

Synthesis and some chemical properties of *s-cis*-diferrocenyltrienes. The role of stereoelectronic factors in cationic dimerization reactions

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Received 22 September 1998

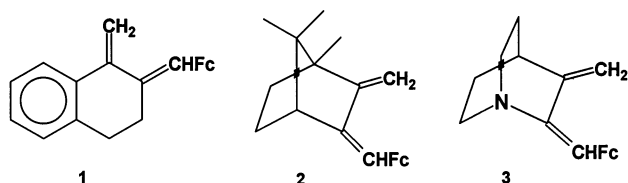
Abstract

Dehydration of 2,6-bis(ferrocenylmethylene)-1-methylcyclohexanol and 2,7-bis(ferrocenylmethylene)-1-methylcycloheptanol gave the corresponding diferrocenyltrienes with a fixed *s-cissoidal* conformation of the double bond system, viz. 1,3-bis(ferrocenylmethylene)-2-methylene-cyclohexane and -cycloheptane, respectively. These trienes easily afford the products of linear and cyclodimerization by a cationic cyclodimerization mechanism as well as [4 + 2]-cyclodimers. They also form Diels–Alder adducts with azodicarboxylic and maleic acid *N*-phenylimides. The latter products undergo stepwise oxidative dehydrogenation on SiO₂ up to the formation of phthalimide derivatives. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkylation; Cycloaddition; Cyclodimerization; Cycloheptane; Cyclohexane; Deprotonation; Ferrocene; Oxidative dehydrogenation; Trienes

1. Introduction

In our previous work we discussed the role of stereoelectronic factors in the chemical behavior of ferrocenyl substituted 1,3-dienes with a fixed *s-cissoidal* conformation of double bonds, viz. 2-ferrocenylmethylene-1-methylenetetraline **1** [1], 3-ferrocenylmethylene-2-methylenecamphane **2** [2], and 2-ferrocenylmethylene-3-methylenequinuclidine **3** [3], prepared by dehydration of the corresponding alcohols.



Diene **1** could not be isolated in the individual state since it easily underwent cyclodimerization irrespective of conditions of dehydration of the starting alcohol. On the contrary, dienes **2** and **3** proved to be stable and were isolated in crystalline state. Dienes **2** and **3** afforded only the products of linear dimerization under the conditions of cationic cycloaddition, unlike other *s-trans/s-cis*-ferrocenylbuta-1,3-dienes examined by us so far [4–6], which produced cyclodimers of a terpenoidal structure. Obviously, the reason for the formation of the linear dimers is strong steric hindrances in molecules of **2** and **3**. It should be noted that this result has served as one of the first proofs of the proposed stepwise mechanism of cationic cyclo-dimerization.

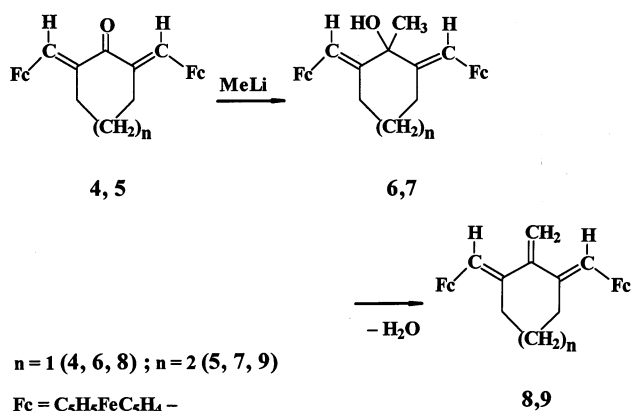
2. Results and discussion

In continuation of our previous investigations in this

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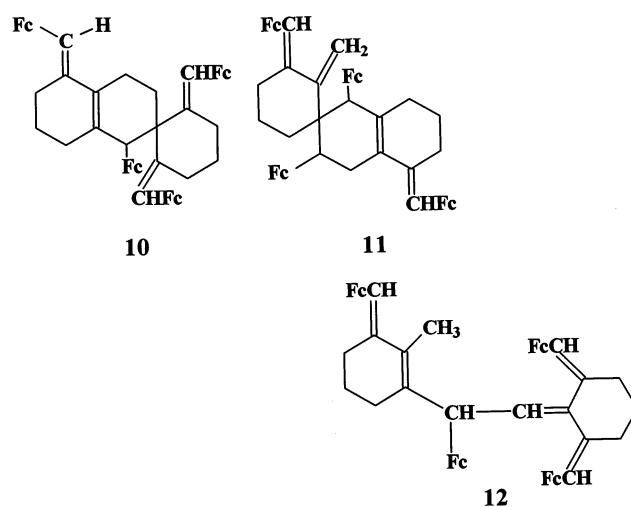
field, in the present work we examined the possibility of synthesizing *s-cis*-diferrocenyltrienes starting from bis-(ferrocenylmethylene)cyclohexanone **4** [7] and -cycloheptanone **5**:



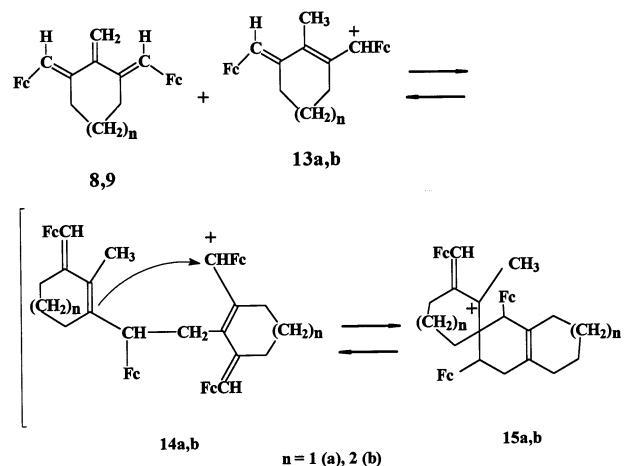
Information on the synthesis and properties of trienes of this type of structure is virtually lacking. However, the chemical behavior of the *exo*-cyclic cross-conjugated trienes under the conditions of both thermal and cationic cycloaddition deserves, in our opinion, special study. *s-cis*-Diferrocenyltrienes **8, 9** are of interest, because at all stages of cationic cyclodimerization, it should form the stable dimeric (linear and cyclic) allyl carbocations [4–6]. One could expect then, that these carbocations could be registered in the reaction mixture by a reaction with *N,N*-dimethylaniline. The final products of this reaction could prove the simultaneous existence of these cations and the stepped mechanism of the cationic cyclodimerization.

The starting *E,E*-chalcones **4** and **5** [7–9] were obtained by condensation of cyclohexanone and cycloheptanone, respectively, with ferrocenecarbaldehyde in the presence of *t*-BuOK. Alcohols **6** [10] and **7** (*E,E*-) were prepared from **4** and **5** and MeLi [4,5].

We found that conventional dehydration of alcohols **6** with POCl_3 in pyridine [4] did not afford the target 1,3-bis(ferrocenylmethylene)-2-methylenecyclohexane **8**. Instead, the following compounds were isolated from the reaction mixture: spiro[2,6-bis(ferrocenylmethylene)cyclohexane-1,2'-(1-ferrocenyl-5-ferrocenylmethylene)-1,2,3,4,5,6,7,8-octahydronaphthalene]] **10** (26%), spiro[3-ferrocenylmethylene-2-methylenecyclohexane-1,2'-(1,3-diferrocenyl-5-ferrocenylmethylene)-1,2,3,4,5,6,7,8-octahydronaphthalene]] **11** (41%), and 1,3-bis(ferrocenylmethylene)-2-[2-ferrocenyl-2-(3-ferrocenylmethylene-2-methylcyclohex-1-enyl)]ethylidenecyclohexane **12** (12%). Earlier, we reported the formation of traces of compounds **10–12** from 1,5-diferrocenyl-3-methyl-2,4-trimethylenepenta-1,4-dienylic carbocation tetrafluoroborate upon treatment with *N,N*-dimethylaniline [10].



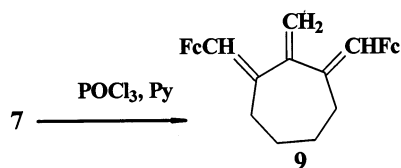
It is quite obvious that compounds **10–12** originate from an intermediate triene **8**, which is formed upon dehydration of alcohol **6**. Thus **10** is the Diels–Alder adduct, while dimers **11** and **12** are formed according to the cationic linear and cyclodimerization schemes, which imply the presence of both triene **8** and the dienyl carbocation **13a**:



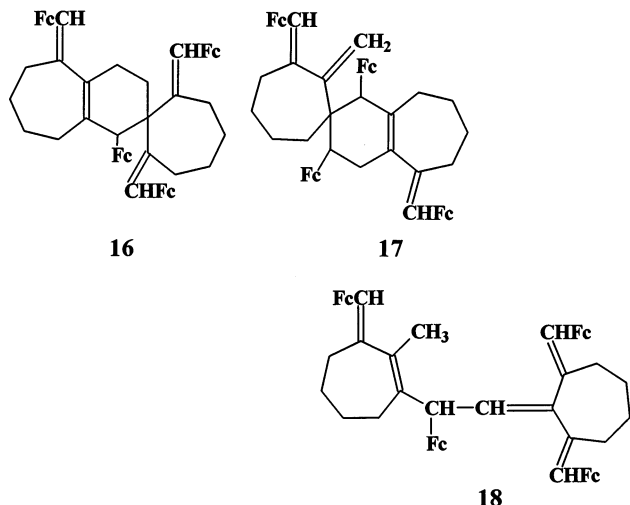
Cation **13a** adds to the methylene group of triene **8** to give a dimeric dienyl cation **14a**, whose intramolecular cyclization affords a cyclodimeric allylic cation **15a**. Deprotonation of cations **14a** and **15a** with a base (pyridine) results in a linear dimer **12** and a cyclodimer **11**, respectively.

In our opinion, this suggests, on the one hand, the enhanced reactivity of triene **8** in cycloaddition and dimerization reactions and, on the other hand, high stability of the monomeric and dimeric carbocations **13a–15a**.

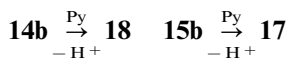
Further, we found that, in contrast to compound **8**, 1,3-bis(ferrocenylmethylene)-2-methylenecycloheptane **9** is a rather stable compound. It is formed in 30% yield upon conventional dehydration of alcohol **7** (POCl_3 , pyridine):



In addition, dimeric products **16**–**18** similar to those formed upon dehydration of alcohol **6** were isolated from the reaction mixture:



Compound **16** is a Diels–Alder adduct, and compounds **17** and **18** are the products of cationic dimerization that obviously occurs by an analogous scheme:



Dimerization and cyclodimerization reactions proceed diastereoselectively. Compounds **10**–**12** and **16**–**18** were isolated as one diastereomeric form. However, the objective spatial structure of these compounds have not been established yet.

The parameters of the ^1H -NMR spectra (number of proton signals, values of chemical shifts and of spin–spin interaction constants) of the aliphatic and olefinic protons in compounds **10**–**12** [10], **16**–**18** confirm the suggested chemical structure of these compounds. Additional information on the structure of compounds **10**–**12**, **16**–**18** is obtained by the ^{13}C -NMR spectra. The presence of four signals from quaternary carbon atoms in the ferrocenyl fragments of compounds **10**–**12**, **16**–**18**, together with the signals from four C_5H_5 groups unambiguously prove the formation of dimers. The presence of C_{spiro} signals confirms the suggested cyclic structure of compounds **10**, **11**, **16** and **17**. The number of ^{13}C -NMR signals from the C, CH, CH_2 and CH_3 groups in compounds **10**–**12**, **16**–**18** correspond to their chemical structure.

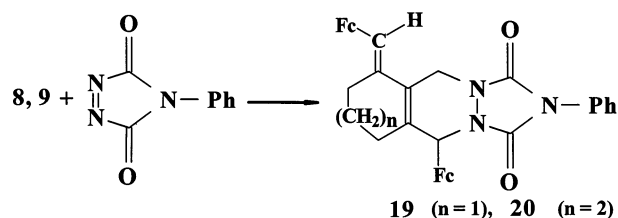
In the search for other methods of dehydration of alcohols **6** and **7** aimed at isolating trienes **8** and **9** in

the individual state, we found that satisfactory results were obtained with alumina (Brockmann activity II). Using this reagent, we managed to isolate as much as 30% of triene **8** and 60% of triene **9**.

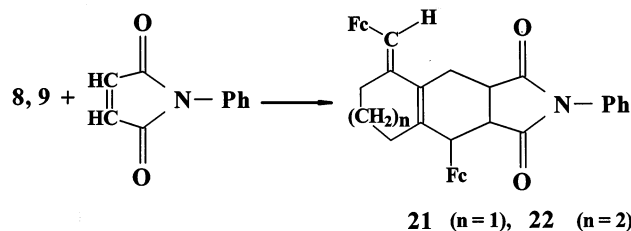
The freshly prepared triene **8** is formed as orange needles, which undergo rapid decomposition even when stored at low temperature (-5 to 0°C) to give cyclodimer **10**. In solution (hexane, benzene), the formation of cyclodimer **10** occurs much faster, and it precipitates as an orange powder.

Thermal cyclodimerization of triene **9** occurs much more slowly. The best results were obtained when it was refluxed in benzene for 1–2 h, the yield of cyclodimer **16** being ca 70%.

With azodicarboxylic acid *N*-phenylimide, compounds **8** and **9** form the Diels–Alder adducts **19** and **20**, respectively, in virtually quantitative yield at 0°C :



With the same ease, compounds **8** and **9** react with *N*-phenylmaleimide to give adducts **21** and **22**, respectively:



The condensations occur stereospecifically, and compounds **21** and **22** were formed as the single isomers, presumably, with *endo*-structures. The *endo*-structures were ascribed to these products based on the previously elaborated ^1H -NMR criteria for the assignment of either *endo*- or *exo*-structures to the ferrocenyl substituted Diels–Alder adducts [9,11]. The fact that one of the protons of the C_5H_4 groups and two protons of the phenyl groups in these compounds resonate at higher fields than the protons of nonsubstituted cyclopentadienyl rings and three other protons of the phenyl rings are evidence of their *endo*-structures.

We found that compounds **21** and **22** undergo smooth auto-oxidation when subjected to thin-layer chromatography on alumina or silica to form phthalimide derivatives as the end products:

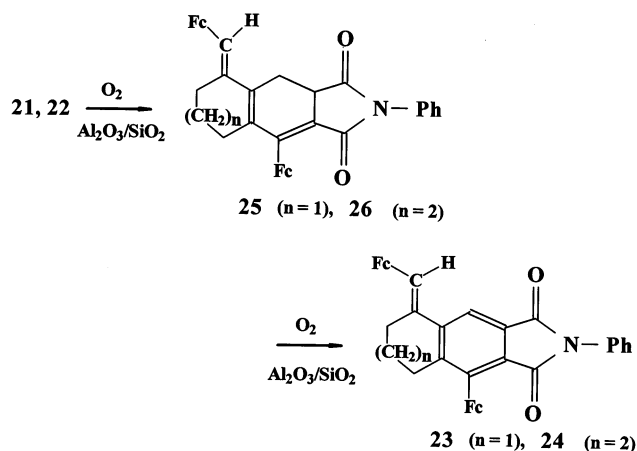
Table 1
¹H-NMR spectral data of compounds **5**, **7–9** and **16–26** (δ , J/Hz)

Compound	C ₅ H ₅	C ₅ H ₄	CH ₂	CH	CH ₃ , OH, Ph
5	4.16 s (10H)	4.38 m (4H), 4.53 m (4H)	1.94 m (4H), 2.60 m (4H)	7.14 s (2H)	–
7	4.12 s (10H)	4.24 m (4H), 4.38 m (2H), 4.40 m (2H)	1.86 bs (4H), 2.25 m (2H), $J = 4.5$, 2.42 m (2H), $J = 4.5$	6.43 s (2H)	1.59 d (3H), $J = 4.5$, 1.63 s (1H)
8	4.10 s, 4.16 s	4.05 m (1H), 4.06 m (1H), 4.07 m (1H), 4.09 m (1H), 4.13 m (2H), 4.21 m (2H)	2.01 m (2H), 2.77 m (4H), 5.32 s (2H)	6.20 s (2H)	–
9	4.14 s (10H)	4.25 m (4H), 4.42 m (4H)	1.87 m (4H), 2.42 m (4H), 4.98 s (2H)	6.42 s (2H)	–
16	4.12 s, 4.16 s (10H), 4.17 s	4.06 m (2H), 4.11 m (2H), 4.14 m (2H), 4.22 m (4H), 4.24 m (2H), 4.27 m (2H), 4.52 m (2H)	1.24–1.30 m (2H), 1.81–1.87 m (4H), 1.89–2.05 m (4H), 2.17–2.42 m (6H), 2.60–2.82 m (4H)	4.20 s (1H), 6.04 s (1H), 6.25 s (1H), 6.57 s (1H)	–
17	4.05 s, 4.08 s, 4.16 s, 4.17 s	3.95–4.07 m (8H), 4.22 m (2H), 4.30 m (2H), 4.33 m (2H), 4.48 m (2H)	1.52–1.65 m (2H), 1.78–1.95 m (4H), 2.00–2.10 m (4H), 2.20–2.30 m (4H), 2.41–2.46 m (2H), 2.78 m (2H), 4.21 d (1H), $J = 1.2$, 5.98 d (1H), $J = 1.2$	4.09 m (1H), $J = 5.8$, 4.22 s (1H) 6.27 s (1H), 6.41 s (1H)	–
18	4.15 s (10H), 4.17 s, 4.20 s	4.06–4.52 m (16H)	1.23–2.81 m (16H)	4.75 d (1H), $J = 10.2$, 6.05 d (1H), $J = 10.2$, 5.94 s (1H), 6.36 s (1H), 6.57 s (1H)	1.89 s (1H)
19	4.16 s, 4.22 s	4.14 m (2H), 4.18 m (2H), 4.26 m (2H), 4.47 m (2H)	1.75–2.82 m (6H), 4.39 bs (1H), 5.12 d (1H), $J = 1.0$	5.68 s (1H), 6.51 s (1H)	7.28–7.60 m (5H)
20	4.14 s, 4.20 s	4.05 m (2H), 4.25 m (2H), 4.28 m (2H), 4.39 m (2H)	1.30–2.85 m (8H), 4.44 bs (1H), 5.24 d (1H), $J = 1.2$	5.69 s (1H), 6.48 s (1H)	7.32–7.61 m (5H)
21	4.11 s, 4.14 s	3.93 m (1H), 4.10 m (2H), 4.26 m (2H), 4.28 m (1H), 4.37 m (1H), 4.39 m (1H)	1.87 m (2H), 2.21 m (2H), 2.58–2.65 m (2H), 2.77 m (1H), 2.98 m (1H)	3.25 m (1H), $J = 12.1$, 3.31 dd (1H), $J = 12.1$, 5.4, 3.88 d (1H), $J = 5.4$, 6.27 s (1H)	7.05 d (2H), $J = 6.9$, 7.38 m (3H)
22	4.12 s, 4.125 s	3.98 m (1H), 4.10 m (1H), 4.14 m (1H), 4.18 m (1H), 4.27 m (2H), 4.38 m (1H), 4.42 m (1H)	1.86 m (4H), 2.35–2.65 m (4H), 2.73 m (1H), 2.81 m (1H)	3.25 m (1H), $J = 12.1$, 3.34 dd (1H), $J = 12.1$; 5.8, 3.89 d (1H), $J = 5.8$	7.09 d (2H), $J = 6.9$, 7.43 m (3H)
23	4.16 s, 4.19 s	4.38 m (2H), 4.47 m (2H), 4.55 m (2H), 4.69 m (2H)	1.90 m (2H), 2.79 m (2H), 3.40 m (2H)	6.94 s (1H), 8.13 s (1H)	7.35–7.71 m (5H)
24	4.14 s, 4.19 s	4.34 m (2H), 4.46 m (2H), 4.52 m (2H), 4.65 m (2H)	1.31 m (2H), 1.43–1.56 m (2H), 1.80–1.86 m (2H), 2.60–3.10 m (2H)	6.38 s (1H), 7.75 s (1H)	7.36–7.58 m (5H)
25	4.15 s, 4.185 s	4.16–4.20 m (8H)	1.25–2.00 m (6H), 2.81 td (1H), $J = 11.8$, 6.2, 4.9, 3.48 dd (1H), $J = 11.8$, 6.2	4.22 dd (1H), $J = 6.2$, 4.9, 6.69 s (1H)	7.11–7.50 m (5H)
26	4.094 s, 4.16 s	4.06–4.20 m (8H)	1.27–2.05 m (8H), 3.01 m (1H), 3.65 m (1H)	4.19 dd (1H), $J = 6.3$, 4.8, 6.33 s (1H)	7.25–7.48m (5H)

Table 2

¹³C-NMR spectral data of compounds **7–9**, **16–18**, **21** and **22** (δ)

Compound	C ₅ H ₅	C ₅ H ₄	C _{ipso} Fe	CH = , CH ₂ =	C	CH, CH ₃	CH ₂	CHFe
7	68.99, 69.08	68.58, 68.64, 68.75, 68.76, 69.12, 69.19, 69.95, 69.97	81.96, 82.14	124.36	40.55, 140.44, 158.27	19.97	30.22, 31.24	–
8	68.80, 69.00	66.45, 66.95, 67.14, 67.30, 69.39, 69.56, 69.65, 70.30	83.58, 90.05	120.48, 129.21	135.29, 136.84, 137.22	–	24.23, 28.23, 31.92	–
9	69.03, 69.06	67.16, 67.51, 68.24, 68.75, 69.35, 69.53, 70.12, 70.35	78.87, 81.80	121.20, 124.38	140.45, 144.48, 144.49	–	29.33, 29.84, 30.20, 31.22	–
16	68.66, 68.85, 68.95, 69.12	66.88, 67.01, 67.38, 67.40, 67.58, 68.16, 68.21, 68.51, 68.78, 68.96, 69.11, 69.19, 69.25, 69.30, 69.34, 69.64	82.30, 82.86, 83.65, 89.15	122.78, 123.43, 124.98	51.23, 132.21, 135.60, 137.15, 142.25, 150.58	–	20.04, 25.93, 26.81, 28.94, 29.74, 30.56, 31.03, 32.22, 41.63	62.45
17	69.12, 69.14, 69.21, 69.27	66.80, 67.38, 67.70, 68.15, 68.22, 68.71, 68.93, 69.05, 69.27, 69.35, 69.39, 69.50, 69.52, 69.61, 70.23, 70.37	81.10, 81.58, 81.99, 82.76	107.76, 124.98, 130.08	50.36, 133.48, 139.03, 141.96, 142.16, 148.78	–	25.98, 26.80, 29.81, 29.83, 30.22, 31.03, 31.49, 47.69, 47.86	63.02, 64.21
18	68.52, 68.88, 69.05, 69.07	65.98, 66.81, 67.04, 67.63, 67.85, 68.26, 68.33, 68.56, 68.64, 68.75, 68.78, 68.94, 69.43, 69.52, 69.76, 69.95	81.95, 82.54, 83.23, 92.63	121.14, 126.78, 132.51, 137.74	122.77, 138.29, 142.09, 142.16, 144.23, 148.17	17.95	22.63, 26.40, 29.59, 31.20, 32.43, 34.31, 36.86, 40.47	55.37
21	68.83, 69.10	67.22, 68.14, 68.55, 68.58, 68.73, 68.85, 69.27, 69.78	82.96, 84.54	119.99	128.32, 130.17, 131.72, 134.28, 136.91, 177.53, 179.14	39.39, 42.75	21.80, 23.21, 27.78, 31.33	46.62
22	68.76, 69.04	67.15, 67.96, 68.40, 68.51, 68.70, 68.76, 69.21, 69.80	82.75, 84.60	118.73	127.73, 129.95, 131.64, 134.18, 137.03, 177.41, 179.20	39.34, 43.06	20.96, 21.99, 22.74, 23.86, 30.87	46.58



The oxidative dehydrogenation occurs in a stepwise manner via intermediate cyclohexadienes **25** and **26**, which were isolated by chromatography and characterized. These compounds are stable in the crystalline state, while in solutions or being absorbed on Al_2O_3 or SiO_2 they undergo smooth oxidation to **23** and **24**.

3. Conclusions

Thus, for the first time we have isolated spiro-cyclodimers **11** and **17** with a methylene fragment, which originate from the diferrocenyldiene systems, together with the linear dimers **12** and **18**. The observed peculiarities of the behavior of trienes **8** and **9** under the conditions of mild acid catalysis seem to be related to the enhanced stability of the intermediate ferrocenyl allylic and dienyl carbocations of the type **13–15** (the electronic effect) and to the absence of substantial steric

hindrances in cycloalkane moieties (the steric effect), which distinguishes these compounds from camphane-[2] and quinuclidine-based [3] *s-cis*-dienes studied by us previously.

The combination of these factors has permitted the isolation of both the cyclic (**11** and **17**) and linear (**12** and **18**) dimers. Thus, we have fixed the principal stages of the asynchronous, stepwise cyclodimerization, viz. the intermediate formation of the linear dienyl carbocations (**14a** and **b**) and cyclic allylic carbocations (**15a** and **b**) resulting from the addition of methyl bisferrocenyldienyl cations **13a** and **b** to the methylene groups of trienes **8** and **9**. The scheme of asynchronous cationic cyclodimerization discussed previously [1–6,12–17] is thereby strongly substantiated.

4. Experimental

All 1H - and ^{13}C -NMR spectra were recorded on a Unity Inova Varian spectrometer (at 300 and 75 MHz) in $CDCl_3$ solutions with Me_4Si as an internal standard (Tables 1 and 2). The elemental analyses data are listed in Table 3.

4.1. 2,6-Bis(ferrocenylmethylene)cyclohexanone **4** and 2,7-bis(ferrocenylmethylene)cycloheptanone **5**

These were obtained from ferrocenecarbaldehyde and the corresponding ketone in *t*-butyl alcohol in the presence of *t*-BuOK. The yield of chalcone **4** was 72% [7] and of chalcone **5**, 38%; orange crystals, m.p. 173–174°C.

Table 3
Elemental analyses data

Compound	Molecular formula	Found (Calculated) (%)			
		C	H	Fe	N
5	$C_{29}H_{28}Fe_2O$	68.93 (69.08)	5.77 (5.60)	22.41 (22.15)	–
7	$C_{30}H_{32}Fe_2O$	69.37 (69.25)	6.03 (6.20)	21.56 (21.47)	–
8	$C_{29}H_{28}Fe_2$	71.51 (71.34)	5.98 (5.78)	22.55 (22.88)	–
9	$C_{30}H_{30}Fe_2$	71.63 (71.74)	5.91 (6.02)	22.37 (22.24)	–
16	$C_{60}H_{60}Fe_4$	71.87 (71.74)	6.19 (6.02)	22.11 (22.24)	–
17	$C_{60}H_{60}Fe_4$	71.58 (71.74)	5.87 (6.02)	22.38 (22.24)	–
18	$C_{60}H_{60}Fe_4$	71.61 (71.74)	5.83 (6.02)	22.43 (22.24)	–
19	$C_{37}H_{33}Fe_2N_3O_2$	67.27 (67.00)	4.83 (5.01)	16.73 (16.84)	6.47 (6.33)
20	$C_{38}H_{35}Fe_2N_3O_2$	67.51 (67.38)	5.06 (5.21)	16.63 (16.48)	6.34 (6.20)
21	$C_{39}H_{35}Fe_2NO_2$	70.71 (70.82)	5.44 (5.33)	17.04 (16.89)	2.26 (2.12)
22	$C_{40}H_{37}Fe_2NO_2$	70.89 (71.13)	5.37 (5.52)	16.73 (16.54)	1.95 (2.07)
23	$C_{39}H_{31}Fe_2NO_2$	71.42 (71.25)	4.54 (4.75)	16.91 (17.00)	2.21 (2.13)
24	$C_{40}H_{33}Fe_2NO_2$	71.30 (71.56)	4.83 (4.95)	16.87 (16.63)	1.91 (2.08)
25	$C_{39}H_{33}Fe_2NO_2$	70.86 (71.04)	4.91 (5.04)	17.08 (16.94)	2.21 (2.12)
26	$C_{40}H_{35}Fe_2NO_2$	71.43 (71.34)	5.11 (5.24)	16.73 (16.59)	1.98 (2.08)

4.2. Alcohols **6** and **7**

These were synthesized from chalcones **4** and **5**, respectively, and methyllithium [4,5]. The yield of cyclohexanol **6** was 73%, yellow crystals, m.p. 156–157°C [10]; the yield of cycloheptanol **7** was 74%, orange crystals, m.p. 167–168°C.

4.3. Dehydration of alcohols **6** and **7** in pyridine in the presence of POCl₃

A total of 1 ml of POCl₃ was added drop-wise to a solution of alcohol **6** (3.0 mmol) in 100 ml of dry pyridine at 5–10°C, the reaction mixture was stirred for 3 h at 10°C, and diluted with water. The reaction products were extracted with benzene. The solvent was removed in vacuo, and the residue was subjected to TLC on SiO₂ (hexane–benzene, 2:1) to give 0.17 g (12%) of the linear dimer **12** (R_f = 0.67), orange crystals, m.p. 226–227°C [8]; 0.38 g (26%) of adduct **10**, (R_f = 0.52), orange crystals, m.p. 259–260°C [8], and 0.60 g (41%) of cyclodimer **11**, orange crystals, m.p. 262–263°C [8].

Under analogous conditions, alcohol **7** (1.56 g, 3.0 mmol) afforded the following products: triene **9** (0.45 g, 30%), (R_f = 0.85), orange needles, m.p. 147–148°C; 1,3-bis(ferrocenylmethylene)-2-[2-ferrocenyl-2-(3-ferrocenylmethylene-2-methylenecyclohept-1-enyl)ethylidenecycloheptane **18**, (0.14 g, 9%) (R_f = 0.68), orange powder, m.p. 183–184°C; spiro[2,7-bis(ferrocenylmethylene)cycloheptane-1,7'-(6-ferrocenyl-1-ferrocenylmethylene-2,3,4,5,6,7,8,9-octahydro-1*H*-benzocycloheptene)] **16**, (0.24 g, 16%) (R_f = 0.61), yellow crystals, m.p. 237–238°C; and spiro[3-ferrocenylmethylene-2-methylenecycloheptane-1,7'-(6,8-diferrocenyl-1-ferrocenylmethylene-2,3,4,5,6,7,8,9-octahydro-1*H*-benzocycloheptene)] **17**, (0.32 g, 21%) (R_f = 0.52), yellow powder, m.p. 254–256°C.

4.4. Dehydration of alcohols **6** and **7** on Al₂O₃

A solution of alcohols **6** or **7** (2 mmol) in 30 ml of chloroform was applied onto 20 g of alumina (Brockmann activity II) and left for 2 h at 20°C. Then it was transferred into a column with alumina of the same activity (layer height, 30 cm) and eluted with hexane. The yield of triene **8** was 0.31 g (30%), orange needles, m.p. 126–127°C, the yield of triene **9** was 0.63 g (61%), orange needles, m.p. 148°C.

4.5. Thermal cyclodimerization of trienes **8** and **9**

Compound **8** (0.5 g, 1.0 mmol) was dissolved in 50 ml of hexane. The solution was kept at 20°C for 12 h. The precipitate that formed was filtered off, washed

with hexane, and dried. Cyclodimer **10** was obtained in a yield of 0.38 g (77%), m.p. 258–259°C.

Triene **9** (0.52 g, 1 mmol) was dissolved in 50 ml of dry benzene, and the solution was refluxed for 2 h. The solvent was removed in vacuo, and the residue was purified by crystallization from acetonitrile to give 0.36 g (70%) of cyclodimer **16**, m.p. 237–239°C.

4.6. Reaction of trienes **8** and **9** with azodicarboxylic acid *N*-phenylimide

To a stirred solution of triene **8** (or **9**) (1 mmol) in 20 ml of dry benzene, was added azodicarboxylic acid *N*-phenylimide (0.18 g) portion-wise as the mixture discolored, in the temperature range 0–5°C. The mixture was stirred for an additional 30 min. The crystals that precipitated were filtered off and purified by crystallization from benzene to give 0.47 g (71%) of 1-ferrocenyl-5-ferrocenylmethylene-2,3-diazabicyclo[4.4.0]dec-9(10)ene-2,3-dicarboxylic acid *N*-phenylimide **19**, yellow crystals, m.p. 293–294°C, and, respectively, 0.46 g (67%) of 1-ferrocenyl-5-ferrocenylmethylene-2,3-diazabicyclo[5.4.0]undec-10(11)ene-2,3-dicarboxylic acid *N*-phenylimide **20**, m.p. 301–303°C.

4.7. Reaction of trienes **8** and **9** with *N*-phenylmaleimide

A mixture of trienes **8** or **9** (1 mmol) and 0.3 g of *N*-phenylmaleimide in 20 ml of dry benzene was stirred for 5 h at 20°C. The solvent was removed in vacuo, and the residue was chromatographed on alumina (Brockmann activity III, hexane–benzene as the eluent) to give 0.43 g (65%) of *endo*-1-ferrocenyl-5-ferrocenylmethylene-1,2,3,4,5,6,7,8-octahydronaphthalene-2,3-dicarboxylic acid *N*-phenylimide **21**, yellow crystals, m.p. 251–252°C, or 0.49 g (72%) of *endo*-1-ferrocenyl-5-ferrocenylmethylenebicyclo[5.4.0]undec-10(11)ene-2,3-dicarboxylic acid *N*-phenylimide **22**, yellow crystals, m.p. 264–265°C.

4.8. Oxidative dehydrogenation of *N*-phenylimides **21** and **22**

A solution of compound **21** (0.22 g) in 10 ml of benzene was applied on thin layer silica gel and left overnight in air. Subsequent chromatography in hexane–benzene (1:1) yielded 0.07 g (30%) of 1-ferrocenyl-5-ferrocenylmethylene-5,6,7,8-tetrahydronaphthalene-2,3-dicarboxylic acid *N*-phenylimide **23**, R_f = 0.72, red crystals, m.p. 236–237°C, and 0.08 g (35%) of 1-ferrocenyl-5-ferrocenylmethylene-3,4,5,6,7,8-hexahydronaphthalene-2,3-dicarboxylic acid *N*-phenylimide **25**, R_f = 0.63, violet crystals, m.p. 258–259°C.

Analogously, 0.22 g of compound **22** yielded 0.08 g (36%) of 1-ferrocenyl-5-ferrocenylmethylene-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-2,3-dicarboxylic acid *N*-phenylimide **24**, $R_f = 0.72$, red powder, m.p. 269–270°C, and 0.05 g (23%) of 1-ferrocenyl-5-ferrocenylmethylene-3,4,6,7,8,9-hexahydro-3*H*,4*H*,5*H*-benzocycloheptene-2,3-dicarboxylic acid *N*-phenylimide **26**, $R_f = 0.64$, red powder, m.p. 241–242°C.

Acknowledgements

Financial support from CONACYT (Mexico) is gratefully acknowledged. We would like to thank Oscar Salvador Yañez Muñoz for the ^1H - and ^{13}C -NMR spectra.

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