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The behavior of 3-ferrocenyl-1-methyl-1,2-pentamethyleneallyl and 1,5-diferrocenyl-3-methyl-2,4-tetramethylene-1,4-dienyl carbocations in the cationic dimerization of 1,3-dienes

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Abstract

3-Ferrocenyl-1-methyl-1,2-pentamethyleneallyl carbocation **9** and 1,5-diferrocenyl-3-methyl-2,4-tetramethylene-1,4-dienyl carbocation **10** are transformed into linear **21** and cyclic **28** dimers, respectively, in low yields under conditions of the cationic dimerization (treatment with *N*,*N*-dimethylaniline). The former is preferentially deprotonated into 1-ferrocenylmethylidene-2-methylidenecycloheptane (**19**) and 3-ferrocenylmethylidene-2-methylcycloheptene (**20**), while the latter is reduced into 1,3-bisferrocenylmethylidene-2-methylcycloheptane (**26**). However, a linear dimer was obtained in the reaction of salt **9** with *s-cis*-diene **19**, while the reaction of salt **10** with 1,3-bisferrocenylmethylidene-2-methylidenecycloheptane (**27**) results in a cyclodimer **28** together with a linear dimer **29**. The results obtained corroborate the stepwise mechanism of cationic cycloaddition of 1,3-dienes and manifest the role of the electronic factor in the intramolecular cyclization of an intermediate linear dimeric allylic cation. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Carbocation; Cyclodimerization; Deprotonation; Reduction; Cycloaddition; Electronic factor; Ferrocene

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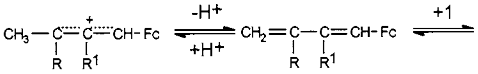
1. Introduction

It is known that ferrocenylmethylcarbocations [1–4] and ferrocenylmethylallylic cations [5–9] undergo deprotonation under the action of nucleophiles (*N*,*N*-dimethylaniline, pyridine) leading to intermediate α-ferrocenylethylenes and ferrocenyl-1,3-dienes, which ultimately give the cationic dimerization and cyclodimerization products, respectively. On the other hand, ferrocenylalkenes and ferrocenyl-1,3-dienes smoothly form intermediate carbenium and allylic cations, respectively, under the action of acids (HCl, AcOH) and then similar linear and cyclic dimers. In addition to these two procedures for performing cationic dimerization/cyclodimerization of ferrocenyl-substituted alkenes or 1,3-dienes, a third route is feasible, viz. the reactions of equimolar amounts of the corresponding olefines/dienes with carbocationic/allyl-cationic components [5–9]. The regio- and stereoselectivities of dimerization/cyclodimerization were rationalized with account of a stepwise mechanism of acid-catalyzed cyclodimerization of aliphatic conjugated dienes postulated by Hoffmann and Ernst [10,11]. According to this mechanism, cyclodimerization of ferrocenyl-1,3-dienes occurs by a scheme [9] involving a series of consecutive steps.



1a-c

2a-c

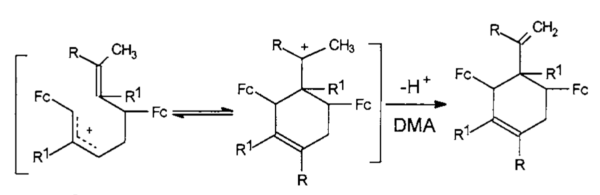
$Fc = C_5H_5FeC_5H_4$

$R = Fc,\ R_1 = H(a)$

$R = Fc,\ R_1 = Me(c)$

$R = Ar,\ R_1 = H(b)$

$DMA = C_6H_5NMe_2$



3a-c

4a-c

5a-c

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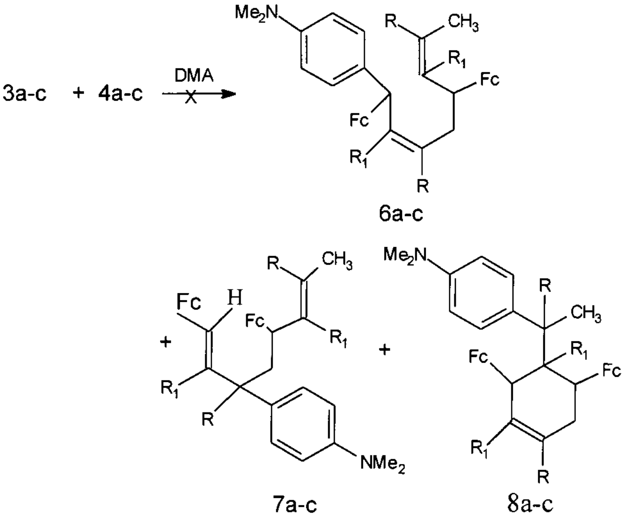
Rigorous proof of this mechanism requires that dimeric linear **3a–c** or cyclic **4a–c** cations or the products of *p*-alkylation of *N*,*N*-dimethylaniline with the corresponding cations were isolated.



However, all attempts at isolating *N*,*N*-dimethylaniline alkylation products **6a–c**, **7a–c**, and **8a–c** to experimentally prove the mechanism suggested have failed, which made us to consider this mechanism as hypothetical.

One of probable reasons for these results seems to be associated with the effect of electronic factors, viz. with lesser stability and higher proneness to deprotonation of the cations **4a–c** compared to the allylic cations **3a–c** [12,13], which shifts the reaction equilibrium.

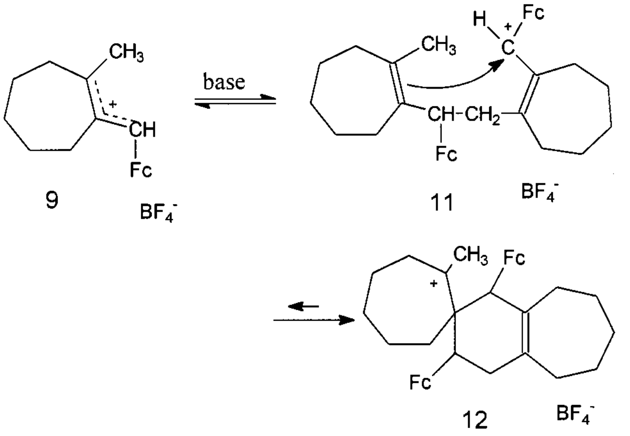
The formation of linear dimeric cations has previously been observed in the study of cationic cyclodimerization of bulky *s*-*cis*-ferrocenyl-1,3-dienes such as 3-ferrocenylmethylidene-2-methylidenecamphane and 2-ferrocenylmethylidene-3-methylidenequinuclidine [14–16]. Both the alkylation products of *N*,*N*-dimethylaniline with linear, dimeric allylic cations and linear dimers were isolated in these cases. The absence of cyclic dimers seems to be associated with a combination of unfavorable steric and electronic factors in the intermediates that formed. These data has been used only to support the idea on the formation of linear dimeric intermediates **3a–c** rather than to prove the entire scheme.

2. Results and discussion

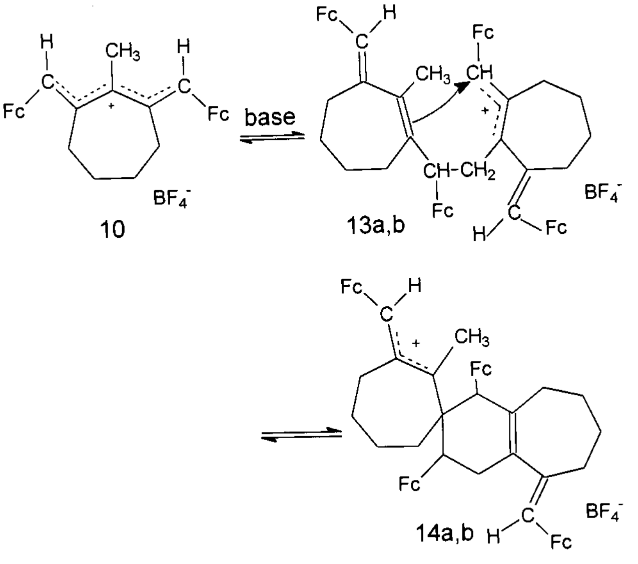
In search for the facts confirming the stepwise character of cationic cyclodimerization of ferrocenyl-1,3-dienes, we have synthesized 1-ferrocenylmethylidene-2-methylcycloheptan-2-yl and 1,3-bis(ferrocenylmethylidene)-2-methylcycloheptan-2-yl tetrafluoroborates (**9** and **10**) and studied their properties.

2.1. Supposed results

In our opinion, the cation **9** presents interest since this should generate linear dimeric allylic cation **11** more stable than the cyclodimeric cation of the type **12** in the intermediate steps of the cationic cyclodimerization.



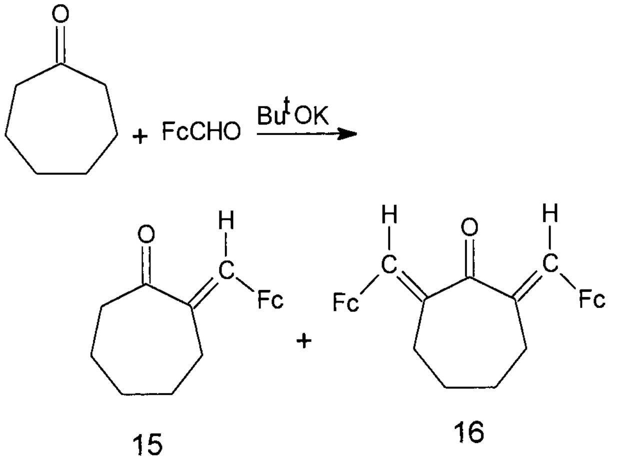
Unlike **9**, the dienyl cation **10** should generate dimeric linear **13a**,**b** and cyclic **14a**,**b** allylic cations of nearly the same stabilities [12,13].



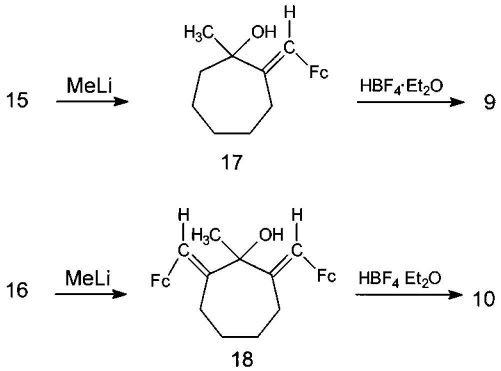
Thus, linear dimers should most probably be formed in the former case, while in the latter case there are good premises for simultaneous detection of linear and cyclic dimers in the reaction mixture. This would be direct proof of an asynchronic mechanism of cationic cyclodimerization.

2.2. Synthesis of starting compounds

The starting *E*-2-ferrocenylmethylidene- and *E*-,*E*-2,7-bis(ferrocenylmethylidene)cycloheptanone (**15** and **16**) prepared by condensation of ferrocenecarbaldehyde with cycloheptanone in the presence of Bu^{t}OK [16–19] served as precursors for tetrafluoroborates **9** and **10**, respectively.



The reaction with methyllithium alllowed conversion of the chalcones **15** and **16** into the alcohols *E*-**17** and *E*-,*E*-**18** [17–19]. Treatment of these alcohols with HBF_4 etherate resulted in the target tetrafluoroborates *E*-**9** and *E*-,*E*-**10** [7,9].

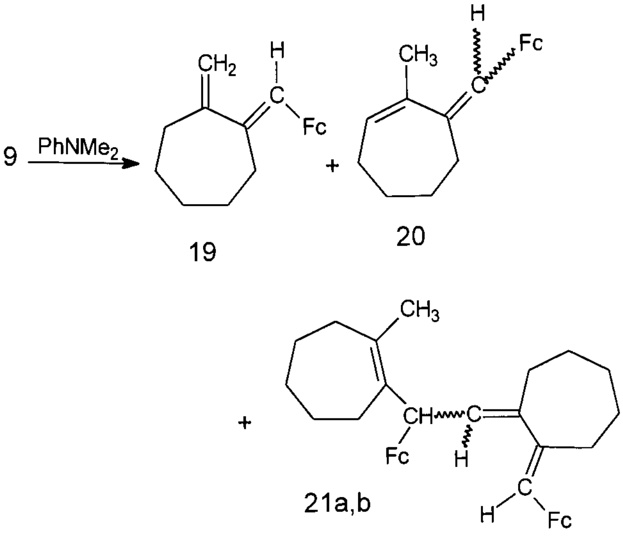


The salts **9** and **10** are solid, virtually black powders sufficiently stable if stored in a dry inert atmosphere. The ^{1}H-NMR spectral data of these salts (Table 1) corroborate completely their structures.

2.3. Chemical transformations of tetrafluoroborate 9

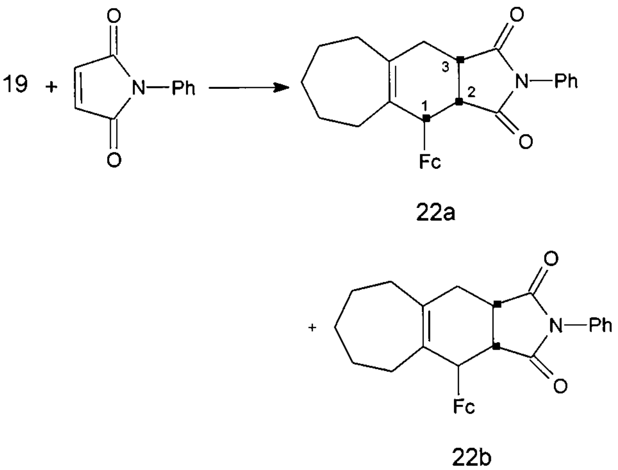
We found that the treatment of tetrafluoroborate **9** with *N*,*N*-dimethylaniline resulted in deprotonation products of (ferrocenyl)methylallyl cation, viz. compounds **19** and **20**, together with a linear dimer **21**.

The structures of these compounds separated by chromatography on alumina (Brockmann activity III) were established based on ^{1}H-NMR spectral data (Table 1). The spectra of compounds **19** and **20** are sufficiently simple and prove their structures unambiguously. According to the NMR spectral data, the dimer **21** represents a ca. 2:1 mixture of isomers **21a** and **21b**. These isomers could not be separated, and their configurations (*Z*- or *E*-) were not determined.



The ^{1}H-NMR spectrum of the dimer **21a**,**b** contains the following characteristic signals which confirm its linear, dimeric structure: two singlets for protons of the methyl groups; two pairs of singlets for the protons of the C_5H_5 groups of the ferrocenyl substituents; two doublets for the protons of the Fc–CH groups, and two doublets for the olefinic protons of the –CH= groups. The integral intensity ratios for all the groups of signals were equal to ca. 2:1.

Compound **19** represents a ferrocenyl-1,3-diene with a fixed *s*-*cis*-configuration of the double bonds. It reacts readily with *N*-phenylmaleimide to give a mixture of *endo*- and *exo*-adducts (**22a** and **22b**, respectively) in a ca. 1:1 ratio (according to ^{1}H-NMR spectral data, Table 1).



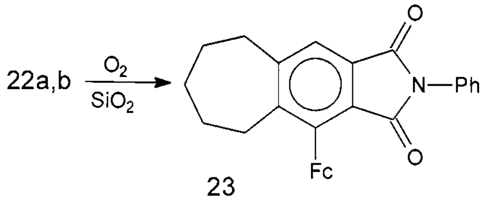
The Diels–Alder adducts **22a** and **22b** were separated by chromatography. The *endo*- and *exo*-structures were ascribed to these products based on the previously elaborated ^{1}H-NMR criteria for the assignment of the ferrocenyl substituted Diels–Alder adducts to either *endo*- or *exo*-isomers [6,20].

Table 1
^{1}H-NMR spectral data of compounds **9**, **10**, **15**, **17**, **19–24**, **26**, **30–33** (300 MHz, $CDCl_3$, TMS); δ (ppm), J (Hz)

Compound	C_5H_5	C_5H_4	CH_2	CH	CH_3, Ar, OH
9	4.58 s (5H)	5.18 m (2H), 5.63 m (2H)	1.44 m (2H), 1.75–1.90 m (4H), 2.20–2.80 m (4H)	8.14 s (1H)	2.09 s (3H)
10	4.65 s (10H)	5.26 m (4H), 5.72 m (4H)	1.93 m (4H), 2.89 m (4H)	8.25 s (2H)	2.18 s (3H)
15	4.14 s (5H)	4.38 m (2H), 4.48 m (2H)	1.78 m (6H), 2.67 m (4H)	7.30 s (1H)	–
17	4.08 s (5H)	4.19 m (1H), 4.21 m (1H), 4.31 m (1H), 4.35 m (1H)	1.38 m (2H), 1.56 m (1H), 1.88 m (3H), 1.93 m (3H), 2.75 m (1H)	6.39 s (1H)	1.33 s (3H), 1.61 s (1H)
19	4.11 s (5H)	4.25 m (1H), 4.48 m (1H), 4.69 m (2H)	1.68 m (2H), 1.83 m (4H), 2.43 m (2H), 2.66 m (2H), 5.03 d (2H), $J=2.4$	6.29 s (1H)	–
E-**20**	4.10 s (5H)	4.22 m (2H), 4.37 m (2H)	1.73 m (4H), 2.17 m (2H), 2.47 m (2H)	5.63 m (1H), $J=5.4$, 6.12 s (1H)	1.93 s (3H)
Z-**20**	4.12 s (5H)	4.14 m (2H), 4.30 m (2H)	1.83 m (4H), 2.21 m (2H), 2.39 m (2H)	5.39 m (1H), $J=6.4$, 5.89 s (1H)	1.88 s (3H)
21a	4.12 s (5H), 4.14 s (5H)	4.24 m (2H), 4.26 m (2H), 4.45 m (2H), 4.47 m (2H)	1.66 m (8H), 1.79 m (8H), 2.40 m (2H), 2.65 m (2H)	4.21 d (1H), $J=10.8$; 5.54 d (1H), $J=10.8$; 7.27 s (1H)	1.84 s (3H)
21b	4.13 s (5H), 4.16 s (5H)	4.22 m (4H), 4.37 m (4H)	1.84 m (6H), 2.17 m (4H), 2.47 m (6H), 2.77 m (4H)	4.26 d (1H), $J=9.6$; 6.30 d (1H), $J=9.6$; 7.40 s (1H)	1.92 s (3H)
22a	4.11 s (5H)	3.89 m (1H), 4.07 m (1H), 4.09 m (1H), 4.11 m (1H)	1.67–1.88 m (4H), 2.25 m (2H), 2.44 m (4H), 2.67 m (2H)	3.14 m (1H), 3.22 dd (1H), $J=5.7$, 9.6; 3.80 d (1H), $J=5.7$	7.00–7.03 m (2H), 7.35–7.40 m (3H)
22b	4.10 s (5H)	4.06 m (1H), 4.12 m (2H), 4.14 m (1H)	1.53 m (3H), 1.82 m (3H), 2.05 m (1H), 2.24 m (1H), 2.41 m (2H), 2.70 m (2H)	3.11 m (1H), 3.20 dd (1H), $J=6.3$, 9.6; 3.78 d (1H), $J=6.3$	6.95–6.98 m (2H), 7.27–7.37 m (3H)
23	4.16 s (5H)	4.45 m (2H), 4.56 m (2H)	1.75 m (4H), 1.94 m (2H), 3.05 m (2H), 3.83 m (2H)	7.65 s (1H)	7.32–7.48 m (5H)
24	4.12 s (5H), 4.19 s (5H)	4.00 m (2H), 4.09 m (2H), 4.15 m (2H), 4.28 m (2H)	1.28–1.50 m (4H), 1.61–1.82 m (4H), 2.08–2.34 m (4H), 2.51–2.83 m (8H), 3.12 d (2H), $J=8.4$	3.64 m (1H), $J=8.4$; 4.42 s (1H)	1.94 s (3H), 2.98 s (6H), 6.54 d (2H), 6.69 d (2H), $J=8.1$
26	4.10 s (5H), 4.12 s (5H)	4.18 m ((2H), 4.20 m (2H), 4.31 m (1H), 4.33 m (1H), 4.35 m (1H), 4.38 m (1H)	1.40–1.60 m (2H), 1.80–2.06 m (4H), 2.20 m (1H), 2.78 m (1H)	3.61 kd (1H), $J=6.9$, 1.5; 5.95 d (1H), $J=1.5$; 6.01 s (1H)	1.31 d (3H), $J=6.9$
30	4.08 s (5H), 4.10 s (5H), 4.13 s (5H), 4.16 s (5H)	4.03–4.35 m (16H)	1.30–1.50 m (4H), 1.72–1.88 m (4H), 2.24–2.43 m (4H), 2.52–2.68 m (4H), 3.06 d (2H), $J=9.06$	3.71 t (1H), $J=9.06$, 4.70 s (1H), 6.18 s (1H), 6.29 s (1H)	2.01 s (3H), 3.02 s (6H), 6.49 d (2H), 6.74 d (2H), $J=8.2$
31	4.07 s (5H), 4.10 s (5H), 4.12 s (5H), 4.14 s (5H)	3.98 m (2H), 4.02 m (2H), 4.06 m (2H), 4.11 m (2H), 4.18 m (2H), 4.21 m (2H), 4.24 m (2H), 4.32 m (2H)	1.35–1.60 m (4H), 2.16–2.60 m (4H), 2.81–3.10 m (4H), 3.14–3.22 m (4H), 3.68 d (2H), $J=6.8$	3.79 m (1H), $J=6.8$; 4.57 s (1H), 4.63 s (1H), 6.25 s (1H)	1.97 s (3H), 3.01 s (6H), 6.40 d (2H), 6.61 d (2H), $J=8.5$
32	4.01 s (5H), 4.04 s (5H), 4.08 s (5H), 4.11 s (5H)	3.93 m (2H), 3.95 m (2H), 4.03 m (2H), 4.07 m (2H), 4.13 m (2H), 4.16 m(2H), 4.19 m (2H), 4.22 m (2H)	1.26–1.53 m (4H), 1.68–1.80 m (4H), 2.43–2.65 m (4H), 2.81–3.05 m (4H), 3.44 d (2H), $J=6.3$	3.60 t (1H), $J=6.3$; 4.75 s (1H), 6.18 s (1H), 6.40 s (1H)	1.94 s (3H), 3.05 s (6H), 6.58 d (2H), 6.74 d (2H), $J=9.1$
33	4.05 s (5H), 4.09 s (5H), 4.16 s (5H), 4.20 s (5H)	4.01 m (2H), 4.07 m (2H), 4.14 m (4H), 4.19 m (4H), 4.24 m (2H), 4.32 m (2H)	1.42–1.61 m (4H), 1.74–1.93 m (4H), 2.14–2.40 m (4H), 2.61–2.73 m (4H), 3.18 m (2H)	3.67 td (1H), $J=6.2$, 1.2; 3.86 t (1H), $J=6.8$; 6.24 d (1H), $J=1.2$; 6.29 s (1H), 6.52 s (1H)	1.94 s (3H)

Complete analysis of the ^{1}H-NMR spectra of compounds **22a** and **22b** was complicated due to a number of circumstances (i.e. partial overlapping of the signals related to $-CH_2-$ groups and masking of the multiplets related to H^1, H^2 and H^3 with that related to the C_5H_4 fragment). As was shown earlier for compounds of the type under consideration, at least one of the protons of the C_5H_4 ring always exhibits in the ^{1}H-NMR spectrum a signal at higher field than the singlet related to the C_5H_5 group in *endo*-isomers and never in *exo*-isomers [6,20]. Thus, the *endo*-structure should be preferably assigned to **22a**, in which the signals for all the protons of the C_5H_4 fragment are located in higher field than the singlet for the protons of unsubstituted cyclopentadienyl ring in ferrocene, and not to **22b**.

We also found that compounds **22a** and **22b** undergo smooth oxidative dehydrogenation by atmospheric oxygen when subjected to TLC on SiO_2 to form phthalimide derivative **23** as the end product.



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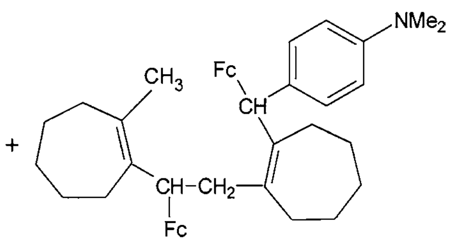
Similar oxidative dehydrogenation of the *N*-phenylmaleimide Diels–Alder adducts has been described by us previously [17]. Compound **20** represents a ferrocenyl-1,3-diene with a fixed *s*-*trans*-configuration of the double bonds. It does not give Diels–Alder adducts with *N*-phenylmaleimide. The treatment of the diene **20** with HBF_4 results in the original tetrafluoroborate **9** in quantitative yield.

Further we have found that the linear dimer **21a**,**b** (ca. 2.1:1) is formed in good yield upon mixing equimolar amounts of diene **19** and salt **9** with *N*,*N*-dimethylaniline as a nucleophile in the final reaction step. In addition, a product of *N*,*N*-dimethylaniline *p*-alkylation with an intermediate dimeric allylic cation (compound **24**) was isolated.

$$9 + 19 \longrightarrow 21a,b$$



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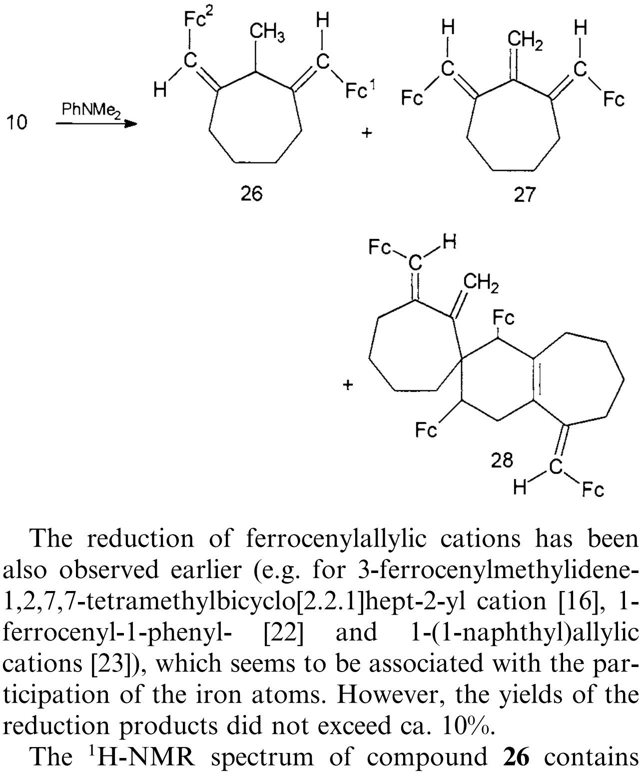
No cyclodimeric products were detected in this reaction, which is in full accord with suggestions on the role of the electronic factors on the cyclization of intermediate, linear dimeric cations (see above).

2.4. Chemical transformations of tetrafluoroborate **10**

In our opinion, the chemical behavior of tetrafluoroborate **10** should resemble that of (3-ferrocenylmethylidene - 2 - methylcyclohex - 1 - enyl)ferrocenylmethylium tetrafluoroborate (**25**). The reaction of the latter with *N*,*N*-dimethylaniline results mainly in all possible alkylation products by monomeric and dimeric linear and cyclic cations [21].

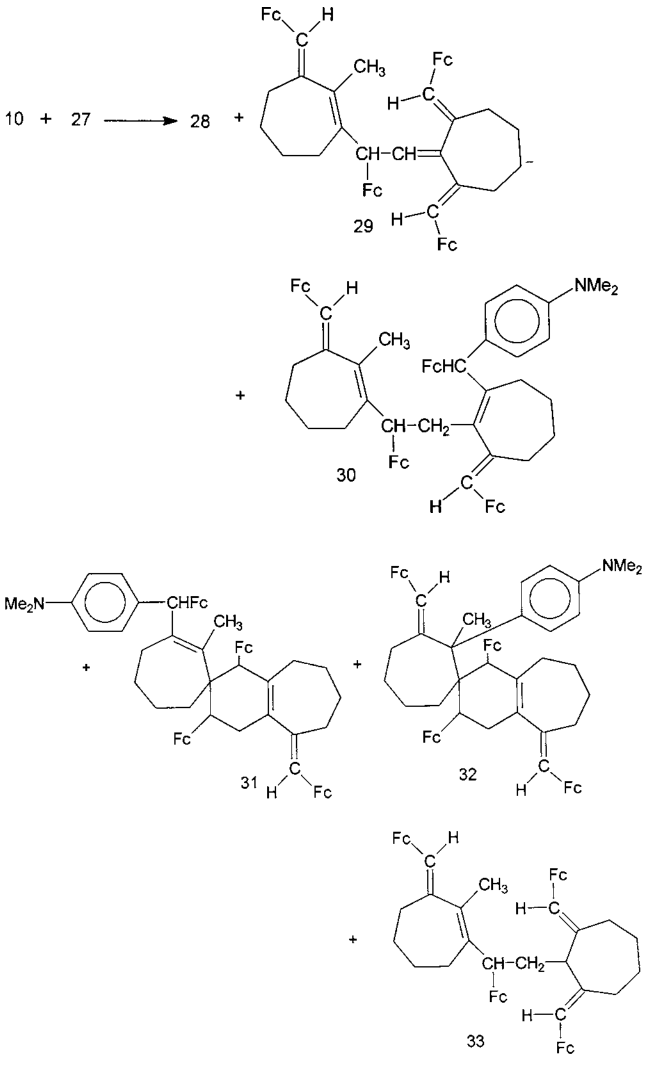
However, unlike **25**, the cation **10** is preferentially reduced to 1,3-bis(ferrocenylmethylidene)-2-methylcycloheptane (**26**, ca. 65%) when treated with *N*,*N*-dimethylaniline. Simultaneously, deprotonation and cyclodimerization occur leading to bisferrocenyltriene (**27**, ca. 7%) and a *spiro* compound (**28** [17], ca. 8%). No products of *N*,*N*-dimethylaniline alkylation were detected.



The reduction of ferrocenylallylic cations has been also observed earlier (e.g. for 3-ferrocenylmethylidene-1,2,7,7-tetramethylbicyclo[2.2.1]hept-2-yl cation [16], 1-ferrocenyl-1-phenyl- [22] and 1-(1-naphthyl)allylic cations [23]), which seems to be associated with the participation of the iron atoms. However, the yields of the reduction products did not exceed ca. 10%.

The ^{1}H-NMR spectrum of compound **26** contains two different signals for the olefinic protons of the Fc^{1}CH= and Fc^{2}CH= groups ($\delta_1 = 5.95$, d, $J = 1.5$ Hz; $\delta_2 = 6.01$, s), which suggests their nonequivalence. Taking into account the equivalence of the analogous protons in the original chalcone **16** and alcohol **18** (see Table 1) and (*E*,*E*)-configuration of the double bonds in these compounds [24], one may suggest that the reduction of the cation **10** is accompanied by *Z*-/*E*-isomerization of one of the ferrocenylmethylidene fragments [19]. Thus, the structure (*Z*,*E*)-1,3-bis(ferrocenylmethylidene)-2-methylcycloheptane should be ascribed to compound **26**.

To avoid formation of considerable amount of the reduction product **26**, we have performed the reaction of salt **10** with pure triene **27** under conditions identical with those described above for the rreaction of tetrafluoroborate **9** with diene **19**. As expected, the following compounds were isolated following treatment of the reaction mixture with *N*,*N*-dimethylaniline: cyclodimer **28** [17], linear dimer **29** [17], three products of *p*-alkylation of *N*,*N*-dimethylaniline (**30–32**), and a reduction product of dimeric linear cation **33**.



All of the reaction products were isolated by column chromatography on alumina (activity III) and by TLC (silica gel). The ^{1}H- and ^{13}C-NMR spectral data of the obtained compounds **30–33** are listed in Tables 1 and 2. The structures of dimers **28** and **29** were discussed earlier [17].

According to the NMR data the dimerization and cyclodimerization occur diastereoselectively. Compounds **28–32** were isolated in just one diastereomeric form. However, their spatial structures are not established yet.

The ^{1}H-NMR spectral data for compounds **30–32**, viz. the number of proton signals, their chemical shift values, and spin–spin coupling constants for aliphatic and olefinic protons, corroborate the assigned structures. Additional information is gained from the ^{13}C-NMR spectra of these compounds. The presence of four C_{ipso} atoms of the ferrocene fragments together with the presence of signals for four nonsubstituted ferrocene cyclopentadienyl rings unambiguously prove their dimeric character. The presence of signals for C_{spiro} atoms proves the structure of compounds **31** and **32**. The number of signals for C, CH, CH_2, and CH_3 groups in compounds **30–32** fully corresponds to their structures.

Obviously, *p*-alkylation of *N*,*N*-dimethylaniline with intermediate dimeric cations **13**, **14a**, and **14b**, deprotonation of these cations, and reduction of the linear dimeric cation **13** are competitive reactions, which results in virtually all theoretically possible reaction products.

3. Conclusions

Thus, we managed to isolate the alkylation products of *N*,*N*-dimethylaniline with mesomeric cyclic dimeric allylic cations **14a** and **14b** together with the alkylation product of *N*,*N*-dimethylaniline with the linear dimeric cation **13**. These results may be regarded as direct evidence for the existence of all consecutive steps in a stepwise mechanism of cationic cyclodimerization of 1,3-dienes, viz. 1) the addition of a carbocation to the methylene group of 1,3-diene through its secondary carbocationic center, which results in a linear dimeric allylic cation of the type **3**; 2) the possibility for intramolecular cyclization of the cation **3** into a cyclic carbocation **4**; 3) base-induced deprotonation of (ferrocenyl)methylcarbocation **4** leading to cyclodimers containing a CH_2= fragment in the molecules of the type **5**.

4. Experimental

All ^{1}H- and ^{13}C-NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) in $CDCl_3$ solutions (except for ^{1}H-NMR spectra of tetrafluoroborates **9** and **10** recorded in CH_2Cl_2) with TMS as internal standard (Tables 1 and 2). The elemental analysis data are listed in Table 3.

Column chromatography was carried out on Al_2O_3 (Brockmann activity III), TLC was performed on plates with a fixed SiO_2 layer.

Table 2
^{13}C-NMR spectroscopy data for compounds **17**, **22**, **24**, **26**, **30–32** (75 MHz, $CDCl_3$, TMS); δ (ppm)

Assignment	**17**	**22a**	**22b**	**24**	**26**	**30**	**31**	**32**
C_5H_5	69.05	68.72	68.67	68.59, 68.91	68.93, 68.96	68.35, 68.53, 68.74, 69.04	68.53, 68.72, 69.03, 69.36	68.50, 68.72. 68.91, 69.11
C_5H_4	68.33, 68.45, 68.51, 69.72	67.16, 67.93, 68.87, 69.06	67.40, 68.20, 68.45, 68.80	66.72, 66.84, 67.11, 67.35, 67.59, 68.14, 68.73, 70.15	68.12, 68.15, 68.23, 68.25, 68.37, 68.40, 69.26, 69.54	65.76, 65.98, 66.07, 66.44, 66.61, 66.83, 67.18, 67.65, 68.14, 68.28, 68.56, 68.79, 68.98, 69.32, 69.51, 69.85	66.72, 66.79, 66.96, 67.19, 68.05, 68.34, 68.48, 68.61, 68.90, 69.12, 69.50, 69.56, 69.83, 70.05, 70.13, 71.12	66.41, 66.62, 66.81, 66.90, 67.82, 68.21, 68.43, 68.56, 68.83, 69.04, 69.46, 69.84, 70.12, 70.21, 70.84, 71.55
C_{ipso}Fc	82.23	84.62	84.70	79.98, 82.17	82.86, 82.90	78.84, 82.09, 82.87, 83.70	79.24, 82.81, 92.05, 94.13	79.15, 81.97, 92.10, 93.30
CH_2	23.66, 28.19, 29.58, 30.29, 42.88	22.24, 27.25, 29.36, 31.83, 35.86, 36.25	26.69, 26.85, 28.39, 29.11, 31.58, 32.15	20.12, 20.31, 21.17, 21.28, 22.18, 22.32, 24.85, 25.01, 28.63, 29.17, 31.01	28.75, 31.57, 32.61, 34.80	20.05, 20.28, 21.10, 22.14, 24.81, 26.19, 28.32, 30.43, 30.89	26.11, 26.28, 27.36, 27.40, 29.70, 29.84, 30.33, 30.58, 40.79	24.83, 26.15, 26.31, 28.27, 29.91, 30.16, 30.73, 33.50, 33.62
CH_3	19.89	–	–	18.25, 40.06	18.21	18.56, 41.12	20.02, 47.44	17.88, 39.98
C	33.50, 137.26	135.34, 137.36	131.73, 132.32	127.83, 129.45, 131.41, 134.17, 145.18	143.40, 145.00	129.92, 130.40, 131.18, 131.24, 134.86, 135.22, 147.72	47.80, 133.60, 133.66, 134.21, 137.06, 138.39, 148.52	47.63, 53.06, 129.82, 132.12, 134.81, 137.26, 145.60
CH=	120.53	126.61, 128.76, 128.95	126.64, 128.25, 128.71	127.86, 128.53, 129.41, 130.72	119.31, 122.98	112.19, 113.91, 128.08, 129.81, 130.40, 134.15	112.27, 122.99, 129.03, 129.30 131.42	116.04, 118.20, 127.82, 129.80, 136.11 136.32
CH	–	39.12, 44.06, 48.12	39.49, 41.23, 48.39	44.13, 45.05	42.61	47.26, 48.30	41.02, 47.20, 57.61	47.62, 56.80
C=O	–	177.68, 178.99	177.64, 178.90	–	–	–	–	–
C_{ipso}	–	148.97	149.25	137.30	–	139.74	143.86	142.10

*4.1. 2-Ferrocenylmethylidenecycloheptanone **(15)** and 2,7-bis(ferrocenylmethylidene)cycloheptanone **(16)***

Obtained from ferrocenecarbaldehyde and cycloheptanone in *tert*-butyl alcohol in the presence of Bu^tOK. The yield of chalcone **15** was 43%, orange crystals, m.p. 78–79°C and the yield of chalcone **16** was 38%, m.p. 173–174°C (lit. [17], m.p. 173–174°C).

*4.2. Alcohols **17** and **18***

Synthesized from chalcones **15** and **16**, respectively, and methyllithium [6,9]. The yield of alcohol **17** was 71.5%, yellow crystals, m.p. 122–123°C; the yield of alcohol **18** was 74%, orange crystals, m.p. 166–168°C (lit. [17], m.p. 167–168°C).

*4.3. Tetrafluoroborates **9** and **10***

Synthesized by addition of HBF_4 etherate to an ethereal solution of the corresponding alcohols **17** and **18**. The precipitated salts **9** and **10** were separated by filtration, washed with dry ether and dry hexane on the filter, and dried in vacuo. The yield of salt **9** was 78%, black powder, m.p. 236–237°C; the yield of salt **10** was 84%, black crystals, m.p. ~320°C (dec.).

*4.4. Reaction of tetrafluoroborate **9** with N,N-dimethylaniline*

N,*N*-Dimethylaniline (1.2 g, 10 mmol) was added to a solution of salt **9** (1.47 g, 5 mmol) in dry CH_2Cl_2 (50 ml) in a dry inert atmosphere. The mixture was stirred for 1 h at 20°C, then the excess of *N*,*N*-dimethylaniline was removed by washing the solution with water, 1% HCl, and again with water. The organic layer was dried with Na_2SO_4 and the solvent was evaporated in vacuo. Chromatography of the residue on alumina in hexane afforded 3-ferrocenylmethylidene-2-methylcycloheptene (**20**) (0.43 g, 28%), orange crystals, m.p. 101–102°C; 1-ferrocenylmethylidene-2-methylidenecycloheptane (**19**) (0.40 g, 26%), orange crystals, m.p. 77–78°C; and 1-ferrocenylmethylidene-2-[2-ferrocenyl-2-(2-methylcyclohept-1-enyl)]ethylidenecycloheptane (**21a**,**b**) (ca. 2:1, 0.30 g, 19%), yellow powder, m.p. 175–177°C.

*4.5. Reaction of tetrafluoroborate **10** with N,N-dimethylaniline*

This reaction was conducted as for the salt **9**. Starting from tetrafluoroborate **10** (2.95 g, 5 mmol) and *N*,*N*-dimethylaniline (1.2 g, 10 mmol) in 100 ml of CH_2Cl_2 the following products were obtained: diene **26** (1.5 g, 60%), orange needles, m.p. 136–137°C; triene **27** (0.25 g, 10%), orange plates, m.p. 147–148°C (lit. [17], m.p. 148°C); and *spiro*-cyclodimer **28**, orange powder, m.p. 255–256°C (lit. [17], m.p. 254–256°C).

*4.6. Reaction of s-cis-ferrocenyldiene **19** with N-phenylmaleimide*

A mixture of dienes **19** (0.3 g, 1 mmol) and 0.3 g of *N*-phenylmaleimide in 50 ml of dry benzene was boiled under reflux for 1 h. The solvent was removed in vacuo, and the residue was chromatographed on alumina (hexane) to give *N*-phenyl-1-ferrocenylbicyclo[5.4.0]undec-10(11)ene-2,3-dicarboximide (**22**) (0.35 g, 72%) as a mixture of *endo*- and *exo*-isomers (**22a** and **22b**, ca. 1:1), yellow crystals, m.p. 161–163°C. The isomers were separated by TLC on silica gel (hexane–benzene, 3:1),

Table 3
Elemental analysis data for the obtained compounds

Compound	Anal. Found (%)				Formula	Calc. (%)			
	C	H	Fe	N, F		C	H	Fe	N, F
9	58.03	5.71	14.37	19.42	$C_{19}H_{23}BF_4Fe$	57.91	5.88	14.18	19.29
10	61.19	5.52	18.71	13.04	$C_{30}H_{31}BF_4Fe_2$	61.06	5.30	18.93	12.88
15	70.29	6.31	18.25	–	$C_{18}H_{20}FeO$	70.14	6.54	18.12	–
17	70.53	7.65	17.01	–	$C_{19}H_{24}FeO$	70.38	7.46	17.22	–
19	74.70	7.41	18.03	–	$C_{19}H_{22}Fe$	74.52	7.24	18.24	–
20	74.36	7.17	18.38	–	$C_{19}H_{22}Fe$	74.52	7.24	18.24	–
21a,**b**	74.73	7.09	18.31	–	$C_{38}H_{44}Fe_2$	74.52	7.24	18.24	–
22a,**b**	72.63	6.03	11.84	2.74	$C_{29}H_{28}FeNO_2$	72.81	5.90	11.68	2.93
23	73.36	5.11	11.99	2.73	$C_{29}H_{25}FeNO_2$	73.27	5.30	11.75	2.95
24	75.41	7.54	15.36	2.04	$C_{46}H_{56}Fe_2N$	75.20	7.70	15.20	1.90
26	71.66	6.18	22.41	–	$C_{30}H_{32}Fe_2$	71.45	6.40	22.15	–
28	71.99	5.84	22.47	–	$C_{60}H_{60}Fe_4$	71.74	6.02	22.24	–
30	72.30	6.48	19.73	1.40	$C_{68}H_{71}Fe_4N$	72.55	6.36	19.85	1.24
31	72.32	6.51	20.03	1.35	$C_{68}H_{71}Fe_4N$	72.55	6.36	19.85	1.24
32	72.41	6.21	19.69	1.12	$C_{68}H_{71}Fe_4N$	72.55	6.36	19.85	1.24
33	71.78	6.38	22.01	–	$C_{60}H_{62}Fe_4$	71.60	6.20	22.20	–

the yield of compound **22b** was 0.14 g, R_f 0.54, m.p. 172–173°C; the yield of the *endo*-adduct **22a** was 0.13 g, R_f 0.47, m.p. 191–192°C.

4.7. Oxidative dehydrogenation of *N*-phenylimides *22a*,*b*

Oxidative dehydrogenation of *N*-phenylimides **22a**,**b** was carried out analogously to the previously published procedure [18]. The yield of *N*-phenyl-1-ferrocenyl-6,7,8,9-tetrahydro-5*H*-benzocycloheptene-2,3-dicarboximide (**23**) was 58%, $R_f = 0.68$ (hexane–benzene, 2:1), red crystals, m.p. 214–215°C.

4.8. Reaction of tetrafluoroborate *9* with diene *19*

A solution of diene **19** (0.61 g, 2 mmol) in 50 ml of dry CH_2Cl_2 was added to a solution of salt **9** (0.86 g, 2.2 mmol) in 50 ml of the same solvent. The mixture was stirred for 30 min at 20°C and then *N*,*N*-dimethylaniline (0.5 ml) was added. Stirring was continued for an additional 30 min, then the reaction mixture was washed with water, 1% HCl, and again with water. The organic layer was dried with Na_2SO_4 and the solvent was evaporated in vacuo. Chromatography of the residue on alumina (4:1 hexane–chloroform) afforded compound **21a**,**b** (ca. 2.1:1), m.p. 174–176°C, and 1-[(4-dimethylaminophenyl)ferrocenyl]methyl-2-[2-ferrocenyl-2-(2-methylcyclohept-1-enyl)]ethylcyclohept-1-ene (**24**) (0.14 g, 11%), yellow powder, m.p. 218–219°C.

4.9. Reaction of tetrafluoroborate *10* with triene *27*

Analogously, the reaction of salt **10** (1.25 g, 2.1 mmol) with triene **27** (1.0 g, 2 mmol) followed by the work-up and chromatography on Al_2O_3 resulted in two fractions (1) yield 1.12 g, eluted with hexane and (2) yield 0.83 g, eluted with a 2:1 hexane–benzene mixture.

Each fraction was rechromatographed on SiO_2 in a 2:1 hexane–benzene mixture to yield (from fraction 1): 1,3-bis(ferrocenylmethylidene)-2-[2-ferrocenyl-2-(3-ferrocenylmethylidene-2-methylcyclohept-1-enyl)]ethylcycloheptane (**33**) (0.16 g, 8%), ($R_f = 0.70$), yellow powder, m.p. 198–199°C; 1,3-bis(ferrocenylmethylidene)-2-[2-ferrocenyl-2-(3-ferrocenylmethylidene-2-methylcyclohept-1-enyl)]ethylidenecycloheptane (**29**) (0.18 g, 9%) ($R_f = 0.66$), orange powder, m.p. 183–185°C (lit. [17], m.p. 183–184°C); and *spiro*[3-ferrocenylmethylidene-2-methylidenecycloheptane-1,7′-(6,8-diferrocenyl-1-ferrocenylmethylidene-2,3,4,5,6,7,8,9-octahydro-1*H*-benzocycloheptene)] (**28**) (0.62 g, 31%) ($R_f = 0.54$), yellow powder, m.p. 254–255°C (lit. [17], m.p. 254–256°C).

From fraction 2 were obtained: 1-[(4-dimethylaminophenyl)ferrocenyl]methyl-2-[2-ferrocenyl-2-(3-ferrocenylmethylidene-2-methylcyclohept-1-enyl)]ethyl-3-ferrocenylmethylidenecyclohept-1-ene (**30**) (0.16 g, 7%), ($R_f = 0.48$), orange oil; *spiro*[2-(4-dimethylaminophenyl)-3-ferrocenylmethylidene-2-methylidenecycloheptane-1,7′-(6,8-diferrocenyl-1-ferrocenylmethylidene-2,3,4,5,6,7,8,9-octahydro-1*H*-benzocycloheptene)] (**32**) (0.25 g, 11%) ($R_f = 0.38$), yellow powder, m.p. 216–217°C, and *spiro*{3-[(4-dimethylaminophenyl)-ferrocenyl]methyl-2-methylcyclohept-2-ene-1,7′-(6,8-diferrocenyl-1-ferrocenylmethylidene-2,3,4,5,6,7,8,9-octahydro-1*H*-benzocycloheptene)} (**31**) (0.29 g, 13%) ($R_f = 0.30$), yellow powder, m.p. 237–238°C.

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