethyl-1-azonia-4-cyclohexyl salt to the terminal methylene group yielding linear and cyclic addition products.

Key words: piperidine, triene, cyclodimerization, dimerization, fragmentation, allylic cation, ferrocene.

Previously we discussed the influence of stereoelectronic factors on the chemical behavior of ferrocenyl-substituted 1,3-dienes with fixed *s-cis*-configuration of double bonds, namely, 3-ferrocenylmethylene-2-methylenecamphane[1] and 2-ferrocenylmethylene-3-methylenequinuclidine.[2] It was found that under conditions of cationic cycloaddition, both dienes form only linear dimerization products **1** and **2**, respectively, unlike all the *s-trans-/s-cis*-ferrocenylbutadienes studied to date.[3—5]



1

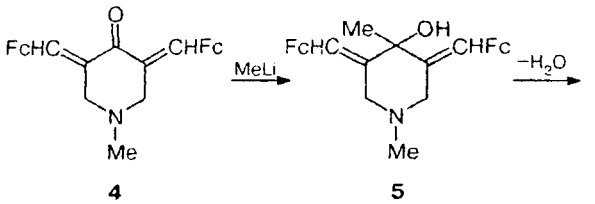


2

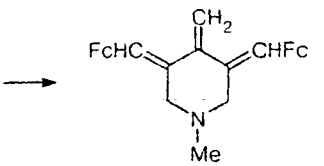
Fc = $C_5H_5FeC_5H_4$

In our opinion, the formation of linear dimers **1** and **2** is due to considerable steric restrictions in the molecules of starting dienes and also to unfavorable electronic factors in the intermediate dimeric carbocations. Meanwhile, the synthesis of linear products **1** and **2** confirmed one important step of the previously discussed[3—7] stepwise mechanism of cationic cyclodimerization, namely, the step of formation of the dimeric linear allylic carbocation, while the mechanism itself remained hypothetical.

In this study, we synthesized 3,5-bis(ferrocenylmethylene)-1-methyl-4-methylenepiperidine (**3**) from 3,5-bis(ferrocenylmethylene)-1-methyl-4-piperidone (**4**) *via* carbinol **5**.



4 **5**



3

The starting chalcone **4** was prepared by condensation of 1-methyl-4-piperidone with ferrocenylcarbaldehyde in a solution of alkali in aqueous alcohol; carbinol **5** was synthesized from **4** on treatment with methyllith-

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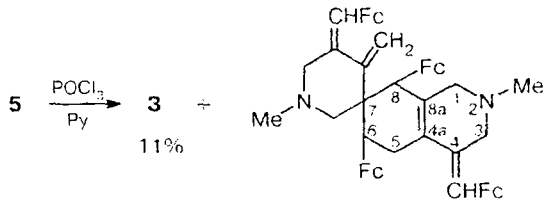
ium.[3,4] Evidently, both molecules are characterized by *E*-configurations of the double bonds and an "external" arrangement of the bulky ferrocenyl substituent.[8,9]

Virtually no data on the synthesis and properties of exocyclic trienes with structures of this type can be found in the literature, except for two preliminary communications dealing with the preparation of relatively unstable 1,3-bis(ferrocenylmethylene)-2-methylenecyclohexane.[10,11] Study of the chemical properties of these trienes and, in particular, their behavior toward cationic cycloaddition deserves attention because specific features of the spatial and electronic structures of these compounds allow one to expect that experimental results would confirm the stepwise mechanism of cationic cyclodimerization.

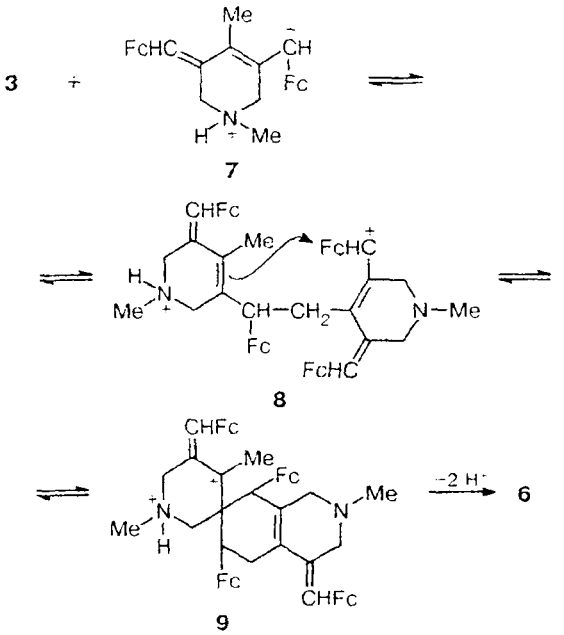
Indeed, we found that diferrocenyltriene **3** is formed in a low yield even during the standard dehydration of alcohol **5** on treatment with $POCl_3$ in pyridine.[3] The major product formed in the reaction was spiro cyclodimer (**6**).



The structures of compounds **3** and **6** were established based on the data of the ^1H and ^{13}C NMR spectra (see Experimental).

The structure of cyclodimer **6** was proved based on the following data. The ^1H NMR spectrum of compound **6** exhibits two singlets with δ 1.98 and 2.35 due to the protons of two methyl groups; two singlets with δ 4.10 (10 H) and 4.24 (10 H) of the protons of the four unsubstituted cyclopentadienyl rings of ferrocene; one singlet of the methine proton of the $-CHFc^1$ group (δ 4.01); five doublets of the protons of five methylene fragments; one triplet of the proton of the $CHFc^2$ group; one doublet for the olefinic protons of the $CH_2=$ group (δ 5.56, J = 1.5 Hz); and two singlets due to the olefinic protons of the two ferrocenylmethylene fragments (δ 6.20 and 6.26). The spin—spin coupling constants of aliphatic and olefinic protons comply with the proposed structure. Additional information was derived from the ^{13}C NMR spectra. The presence of four signals corresponding to quaternary carbon atoms of the ferrocenyl fragments in compound **6** together with the signals due to the four C_5H_5 groups of ferrocene points unambiguously to a dimeric structure. The number of signals of C, CH, CH_2, and Me groups in dimer **6** and the ^{13}C NMR chemical shifts fully comply with structure **6**.

It is clear that cyclodimer **6** could have formed from triene **3**, resulting upon dehydration of carbinol **5**, according to the cationic cyclodimerization pattern, which implies the presence of both triene **3** and the dienyl carbenium ammonium dication (**7**) in the reaction mixture.



Cation **7** adds to the methylene group of diferrocenyl triene **3** to give dimeric dienyl cation **8**. Intramolecular cyclization of cation **8** affords cyclodimeric allylic cation **9**. Deprotonation of **9** on treatment with pyridine results in the formation of cyclodimer **6**.

In our opinion, these results indicate that triene **3** is highly prone to participate in cationic cyclodimerization, apparently, due to the favorable electronic and steric effects. Thus the electronic effect, manifested as the high capacity of the ferrocenyl substituent to stabilize a neighboring carbocationic center,[1,2,12–14] is known to direct the addition of cation **7** exclusively at the exocyclic methylene[4] $CH_2=$ group in triene **3**, giving rise to stabilized dimeric α-ferrocenylallyl cation **8**. The *E*-configurations of the double bonds in the ferrocenylmethylene fragments in triene **3** do not hamper this addition route (steric factor). It is also known that intramolecular alkylation giving cyclodimeric cations can occur only when there are no substantial conformational steric restrictions in the intermediate linear dimeric allylic cations.[1–7] The configuration of the piperidine fragments in **8** apparently complies with these requirements and does not create significant steric hindrance to the realization of the conformation most convenient for the intramolecular cyclization of cation **8** to proceed giving cyclic carbocation **9**. The latter, in turn, is a ferrocenylallylic cation; apparently, it is not inferior in stability to the linear cation **8** (electronic factor). All these prerequisites appear to create conditions for the simultaneous existence of cations **8** and **9** in the reaction mixture and, hence, for the experimental detection of both species. This fact could be regarded as an adequate

proof for the stepwise mechanism of cationic cyclodimerization of conjugated dienes.

To confirm this scheme, we synthesized the bis(tetrafluoroborate) of cation 7 by treatment of carbinol 5 with HBF_4 etherate.

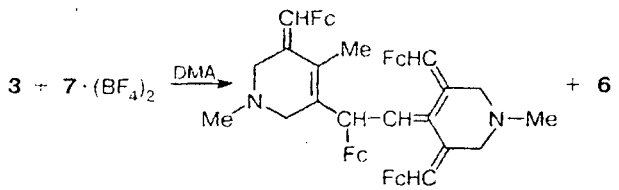
$$\mathbf{5} \xrightarrow{Et_2O \cdot HBF_4} \mathbf{7} \cdot (BF_4)_2$$

We found that the same salt of 7 is also formed in a quantitative yield on treatment of dimer **6** with HBF_4 etherate due to fragmentation of the spiro dimer.

$$\mathbf{6} \xrightarrow{2\ Et_2O \cdot HBF_4} 2\ \mathbf{7} \cdot (BF_4)_2$$

In order to find strong evidence for the participation of the triene and cationic components in the cyclodimerization, we made diferrocenyltriene **3** to react with salt $\mathbf{7} \cdot (BF_4)_2$. Cycloaddition was performed by mixing solutions of bis(tetrafluoroborate) of 7 and triene **3** at room temperature followed by treatment of the reaction mixture with *N*,*N*-dimethylaniline (DMA).

The reaction gave two products, spiro cyclodimer **6** and linear dimer **10**.



10

Reaction time/min	Yield (%)	
	10	**6**
5	23.0	47.0
15	16.0	58.0
30	10.3	69.5

The maximum yield of the linear product (23%) was attained for short reaction times (3–5 min). An increase in the time of the contact of the reactants diminishes the yield of the linear dimer and increases the yield of the cyclic dimer.

The structure of dimer **10** was established based on the data of the ^1H NMR spectrum. The presence of three singlets of the three methyl groups, four doublets of the four methylene groups, doublets of the aliphatic proton of the —CH—Fc group and the olefinic proton of the —CH= group with a mutual spin—spin coupling constant (δ 4.83 and 6.25, J = 7.8 Hz), and three singlets of the olefinic protons of the ferrocenylmethylene fragments (δ 6.58, 6.79, and 6.86) in addition to the signals corresponding to the four ferrocene substituents confirms unambiguously the linear structure of compound **10**.

It is beyond doubt that dimer **10** can form upon deprotonation of the intermediate linear dimeric cation **8** that has not had time to undergo intramolecular cyclization on treatment with DMA.

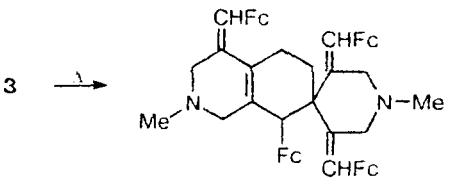
One known variant of performing the cationic cyclodimerization of ferrocenyl-1,3-dienes includes treatment of salts of methylferrocenylallyl cations with bases (Py, DMA),[4] resulting in the intermediate generation of the diene component. By applying this procedure to the bis(tetrafluoroborate) of 7, we found that dimeric products **6** and **10** are formed on slow addition of a solution of a base to a solution of the salt of 7. The reverse order of mixing the reactants (a solution of the salt of 7 is added to a solution of a base) results in triene **3** being formed predominantly (67%).

$$2\ PhNMe_2 + \mathbf{7} \longrightarrow \mathbf{3} + 2\ PhNHMe_2^+ \cdot BF_4^-$$

$$\mathbf{7} + 2\ PhNMe_2 \longrightarrow \mathbf{6} + \mathbf{10}$$

Freshly prepared compound **3** is an orange finely crystalline powder, fairly stable during storage in a sealed tube. On storage under ambient conditions, the product gradually cyclodimerizes to give cyclodimer **6**. Compound **6** is formed especially rapidly in a $CHCl_3$ solution, where it precipitates as an orange powder, or in a benzene solution in the presence of AcOH.

Thermal cyclodimerization of triene **3** proceeds much more slowly. The yield of the cyclodimeric Diels—Alder adduct **11** was 43% even on refluxing in *m*-xylene for 4 h.

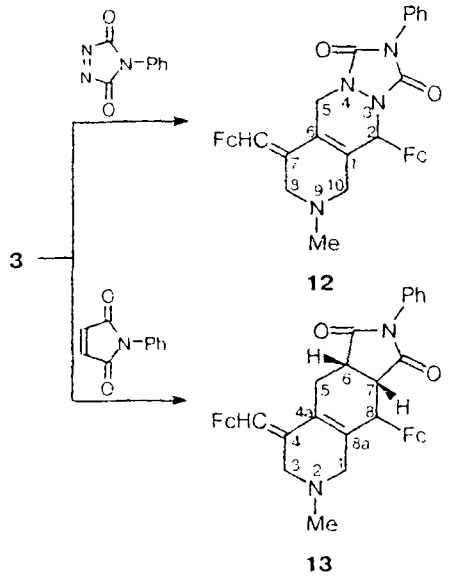


11

The structure of compound **11** was determined relying on the ^1H NMR spectral data, which fully conform to the proposed structure (see Experimental). Unlike cyclodimer **6**, adduct **11** does not undergo fragmentation to give two molecules of the salt of 7 on treatment with HBF_4 etherate.

Diferrocenyltriene **3** reacts with *N*-phenylimides of azodicarboxylic and maleic acids to give Diels—Alder adducts **12** and **13**, respectively.

The formation of adduct **13** occurs stereospecifically. Compound **13** was isolated as only one, presumably, *endo*-isomer. The assignment to the *endo*-form was based on the previously elucidated NMR criteria for the identification of *endo*- and *exo*-isomers of ferrocenyl-substituted Diels—Alder adducts.[12] Compound **13** was identified as the *endo*-adduct based on the fact that the signals of each of the four protons of the ferrocene Fc^1 substituted cyclopentadienyl ring are manifested as separate multiplets, two of which are located in a higher field than the singlet corresponding to the C_5H_5 group of the same ferrocene fragment.



Thus, we showed that 3,5-bis(ferrocenylmethylene)-1-methyl-4-methylenepiperidine (**3**) readily forms a heterocyclic spiro dimer **6** with an exocyclic methylene group according to the cationic cycloaddition pattern. The reaction proceeds *via* the intermediate formation of linear dimeric dienyl cation **8**, which is confirmed by the isolation of linear dimer **10**. Cation **8** undergoes intramolecular cyclization giving rise to spiro allylic cation **9**. The last-mentioned process predominates.

Thus, we believe that the specific features in the behavior of triene **3** under the conditions of cationic cycloaddition are actually associated with the high and comparable stabilities[13,14] of allylic cations **8** and **9** and with the absence of substantial steric hindrance in the piperidine fragments. The combination of these factors allowed us to isolate simultaneously cyclic **6** and linear **10** dimers and thus to detect the main steps of the nonsynchronous stepwise cyclodimerization, which confirms the scheme discussed previously.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ using Me_4Si as the internal standard. The ^1H NMR spectrum of the bis(tetrafluoroborate) of **7** was obtained in a CD_2Cl_2 solution. A column with Al_2O_3 (Brockman activity III) and plates with a fixed SiO_2 layer were used for chromatography. All the syntheses were carried out under dry argon in anhydrous solvents. The data of elemental analysis of the compounds synthesized are summarized in Table 1.

3,5-Bis(ferrocenylmethylene)-1-methyl-4-piperidone (4) was prepared from 1-methyl-4-piperidone and ferrocenecarbaldehyde in 70% EtOH in the presence of NaOH.[4] The yield of chalcone **4** was 73%, violet crystals, m.p. 197–198 °C. ^1H NMR, δ: 2.53 (s, 3 H, Me); 3.61 (t, 4 H, 2 CH_2, J = 1.36 Hz); 4.18 (s, 10 H, 2 C_5H_5); 4.46 (m, 4 H, C_5H_4); 4.49 (m, 4 H, C_5H_4); 7.61 (s, 2 H, 2 CH=).

Table 1. Data of elemental analysis of the compounds synthesized

Compound	Found / Calculated (%)				Molecular formula
	C	H	Fe	N	
3	69.43 / 69.21	6.04 / 5.81	22.37 / 22.20	2.51 / 2.78	$C_{29}H_{29}Fe_2N$
4	66.74 / 66.56	5.21 / 5.39	22.35 / 22.11	2.58 / 2.77	$C_{28}H_{27}Fe_2NO$
5	67.03 / 66.82	5.87 / 6.00	21.58 / 21.43	2.44 / 2.68	$C_{29}H_{31}Fe_2NO$
6	69.36 / 69.21	6.03 / 5.81	22.39 / 22.20	2.63 / 2.78	$C_{58}H_{58}Fe_4N_2$
7	51.48 / 51.30	4.41 / 4.60	16.71 / 16.45	1.87 / 2.06	$C_{29}H_{31}B_2F_8Fe_2N$
10	69.05 / 69.21	5.74 / 5.81	22.44 / 22.20	2.87 / 2.78	$C_{58}H_{58}Fe_4N_2$
11	69.11 / 69.21	5.65 / 5.81	22.01 / 22.20	2.98 / 2.78	$C_{58}H_{58}Fe_4N_2$
12	65.73 / 65.51	4.79 / 5.05	16.62 / 16.47	8.06 / 8.25	$C_{37}H_{34}Fe_2N_4O_2$
13	69.07 / 69.24	5.52 / 5.37	16.71 / 16.52	4.28 / 4.14	$C_{39}H_{36}Fe_2N_2O_2$

3,5-Bis(ferrocenylmethylene)-1,4-dimethyl-4-piperidol (5) was prepared from chalcone **4** and methyllithium as described previously,[4] yield 71%, yellow crystals, m.p. 184–185 °C. ^1H NMR, δ: 1.68 (s, 3 H, Me); 1.70 (s, 1 H, OH); 2.43 (s, 3 H, Me); 3.10 (dd, 2 H, CH_2, J = 2.0 Hz, 15.1 Hz); 3.74 (d, 2 H, CH_2, J = 15.1 Hz); 4.10 (s, 10 H, 2 C_5H_5); 4.21 (m, 4 H, C_5H_4); 4.28 (m, 4 H, C_5H_4); 6.27 (d, 2 H, 2 CH=, J = 2.0 Hz).

Dehydration of carbinol 5 in pyridine on treatment with $POCl_3$.[10] Phosphorusoxychloride (1 mL, 1.1 mmol) was added dropwise at 5–10 °C to a solution of alcohol **5** (2.1 g, 5 mmol) in 120 mL of Py. The mixture was stirred at 20 °C for 4 h, and 200 mL of water was added. The reaction products were extracted with benzene (3×50 mL). After the solvent had been evaporated *in vacuo*, the residue was chromatographed on Al_2O_3 (using benzene as the eluent) to give 0.22 g (11%) of 3,5-bis(ferrocenylmethylene)-1-methyl-4-methylenepiperidine (**3**) and 1.26 g (63%) of 6,8-diferrocenyl-4,5′-bis(ferrocenylmethylene)-2,1′-dimethyl-4′-methylenespiro[1,2,3,4,5,6,7,8-octahydroisoquinoline-7,3′-piperidine] (**6**).

Compound 3, orange crystals, m.p. 201–202 °C. ^1H NMR, δ: 2.38 (s, 3 H, Me); 2.89 (d, 2 H, CH_2, J = 16.03 Hz); 3.44 (d, 2 H, CH_2, J = 16.03 Hz); 4.12 (s, 10 H, 2 C_5H_5); 4.31 (m, 4 H, C_5H_4); 4.38 (m, 4 H, C_5H_4); 5.52 (s, 2 H, CH_2=); 6.36 (s, 2 H, 2 CH=). ^{13}C NMR, δ: 40.72 (Me); 46.23 (CH_2); 67.54, 68.47, 68.64, 69.50 (2 C_5H_4); 68.83, 69.06 (2 C_5H_5); 77.20, 82.03 (2 C_{ipso}Fc); 112.41 (CH_2=); 129.07 (2 CH=); 126.19, 149.02 (2 C, C=CH_2 + 2 C=CHFc).

Compound 6, yellow powder, dec.p. 270 °C. ^1H NMR, δ: 1.98 (s, 3 H, Me); 2.35 (s, 3 H, Me); 2.52 (d, 2 H, CH_2, J = 6.3 Hz); 2.91 (d, 2 H, CH_2, J = 15.0 Hz); 3.21 (d, 2 H, CH_2, J = 16.5 Hz); 3.65 (d, 2 H, CH_2, J = 15.0 Hz); 3.77 (d, 2 H, CH_2, J = 16.5 Hz); 3.92 (t, 1 H, CH, J = 6.3 Hz); 4.01 (s, 1 H, CH); 4.10 (s, 10 H, 2 C_5H_5); 4.24 (s, 10 H, 2 C_5H_5); 4.16 (m, 2 H), 4.18 (m, 4 H), 4.23 (m, 4 H), 4.27 (m, 4 H),

4.32 (m, 2 H) (4 C_5H_3); 5.56 (d, 2 H, CH_2=, J = 1.5 Hz); 6.22 (s, 1 H, CH=); 6.27 (s, 1 H, CH=). ^{13}C NMR, δ: 22.59 (CH_2); 28.10 (Me); 30.42 (C); 37.62 (Me); 43.84, 43.90, 45.56, 45.60 (4 CH_2); 53.43, 55.65 (Fc—CH); 65.66, 66.50, 67.07, 67.12, 67.17, 67.59, 67.61, 68.11, 68.50, 68.66, 68.77, 68.82, 68.90, 69.51, 69.67, 69.70 (4 C_5H_4); 68.52, 68.54, 68.70, 69.09 (4 C_5H_5); 72.81, 77.20, 82.39, 92.35 (4 C_{ipso}Fe); 121.04 (CH_2=); 127.44, 127.48 (2 CH=); 128.61 (C), 130.59 (2 C), 134.23 (C), 134.26 (C).

5-Ferrocenylmethylene-3-(ferrocenylmethan-1-ylium-1-yl)-1,4-dimethyl-1,2,5,6-tetrahydropyridinium bis(tetrafluoroborate) (7·$(BF_4)_2$) was synthesized from alcohol **5** in anhydrous ether on treatment with HBF_4 etherate.[8] The yield of the salt was nearly quantitative, black hygroscopic crystals, dec.p. 320 °C. ^1H NMR, δ: 2.42 (s, 3 H, Me); 3.45 (s, 3 H, Me); 3.89 (m, 4 H, 2 CH_2); 5.18 (s, 10 H, 2 C_5H_5); 4.93 (m, 2 H), 5.31 (m, 2 H), 6.23 (m, 2 H), 6.26 (m, 2 H) (2 C_5H_4); 7.58 (s, 2 H, 2 FcCH=); 8.73 (br.s, 1 H, NH).

Fragmentation of cyclodimer 6. HBF_4 etherate (1.0 mL) was added dropwise with stirring to a solution of compound **6** (1.3 g, 1.5 mmol) in 100 mL of anhydrous ether. The mixture was stirred for 1 h at 20 °C. The precipitate was filtered off, washed on the filter with several portions of anhydrous ether and anhydrous hexane, and dried *in vacuo* to give 1.55 g (89%) of salt 7·$(BF_4)_2$, dec.p. 321 °C.

The reaction of triene 3 with bis(tetrafluoroborate) of 7. A solution of triene **3** (1.0 g, 2 mmol) in 50 mL of CH_2Cl_2 was added with stirring (0—5 °C) to a solution of salt 7·$(BF_4)_2$ (1.32 g, 2 mmol) in 50 mL of CH_2Cl_2. The mixture was stirred for 5 min and DMA (0.6 g) was added. Stirring was continued at ~20 °C for 30 min. The reaction mixture was washed with water, the organic layer was dried with Na_2SO_4, and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 (hexane—AcOEt, 3 : 1) to give 0.46 g (23%) of 3,5-bis(ferrocenylmethylene)-4-[2-ferrocenyl-2-(5-ferrocenylmethylene-1,4-dimethyl-1,2,5,6-tetrahydro-3-pyridyl)-ethylidene]-1-methylpiperidine (**10**), R_f 0.52, and 0.95 g (47%) of cyclodimer **6**, R_f 0.41, dec.p. 273—275 °C.

Compound 10, orange powder, m.p. 315—317 °C. ^1H NMR, δ: 1.84 (s, 3 H, Me); 2.31 (s, 3 H, Me); 2.43 (s, 3 H, Me); 2.63 (d, 2 H, CH_2, J = 11.03 Hz); 2.80 (d, 2 H, CH_2, J = 15.14 Hz); 3.11 (d, 2 H, CH_2, J = 11.0 Hz); 3.50 (d, 2 H, CH_2, J = 15.40 Hz); 4.18 (s, 5 H), 4.23 (s, 5 H), 4.28 (s, 10 H, 4 C_5H_5); 4.09—4.68 (m, 16 H, 4 C_5H_4); 4.83 (d, 1 H, Fc—CH, J = 7.8 Hz); 6.25 (d, 1 H, CH=, J = 7.8 Hz); 6.58 (s, 1 H), 6.79 (s, 1 H), 6.86 (s, 1 H, 3 Fc—CH=).

The reaction of bis(tetrafluoroborate) 7 with DMA. ***A.*** A solution of salt 7·$(BF_4)_2$ (1.31 g, 2 mmol) in 50 mL of CH_2Cl_2 was added dropwise with stirring (0—5 °C) to a solution of DMA (0.6 g) in 30 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h at ~20 °C and washed with water. The organic layer was dried with Na_2SO_4 and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 (hexane—benzene, 3 : 1) to give 0.67 g (67%) of triene **3**, R_f 0.71, m.p. 203 °C, and 0.09 g (9%) of compound **6**, R_f 0.42, dec.p. 293 °C.

B. A solution of DMA (0.6 g) in 30 mL of CH_2Cl_2 was added dropwise at 20 °C to a solution of salt 7·$(BF_4)_2$ (1.31 g) in 50 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h. A similar workup and chromatography gave 0.14 g (14%) of dimer **10**, R_f 0.52, m.p. 316—317 °C, and 0.65 g (65%) of cyclodimer **6**, R_f 0.42, dec.p. 275 °C.

Thermal cyclodimerization of triene 3. A solution of triene **3** (0.5 g, 1 mmol) in 50 mL of *m*-xylene was refluxed for 4 h. After evaporation of the solvent *in vacuo*, the residue was chromatographed on Al_2O_3 (using benzene as the eluent) to give 0.22 g (43%) of 8-ferrocenyl-4,3′,5′-tris(ferrocenylmethylene)-2,1′-dimethylspiro[1,2,3,4,5,6,7,8-octahydroisoquinoline-7,4′-piperidine] (**11**) as orange powder, dec.p. 287 °C. ^1H NMR, δ: 2.17 (s, 3 H, Me); 2.22 (s, 3 H, Me); 2.40 (m, 2 H), 2.52 (m, 2 H), 2.72 (d, 2 H, J = 11.8 Hz), 3.10 (d, 2 H, J = 15.3 Hz), 3.25 (d, 2 H, J = 16.2 Hz), 3.50 (d, 2 H, J = 11.8 Hz, 6 CH_2); 4.08 (s, 1 H, CH); 4.10 (s, 5 H), 4.11 (s, 5 H), 4.13 (s, 5 H), 4.14 (s, 5 H, 4 C_5H_5); 4.06 (m, 2 H), 4.13 (m, 2 H), 4.16 (m, 2 H), 4.17 (m, 2 H), 4.19 (m, 2 H); 4.22 (m, 2 H), 4.25 (m, 2 H), 4.27 (m, 2 H, 4 C_5H_4); 6.20 (s, 1 H), 6.22 (s, 1 H), 6.83 (s, 1 H, 3 CH=).

Reaction of triene 3 with azodicarboxylic acid *N*-phenylimide. Azodicarboxylic acid *N*-phenylimide (0.18 g) (Aldrich, 28, 099-2) was added in portions, as the solution decolorized, to a solution of compound **3** (1.0 mmol) in 30 mL of benzene, the temperature of the reaction mixture being maintained between 0 and 5 °C. Stirring was continued for an additional 30 min. The precipitate was filtered off and recrystallized from benzene to give 0.52 g (76%) of 2-ferrocenyl-7-ferrocenylmethylene-9-methyl-3,4,9-triazabicyclo[4.4.0]dec-1(6)-ene-3,4-dicarboxylic acid *N*-phenylimide (**12**) as yellow crystals, m.p. 316—317 °C. ^1H NMR, δ: 2.23 (s, 3 H, Me), 2.46 (m, 2 H), 3.60 (s, 2 H, 2 CH_2); 4.21 (s, 5 H), 4.26 (s, 5 H, 2 C_5H_5); 3.98 (m, 2 H), 4.10 (m, 2 H), 4.48 (m, 4 H, 2 C_5H_4); 4.41 (s, 1 H), 4.87 (s, 1 H, 1 CH_2); 6.07 (s, 1 H, CH=); 7.28—7.49 (m, 5 H, C_6H_5).

The reaction of triene 3 with *N*-phenylmaleimide. A solution of compound **3** (1.0 mmol) and *N*-phenylmaleimide (0.3 g) (Reachim) in 50 mL of benzene was refluxed for 1 h. After evaporation of the solvent, the residue was chromatographed on SiO_2 (hexane—AcOEt, 4 : 1) to give 0.48 g (72%) of 8-ferrocenyl-4-ferrocenylmethylene-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline-6,7-dicarboxylic acid *endo*-*N*-phenylimide (**13**), R_f 0.53, as yellow crystals, m.p. 296—297 °C. ^1H NMR, δ: 2.50 (s, 3 H, Me); 2.64 (dd, 1 H, CH_2, J = 15.6 Hz, 6.6 Hz); 3.05 (dd, 1 H, CH_2, J = 15.6 Hz, 9.5 Hz); 3.23 (d, 2 H, CH_2, J = 16.5 Hz); 3.27 (m, 1 H, CH); 3.35 (dd, 1 H, J = 9.5 Hz, 5.7 Hz); 3.63 (d, 2 H, CH_2, J = 14.1 Hz); 3.89 (d, 1 H, Fc^1—CH, J = 5.7 Hz); 4.13 (s, 5 H, C_5H_5 Fc^1); 4.15 (s, 5 H, C_5H_5 Fc^2); 3.92 (m, 1 H), 4.11 (m, 1 H), 4.14 (m, 1 H), 4.24 (m, 1 H) (C_5H_4 Fc^1); 4.29 (m, 2 H), 4.34 (m, 2 H) (C_5H_4 Fc^2); 6.34 (s, 1 H, CH=); 7.01—7.05 (m, 2 H), 7.34—7.45 (m, 3 H) (C_6H_5). ^{13}C NMR, δ: 31.86 (Me); 38.89, 40.53, 45.67 (3 CH_2); 46.67, 55.72 (2 CH); 59.00 (FcCH); 67.42, 68.09, 68.80, 68.85, 68.90, 68.95, 69.32, 69.89 (2 C_5H_4); 68.94, 69.18 (2 C_5H_5); 81.88, 84.28 (2 C_{ipso}Fe); 120.25 (CH=); 126.66, 128.32, 128.91 (C_6H_5); 128.49 (C), 131.53 (C), 134.05 (C); 177.24 (C_{ipso}Ph); 178.92 (C=O).

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