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Mutual *Z*-/*E*-isomerization of ferrocenylmethylene- and arylidene-substituted carbo- and heterocycles

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Abstract

The treatment of *Z*-2-ferrocenylmethylene-, *Z*-2-arylidene-3-quinuclidinones and 3-methylene-quinuclidines, as well as *E*-3-ferrocenylmethylenecamphor, -menthone, and -cyclohexanone with $NaBPh_4$ in acetic acid results in their reversible *Z*-/*E*-isomerization. The reaction proceeds via hydroxyallyl and crotyl carbocations with a fixed *s-cis*-conformation.

Keywords: Ferrocene; Quinuclidinone; Carbocation; *Z*-/*E*-isomerization

1. Introduction

Incorporation of a ferrocene fragment into a molecule of an organic compound imparts the chemical and physicochemical properties that are absent or little manifested in the parent substance. This allows one to use ferrocene derivatives as models suitable to reveal the features that have not been observed in, albeit inherent to, the analogous classes of compounds [1,2]. In addition, ferrocene-containing compounds often possess unexpected biological activity, which is rationalized as being due to their different membrane-permeation properties and anomalous metabolism [3–6].

Recently, we have reported on the sufficiently high antiviral activity of compounds containing ferrocene and quinuclidine [7] and camphane [8] moieties. They were synthesized starting from *Z*-2-ferrocenylmethylene-3-quinuclidinone **1** or *E*-3-ferrocenylmethylenecamphor **2**, which in turn were prepared by a base-promoted, high-yielding condensation of 3-quinuclidinone hydrochloride or camphor, respectively, with ferrocenecarbaldehyde. *Z*- and *E*-Configuration of C(1)=C(2) double bond was retained in *s-cis*-ferrocenyl-1,3-dienes **3** and **4** obtained from the chalcones **1** and **2**:

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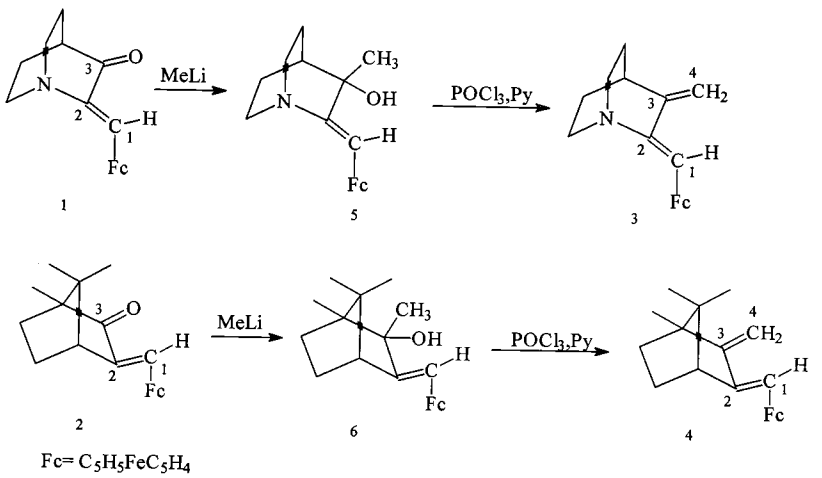
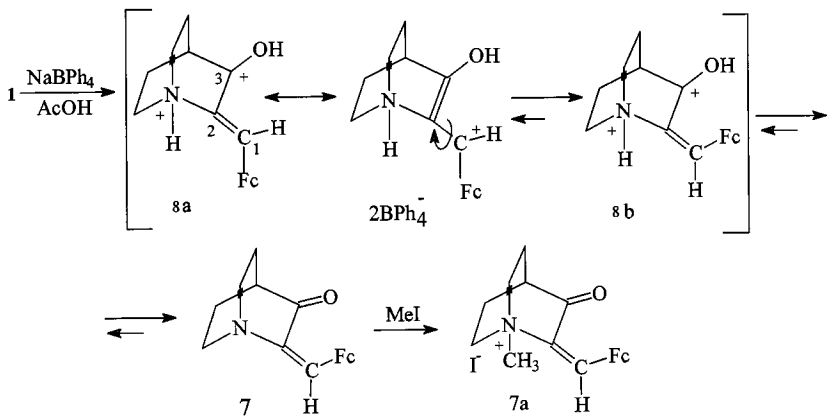


It is well known that isomeric compounds may possess different biological activity. Therefore, the comparative structure-activity study of derivatives of isomeric (*E*- and *Z*-) compounds with *s*-cisoid conformation is desirable. However, the methods of synthesis of such difficult to access geometrical isomers with 'internal' position of the bulky substituents in compounds with *s*-cisoid conformation have never been reported in literature. In the present work, we describe the *Z*-/*E*-isomerization of ferrocenylmethylene and arylidene derivatives of some carbo- and heterocycles which allows to obtain pure *Z*- and *E*-isomers with satisfactory yield.

2. Results and discussion

2.1. Mutual Z-/E-isomerization of 2-ferrocenylmethylene- and 2-arylidene-substituted 3-quinuclidinones

We have found that *Z*-2-ferrocenylmethylene-3-quinuclidinone **1** underwent smooth isomerization on treatment with $NaBPh_4$ in acetic acid to give 80% of the *E*-isomer **7**. The isomerization occurs presumably via the ferrocenylhydroxyallyl carbenium–ammonium ion **8**:



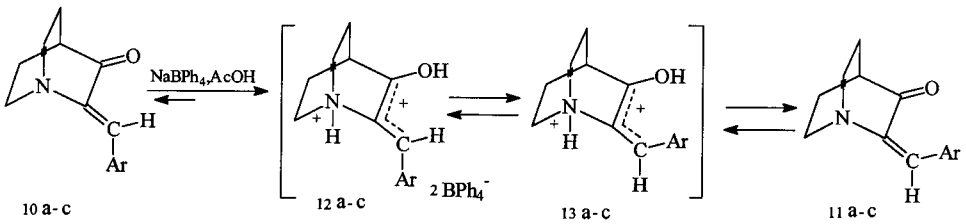
The hindered rotation around the bond with the order of 1.5 [9–11], the geometry of allyl cations and steric interactions between bulky substituents therein [11–13] are studied with hydroxyallyl carbocations including ferrocenyl-substituted ones [14]. Ferrocenylchalcones that have been used previously for the protonation and generation of hydroxyallyl cations possessed linear structure and existed as mixtures of *s-cis*- and *s-trans*-conformers. With account of chirality of α-ferrocenylcarbocations [13,14], the cations could be present in solutions as mixtures of two diastereomers due to the free rotation around the C(2)–C(3) ordinary bond in the initial compounds [14].

Ferrocenylmethylenequinuclidinone **1** exists in a fixed *s-cis*-conformation, and the isomerization can only result from the rotation around the C(1)···C(2) bond of the order 1.5 despite the hindered character of this rotation. In our opinion, this is facilitated by the following factors.

1. The pronounced ability of ferrocene to stabilize the positive charge in α-ferrocenylcarbocations [9,10]. In the absence of other potent stabilizers of the carbocationic center at position 3 of the allylic system, this results in the concentration of the positive charge at position 1 (see the above scheme).
2. Strong steric interactions of the 'outer' and 'apical' *Z* substituents [15–17] that may manifest themselves only in the change in arrangement of substituents relative to the C(1)···C(2) bond.

3. The effect of a bulky anion BPh_4^-, which facilitates the isomerization with the 'inward' orientation of the OH and Fc groups. This effect should be manifested the most strongly for nitrogenous heterocycles possessing an additional cationic center.

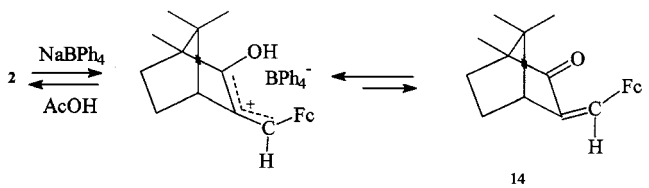
A detailed examination of this process has shown that *Z*-2-arylidene-3-quinuclidinones **10a–c** isomerize under similar conditions to give 40–50% of the *E*-isomers **11a–c**:



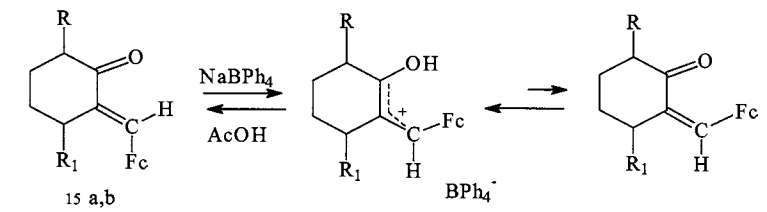
Ar= Ph(a); n-C_6H_4-F (b); 2,4-C_6H_3/ $(OCH_3)_2$ (c)

2.2. Mutual *Z*-/*E*-isomerization of ferrocenylmethylene-substituted camphor and cyclohexanones

E-3-Ferrocenylmethylenecamphor **2** [8,18] also isomerizes to give 40% of the corresponding *Z*-isomer **14** on treatment with $NaBPh_4$ in acetic acid:



Likewise, ferrocenylmethylene-substituted cyclohexanones **15a,b** undergo *E*-/*Z*-isomerization, although the extent of inversion of configuration (ca. 20%) is much less than that for quinuclidine derivatives:



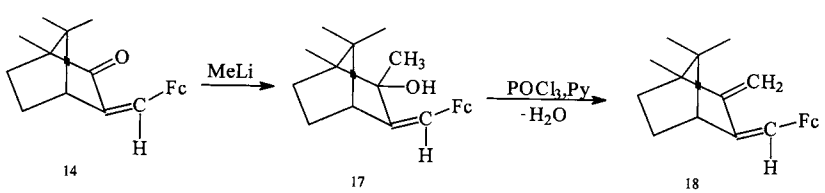
R=R_1= H (a)[18,19]; R=CH$(CH_3)_2$, R_1= CH_3 (b)

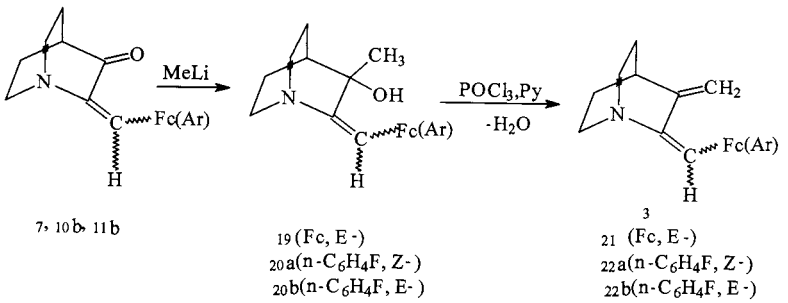
These data are in full agreement with the concept of the factors that favor the isomerization and confirm the suggestion on the participation of the tetraphenylborate anion in this process.

Satisfactory ^{1}H NMR spectra could be obtained in CF_3COOH, which show the protonation of the carbonyl group and the formation of hydroxyallyl carbenium–ammonium cations **8a** and **8b** thereby. Decomposition of the samples precluded monitoring of the dynamics of the chalcone *Z*-/*E*-isomerization.

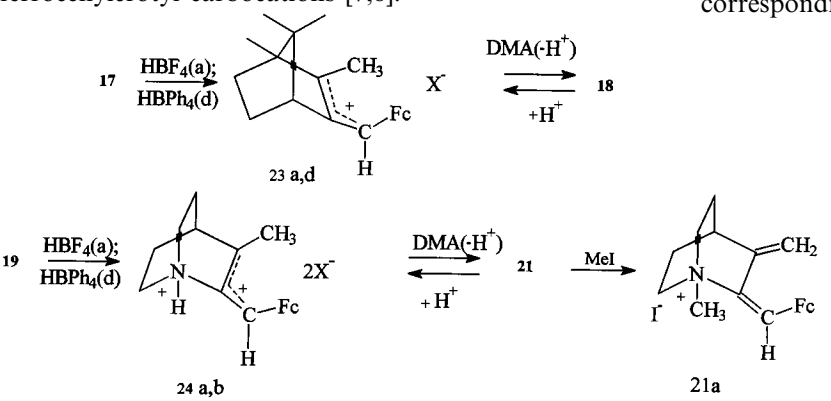
2.3. Synthesis of *Z*- and *E*-isomeric *s*-*cis*-1,3-dienes

The reaction of carbo- and hetero-cyclic *Z*- (**14** and **10b**) and *E*-chalcones (**7** and **11b**) with methyllithium afforded the corresponding alcohols (**17**, **19**, **20a**, **20b**). Their dehydration by POCl3 in pyridine resulted in 1,3-dienes (**18**, **21**, **22a**, **22b**) with the fixed *s*-*cis*-conformation of the double bonds:

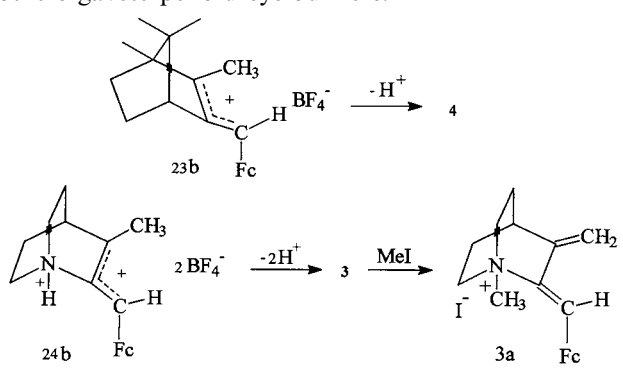




The dienes **18** (*Z*-) and **21** (*E*-) were also smoothly prepared by base-promoted deprotonation of salts of ferrocenylcrotyl carbocations [7,8]:



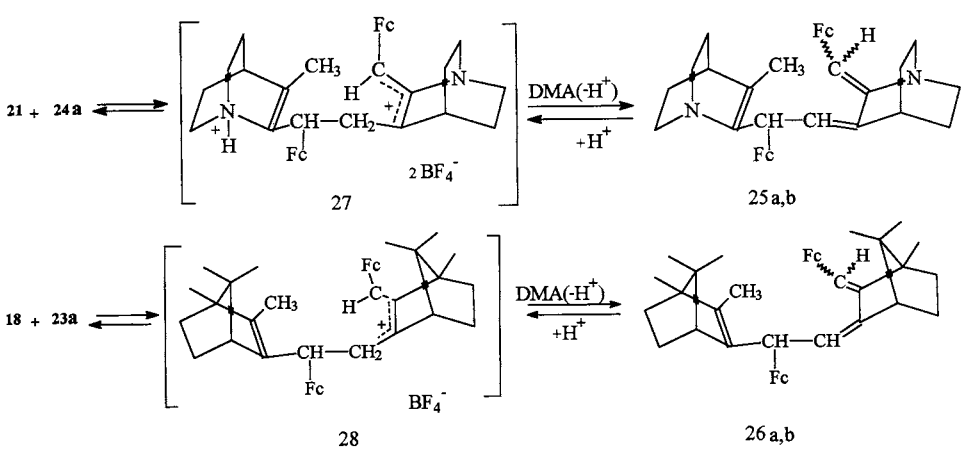
Of many salts of ferrocenylcrotyl carbocations studied so far [1,2,20,21] only **23b** and **24b** underwent deprotonation under analogous conditions, whereas all others gaveterpenoid cyclodimers.



Neither could *Z*- and *E*-2-arylidene-3-quinuclidinones **22a** and **22b** be prepared by deprotonation of the corresponding salts of arylcrotyl carbocations. Unlike ferrocenyl-substituted analogs, they underwent dimerization and polymerization resulting in a complex mixture of unidentified products.

*2.4. Synthesis and fragmentation reactions of the linear dimers of 1,3-dienes **21** and **18***

These dienes do not produce linear or cyclic dimers in acidic medium (proton-catalyzed dimerization) either, which is typical of many ferrocenyl-1,3-dienes [1,2,5,8,20–22]. The linear dimers **25** and **26** were obtained as mixtures of two isomers (**25a**:**25b** ca. 1:2, **26a**:**26b** ca. 1:1, according to NMR data) by the reaction of the *E*- and *Z*-dienes **21** and **18** with the corresponding *E*- and *Z*-carbocations **24a** and **23a**, respectively. One of the isomers (**25b**) was isolated in the pure state. The *E*- or *Z*-configuration of the dimers has not been assigned yet.



The linear dimers **25** and **26** are obviously formed upon base-promoted deprotonation of the intermediate, dimeric allylic carbocation salts **27** and **28**, respectively, which result from the addition of the secondary cationic center of the cations **24a** and **23a** at the methylene group of the dienes **21** and **18** [7,8,20,21].

The action of HBF_4 etherate on the dimers **25** and **26** results in their complete fragmentation, which is similar to that found earlier for terpenoid ferrocenylcyclodimers [23]. The fragmentation of the dimers **25a** and **25b** affords mixtures of isomeric tetrafluoroborates **24a** and **24b** (~3:1, ^{1}H NMR data), whereas that of **26a**,**b** gives a mixture of **23a** and **23b** (~2:3).

Obviously, the fragmentation is the process opposite to the dimerization. It occurs in the presence of large excess of a strong acid necessary to protonate the C(3)=C(4) double bond of the linear dimers (see the above scheme).

2.5. Mutual *Z*-/*E*-isomerization of *s*-*cis*-1,3-dienes

The formation of mixtures of isomeric linear dimers **25a**,**b** and **26a**,**b** from the homoisomeric reactants suggests that the isomerization accompanies the dimerization. Hence, either the original ferrocenylcrotyl cations **24a** and **23a** or the intermediate dimeric cations **27** and **28** undergo the isomerization in solutions. Therefore, we have studied by NMR spectroscopy the solution behaviour of the salts **24a**,**b** and **23a**,**b** in more detail.

The terafluoroborates **24a**, **24b**, **23a**, and **23b**, which were prepared as black powders from the alcohols **19**, **5**, **17**, and **6**, are sufficiently stable on storage in a dry, inert atmosphere. The ^{1}H NMR spectra of the salts **24b** and **23b** in CD_2Cl_2 revealed their gradual isomerization into **24a** and **23a**, respectively, which followed from the duplication of all the signals. In the respective equilibrium mixtures *A* and *B* after 16 h, the isomers **24a** and **23b** predominated (**24a**:**24b** ca. 3:1 and **23b**:**23a** ca. 3:2):

The mutual, reversible isomerization of the tetraphenylborate **24c** into **24d** and of **23c** into **23d**, and vice versa, occurs faster. The equilibrium is attained already after 5 h at ambient temperature, the isomer ratios in the mixtures *A* and *B* being **24c**:**24d** ca. 1:4 and **23c**:**23d** ca. 1:1.

Treatment of the equilibrium mixtures *A* and *B* with *N*,*N*-dimethylaniline yielded the isomeric *s*-*cis*-1,3-dienes: **3b** (16%), **21** (80%), **4** (45%), and **18b** (40%). The same results were obtained on the treatment of the alcohols **5** and **6b** with $NaBPh_4$ in acetic acid.

Obviously, the mutual *Z*-/*E*-isomerization of ferrocenylcrotyl carbocations **24b**/**24a**, **24c**/**24d**, **23b**/**23a**, and **23c**/**23d**, as well as the governing factors are the same as those discussed above for the ferrocenylhydroxyallyl carbocations.

2.6. Biological activity of the synthesized compounds

According to a preliminary biological assay, ferrocene-containing compounds **3a**, **7**, **7a**, **19**, **21**, **21a**, **25**, and **26** possess high antiviral (relative to smallpox, tick caused encephalitis, type I and II herpes viruses) and also antistaphylococcus activity. It should be mentioned, that the biological activity of water-soluble methyliodides is higher than that of the initial bases. In addition we observed higher biological activity of the *E*-isomeric derivatives of quinuclidine as compared to that of the corresponding *Z*-isomers.

3. Experimental

^{1}H and ^{13}C NMR spectra were recorded on a 'Gemini 200 Varian' spectrometer (200 and 50 MHz) for solutions in $CDCl_3$, CD_2Cl_2, and CF_3COOH with Me_4Si as the internal standard. Column chromatography was carried out on Al_2O_3 (activity grade III according to Brockmann).

3.1. *Z*-2-ferrocenylmethylene-3-quinuclidinone **1**

Z-2-ferrocenylmethylene-3-quinuclidinone **1** was obtained by a standard procedure [7] from ferrocenecarbaldehyde and 3-quinuclidinone hydrochloride in an aqueous-ethanolic alkali as dark-red crystals, yield 85%, m.p. 122–123°C [6].

3.2. *Z*-2-ferrocenylmethylene-3-hydroxyquinuclidinium-3-cation **8a**

Compound **1** was dissolved in CF^3COOH, and the ^{1}H NMR spectrum of *Z*-2-ferrocenylmethylene-3-hydroxyquinuclidinium-3-cation **8a** was recorded at 20°C, (δ): 2.12 (2 H, m), 2.28 (2 H, m), 2.98 (1 H, m), 3.25 (2 H, m), 3.71 (2 H, m), 5.68 (1 H, m, C_5H_4), 5.73 (1 H, m, C_5H_4), 5.78 (5 H, s, C_5H_5), 6.25 (2 H, m, C_5H_4), 8.05 (1 H, s, =CH–Fc), 8.40 (1 H, br.s, $^+$NH).

3.3. *Z*-2-Arylidene-3-quinuclidinones **10a–c**

Z-2-Arylidene-3-quinuclidinones **10a–c** were obtained analogously from the corresponding aromatic aldehydes and 3-quinuclidinone hydrochloride.

10a (71%), yellow crystals, m.p. 134–135°C [24].

10b (76%), yellow crystals, m.p. 119–120°C, ^{1}H NMR ($CDCl_3$), δ: 2.04 (4 H, m, CH_2), 2.65 (1 H, m, CH), 3.15 (4 H, m, CH_2), 6.99 (1 H, s, CH=), 7.07 (2 H, m, C_6H_4), 8.08 (2 H, m, C_6H_4). ^{13}C NMR ($CDCl_3$), δ:

25.79 (CH_2), 40.15 (CH), 47.34 (CH_2), 115.24, 115.53, 123.71, 134.01, 134.15 (CH), 144.13, 161.47, 206.11 (C), 147.5 (d, $^1J_{CF}$ 259.9 Hz, CF). Anal. Calcd. for $C_{14}H_{14}FNO$, %: C, 72.71; H 6.10; F, 8.21; N, 6.06. Found: C, 71.83; H, 5.89; F, 8.19; N, 5.84%.

10c (74%), yellow crystals, m.p. 102–103°C, ^{1}H NMR ($CDCl_3$), δ: 1.98 (4 H, m, CH_2), 2.60 (1 H, m, CH), 3.03 (4 H, m, CH_2), 3.76 (3 H, s, CH_3), 3.80 (3 H, s, CH_3), 6.50 (2 H, m, $J = 9.1$ Hz, C_6H_3), 7.53 (1 H, s, CH=), 8.63 (1 H, d, $J = 9.1$ Hz, C_6H_3). Anal. Calcd. for $C_{16}H_{19}NO_3$, %: C, 70.31; H 7.01; N, 5.12. Found: C, 70.48; H, 6.79; N, 5.27%.

3.4. *E*-3-ferrocenylmethylenecamphor **2**

A solution of ferrocenecarbaldehyde (2.1 g, 10 mmol) and camphor (2.3 g, 15 mmol) in dry benzene (100 ml) was added to a solution of Bu^{t}OK (from 0.1 g of metallic K) in dry Bu^{t}OH (20 ml), and the mixture was refluxed for 6 h. The solvent was evaporated in vacuo, and the residue was chromatographed on alumina to give *Z*-3-ferrocenylmethylenecamphor **14** and *E*-3-ferrocenylmethylenecamphor **2**.

14, eluted with hexane, yield 0.21 g (6%), red crystals, m.p. 78–79°C [18].

2, eluted with 3:1 hexane–benzene, yield 2.34 g (67%), dark-orange plates, m.p. 130–131°C (cf. [8,18]).

3.5. *E*-2-ferrocenylmethylenecyclohexanone **15a**

E-2-ferrocenylmethylenecyclohexanone **15a** was obtained by the standard procedure from ferrocenecarbaldehyde (10 mmol) and cyclohexanone (25 mmol) in aqueous-ethanolic alkali. The precipitate was filtered off and washed with ethanol to give 2,6-bis(ferrocenylmethylene)cyclohexanone (3.0 g, 60%), m.p. 163–164°C (cf. [18]). The filtrate was diluted with water (100 ml) and the product was extracted with benzene (3×50 ml). Following concentration of the extract and column chromatography on alumina with hexane as the eluent, the monochalcone **15a** was obtained, yield 0.3 g (10%), m.p. 113–114°C (cf. [18]).

3.6. *E*-3-ferrocenylmethylenementhone **15b** and its *Z*-isomer **16b**

E-3-Ferrocenylmethylenementhone **15b** and its *Z*-isomer **16b** were obtained analogously from ferrocenecarbaldehyde (2.1 g, 10 mmol) and menthone (2.3 g, 15 mmol).

16b, eluted with hexane, yield 0.18 g (5%), red crystals, m.p. 76–77°C. ^{1}H NMR ($CDCl_3$), δ: 0.68 (3 H, d, $J = 6.8$ Hz, CH_3), 0.98 (3 H, d, $J = 6.8$ Hz, CH_3), 1.23 (3 H, d, $J = 7.0$ Hz, CH_3), 1.60 (1 H, m), 1.75 (1 H, m), 1.80–2.10 (4 H, m), 3.35 (1 H, m), 4.16 (5 H, s, C_5H_5), 4.38 (1 H, m, C_5H_4), 4.43 (2 H, m, C_5H_4), 4.51 (1 H, m, C_5H_4), 6.68 (1 H, s, CH=). Anal. Calcd. for $C_{21}H_{26}FeO$, %: C, 72.01; H 7.48; Fe, 15.94. Found: C, 71.81; H, 7.62; Fe, 16.08%.

15b, eluted with 3:1 hexane–benzene, yield 2.27 g (65%), red crystals, m.p. 210–211°C. ^{1}H NMR ($CDCl_3$), δ: 0.89 (3 H, d, $J = 6.85$ Hz, CH_3), 0.91 (3 H, d, $J = 6.85$ Hz, CH_3), 1.28 (3 H, d, $J = 7.16$ Hz, CH_3), 1.55 (1 H, m), 1.70 (1 H, m), 1.80–2.20 (4 H, m), 3.18 (1 H, m), 4.15 (5 H, s, C_5H_5), 4.46 (2 H, m, C_5H_4), 4.53 (2 H, m, C_5H_4), 7.45 (1 H, s, CH=). Anal. Calcd. for $C_{21}H_{26}FeO$, %: C, 72.01; H 7.48; Fe, 15.94. Found: C, 71.93; H, 7.23; Fe, 16.18%.

3.7. *E*-2-ferrocenylmethylene-3-quinuclidinone **7**

A mixture of the chalcone **1** (0.96 g, 3 mmol) and $NaBPh_4$ (2.60 g, 7.5 mmol) in glacial acetic acid (50 ml) was stirred in an atmosphere of argon at 40–50°C for 6 h. Then it was cooled to room temperature, poured in 10% aqueous Na_2CO_3 (200 ml), and the product was extracted with benzene (3×50 ml). The solvent was evaporated in vacuo and the residue was chromatographed on alumina to give the original chalcone **1** (eluted with hexane, yield 0.15 g, 15%), m.p. 122–124°C [7], and its isomer **7** eluted with benzene, yield 0.77 g (80%), violet crystals, m.p. 113–114°C. ^{1}H NMR ($CDCl_3$), δ: 1.94 (4 H, m), 2.61 (1 H, m), 3.06 (4 H, m), 4.13 (5 H, s, C_5H_5), 4.44 (2 H, m, C_5H_4), 5.00 (2 H, m, C_5H_4), 6.61 (1 H, s, CH=). ^{13}C NMR ($CDCl_3$), δ: 25.50 (CH_2), 42.42 (CH), 49.22 (CH_2), 69.54 (C_5H_5), 71.39, 72.93 (C_5H_4), 82.34 (C_{ipso} Fc), 135.88 (CH=), 139.91, 203.05 (C). Anal. Calcd. for $C_{18}H_{19}FeNO$, %: C, 67.30; H 5.98; Fe, 17.39; N, 4.36. Found: C, 67.12; H, 6.12; Fe, 17.50; N, 4.21%.

3.8. *E*-2-ferrocenylmethylene-3-quinuclidinone methiodide **7a**

To a solution of the chalcone **7** (0.32 g, 1 mmol) in chloroform, MeI (0.5 ml) was added, and the precipitation of violet needles of the methiodide **7a** began after several min. The reaction mixture was left for 1 h at 20°C, and the crystals that sedimented were filtered off, yield 0.40 g (87%), m.p. ca. 315°C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 2.30–2.65 (4 H, m), 3.20 (1 H, m), 3.70 (3 H, s), 3.85–4.30 (4 H, m), 4.61 (5 H, s, C_5H_5), 5.05 (2 H, m, C_5H_4), 5.42 (2 H, m, C_5H_4), 8.40 (1 H, br.s, CH=). Anal. Calcd. for $C_{19}H_{22}FeINO$, %: C, 49.26; H, 4.78; Fe, 12.06; I, 27.42; N, 3.02. Found: C, 49.43; H, 4.49; Fe, 11.89; I, 27.46; N, 2.95%.

3.9. *E*-2-ferrocenylmethylene-3-hydroxyquinuclidinium-3-cation **8b**

Compound **1** was dissolved in CF_3COOH, and the ^{1}H NMR spectrum of *E*-2-ferrocenylmethylene-3-hy-

droxyquinuclidinium-3-cation **8b** was recorded at 20°C: (δ): 2.10 (2 H, m), 2.30 (2 H, m), 2.87 (1 H, m), 3.34 (2 H, m), 3.84 (2 H, m), 5.28 (1 H, m, C_5H_4), 5.64 (5 H, m, C_5H_5), 5.68 (1 H, m, C_5H_4), 6.23 (2 H, m, C_5H_4), 7.98 (1 H, s, =CH–Fc), 8.23 (1 H, br.s, $^+$NH).

3.10. E-2-arylmethylene-3-quinuclidinones 11a–c

E-2-Arylmethylene-3-quinuclidinones **11a–c** were obtained by a procedure identical with that used in the synthesis of **7**: 3 mmol of the corresponding chalcone **10a–c** in acetic acid (50 ml) was treated with 7.5 mmol of $NaBPh_4$. The following products were isolated by column chromatography on alumina.

10a , eluted with 3:1 hexane–benzene, yield 45%, m.p. 134–135°C [24], and **11a**, eluted with 2:1 hexane–benzene, yield 50%, yellow crystals, m.p. 74–75°C. ^{1}H NMR ($CDCl_3$), δ: 2.00 (4 H, m, CH_2), 2.62 (1 H, m, CH), 2.90–3.30 (4 H, m, CH_2), 7.016 (1 H, s, CH=), 7.35 (3 H, m, Ph), 8.05 (2 H, m, Ph). Anal. Calcd. for $C_{14}H_{15}NO$, %: C, 78.84; H 7.09; N, 6.56. Found: C, 79.03; H, 6.85; N, 6.49%.

10b, eluted with 2:1 hexane–benzene, yield 29%, m.p. 119–120°C, and **11b**, eluted with 1:3 hexane–benzene, yield 60%, m.p. 84–85°C. ^{1}H NMR ($CDCl_3$), δ: 2.01 (4 H, m, CH_2), 2.64 (1 H, m, CH), 2.97 (2 H, m, CH_2), 3.13 (2 H, m, CH_2), 6.78 (1 H, s, CH=), 7.05 (2 H, m, C_6H_4), 7.95 (2 H, m, C_6H_4). ^{13}C NMR ($CDCl_3$), δ: 25.32 (CH_2), 42.58 (CH), 48.94 (CH_2), 114.87, 115.16, 123.76, 133.25, 133.36 (CH), 143.45, 161.83, 203.69 (C), 147.30 (d, $^1J_{CF}$ 267 Hz, CF). Anal. Calcd. for $C_{14}H_{14}FNO$, %: C, 72.71; H 6.10; F, 8.21; N, 6.06. Found: C, 72.54; H, 5.93; F, 8.32; N, 5.85%.

10c, eluted with 1:1 hexane–benzene, yield 40%, m.p. 102–103°C, and **11b**, eluted with 3:1 benzene–ethyl acetate, yield 45%, yellow crystals, m.p. 117–118°C. ^{1}H NMR ($CDCl_3$), δ: 1.99 (4 H, m, CH_2), 2.61 (1 H, m, CH), 3.10 (4 H, m, CH_2), 3.80 (3 H, s, CH_3), 3.83 (3 H, s, CH_3), 6.50 (2 H, m, $J = 9.4$ Hz, C_6H_3), 7.37 (1 H, s, CH=), 8.36 (1 H, d, $J = 9.4$ Hz, C_6H_3). Anal. Calcd. for $C_{16}H_{19}NO_3$, %: C, 70.31; H 7.01; N, 5.12. Found: C, 70.28; H, 6.82; N, 4.95%.

The isomerization of *E*-configurated chalcones into *Z*-isomers was performed analogously to yield ca. 17% of **1**, ca. 40% of **10a**, ca. 32% of **10b**, and ca. 50% of **10c**.

3.11. Z-3-ferrocenylmethylenecamphor 14

A mixture of the chalcone **2** (0.7 g, 2 mmol) and $NaBPh_4$ (1.02 g, 3 mmol) in glacial acetic acid (50 ml) was boiled under reflux for 6 h. The reaction mixture was poured in water, the products were extracted with benzene to give after column chromatography 0.36 g (50%) of the original chalcone **2** and 0.28 g (40%) of the chalcone **14**, m.p. 78–80°C (cf. [18]).

3.12. Z-2-ferrocenylmethylenementhone 16b

Z-2-ferrocenylmethylenementhone **16b** was obtained analogously from 0.7 g (2 mmol) of **15b**, yield 0.16 g (20%), m.p. 76–77°C; recovery of **15b** was 0.45 g (65%), m.p. 210–211°C.

3.13. Z-2-ferrocenylmethylenecyclohexanone 16a

Z-2-ferrocenylmethylenecyclohexanone **16a** was obtained analogously from 0.6 g (2 mmol) of **15a**, yield 0.13 g (20%), dark red crystals, m.p. 182–183°C (cf. [19]); recovery of **15a** was 0.42 g (70%), m.p. 113–115°C. (cf. [18]).

3.14. E-2-ferrocenylmethylene-3-hydroxy-3-methylquinuclidine 19

A suspension of the chalcone **7** (3.2 g, 10 mmol) in dry benzene (50 ml) was added to an ethereal solution of methyllithium (30 mmol) with stirring, stirring was continued for 1 h, and the reaction mixture was quenched with 5% aqueous NaOH. The organic layer was separated, washed with water, and dried with Na_2SO_4. Following evaporation of the solvent in vacuo, the residue was crystallized from ethanol to give 2.75 g (78%) of the alcohol **19** as orange crystals, m.p. 206–207°C. ^{1}H NMR ($CDCl_3$), δ: 1.40–2.20 (4 H, m), 1.60 (3 H, s), 2.33 (1 H, s, OH), 2.85 (1 H, m), 3.00–3.08 (4 H, m), 4.17 (5 H, s, C_5H_5), 4.29 (2 H, m, C_5H_4), 4.48 (1 H, m, C_5H_4), 4.78 (1 H, m, C_5H_4), 6.32 (1 H, s, CH=); ^{13}C NMR ($CDCl_3$), δ: 21.79, 24.24 (CH_2), 24.16 (CH_3), 37.48 (CH_2), 47.54 (CH_2), 49.89 (CH), 68.91 (C), 69.19 (C_5H_5), 70.01, 71.10, 71.91 (C_5H_4), 79.13 (C_{ipso} Fc), 122.52 (CH=), 131.4 (C). Anal. Calcd. for $C_{19}H_{23}FeNO$, %: C, 67.66; H 6.87; Fe, 16.56; N, 4.15. Found: C, 67.48; H, 7.01; Fe, 16.34; N, 3.94%.

The alcohol **5** was obtained analogously from the chalcone **1**, yield 70%, m.p. 161–162°C (cf. [7]).

3.15. E- and Z-2-ferrocenylmethylene-3-methylquinuclidinium-3-cation tetrafluoroborates (24a and 24b)

E- and *Z*-2-ferrocenylmethylene-3-methylquinuclidinium-3-cation tetrafluoro-borates (**24a** and **24b**) were prepared by the addition of HBF_4 etherate to solutions of the alcohols **19** and **5**, respectively, in dry ether [7].

24a, yield 71%, black powder, decomposes on heating. ^{1}H NMR (CD_2Cl_2), δ: 2.06 (2 H, m), 2.25 (2 H, m), 2.37 (3 H, s), 3.25 (1 H, m), 3.44 (2 H, m), 3.96 (2 H, m), 4.97 (1 H, m, C_5H_4), 5.26 (5 H, s, C_5H_5), 5.30 (1 H, m, C_5H_4), 6.47 (1 H, m, C_5H_4), 6.50 (1 H, m, C_5H_4), 7.80 (1 H, s, =CH–Fc), 8.80 (1 H, s, $^+$NH). Anal. Calcd. for $C_{19}H_{23}B_2F_8FeN$, %: C, 46.08; H 4.68; Fe,

11.28; N, 2.82. Found: C, 45.48; H, 4.33; Fe, 11.12; N, 3.01%.

24b, yield 80%, black powder, decomposes on heating. ^{1}H NMR (CD_2Cl_2), δ: 2.08 (2 H, m), 2.32 (2 H, m), 2.42 (3 H, s), 3.30 (1 H, m), 3.46 (2 H, m), 3.98 (2 H, m), 4.98 (1 H, m, C_5H_4), 5.29 (5 H, s, C_5H_5), 5.34 (1 H, m, C_5H_4), 6.52 (2 H, m, C_5H_4), 7.84 (1 H, s, =CH–Fc), 9.01 (1 H, s, $^+$NH). Anal. Found: C, 46.12; H, 4.77; Fe, 11.31; N, 3.07%.

3.16. Tetraphenylborates *24c* and *24d*

Tetraphenylborates **24d** and **24c** were obtained by the standard procedure, viz., using $NaBPh_4$ in glacial acetic acid [7,8] at 10–15°C. After 20 min, the crystalline salts were filtered off and washed on the filter with dry ether.

24c, yield 65%, brown powder, decomposes on heating. Anal. Calcd. for $C_{67}H_{63}B_2FeN$, %: C, 83.82; H, 6.61; Fe, 5.82; N, 1.46. Found: C, 83.97; H, 6.42; Fe, 5.59; N, 1.58%.

24d, yield 68%, brown powder, decomposes on heating. Anal. Found: C, 83.75; H, 6.82; Fe, 6.01; N, 1.21%.

3.17. 3-ferrocenylmethylene-2-hydroxy-2-methylcamphanes *6* and *17*

3-Ferrocenylmethylene-2-hydroxy-2-methylcamphanes (**6** [7] and **17**) were synthesized from the corresponding chalcones, **2** and **14**. A suspension of the chalcone **2** (1.05 g, 3 mmol) in dry benzene (50 ml) was added to an ethereal solution of methyllithium (10 mmol) with stirring, stirring was continued for 1 h, and the reaction mixture was quenched with 5% aqueous NaOH. The organic layer was separated, concentrated in vacuo, and the residue was dissolved in ethanol (25 ml) with heating. The product that crystallized on cooling was filtered off, washed with ethanol, and dried to give 3-(1-ferrocenylethyl)camphor, yield 0.44 g (40%) from **2** and 0.65 g (60%) from **14**, yellow crystals, m. p. 152–153°C. ^{1}H NMR ($CDCl_3$), δ: 0.86 (3 H, s), 0.89 (3 H, s), 0.92 (3 H, s), 1.15–1.70 (4 H, m), 1.62 (3 H, d, $J = 6.6$ Hz), 1.82 (1 H, m), 2.52 (1 H, m, $J = 6.6$ Hz), 3.98 (1 H, m, C_5H_4), 4.01 (1 H, m, C_5H_4), 4.11 (2 H, m, C_5H_4), 4.14 (5 H, s, C_5H_5). Anal. Calcd. for $C_{22}H_{28}FeO$, %: C, 72.53; H, 7.74; Fe, 15.33. Found: C, 72.71; H, 7.58; Fe, 15.43%.

The ethanolic filtrate was taken to dryness and the residue was chromatographed on alumina in benzene to yield 0.46 g (42%) of alcohol **6** (from **2**), m.p. 96–97°C (cf. [7]), and 0.33 g (30%) of alcohol **17** (from **14b**), orange oil. ^{1}H NMR ($CDCl_3$), δ: 0.84 (3 H, s), 0.96 (3 H, s), 1.00 (3 H, s), 1.35 (3 H, s), 1.25–2.00 (4 H, m), 2.76 (1 H, m), 4.10 (1 H, m, C_5H_4), 4.12 (5 H, s, C_5H_5), 4.15 (1 H, m, C_5H_4), 4.30 (2 H, m, C_5H_4), 6.38 (1 H, s, CH=). Anal. Found: C, 72.29; H, 7.91; Fe, 15.52%.

3.18. E- and Z-3-ferrocenylmethylene-1,2,7,7-tetramethylbicyclo[2.2.1]heptane-2-cation tetra-fluoroborates (*23a* and *23b*)

E- and *Z*-3-Ferrocenylmethylene-1,2,7,7-tetramethylbicyclo[2.2.1]heptane-2-cation tetra-fluoroborates (**23a** and **23b** [8]) were prepared as described above, starting from the alcohols **6** and **17**, respectively, and HBF_4 etherate.

23a, yield 70%, dark brown powder, decomposes on heating. ^{1}H NMR (CD_2Cl_2), δ: 0.79 (3 H, s), 0.92 (3 H, s), 1.13 (3 H, s), 1.81 (3 H, s), 1.65 (2 H, m), 1.72–1.83 (2 H, m), 3.46 (1 H, m), 4.85 (5 H, s, C_5H_5), 4.96 (1 H, m, C_5H_4), 5.38 (1 H, m, C_5H_4), 6.07 (1 H, m, C_5H_4), 6.20 (1 H, m, C_5H_4), 8.42 (1 H, s, =CH–Fc). Anal. Calcd. for $C_{22}H_{27}BF_4Fe$, %: C, 60.87; H 6.27; Fe, 12.86. Found: C, 60.59; H, 6.32; Fe, 13.01%.

3.19. Tetraphenylborates *23c* and *23d*

Tetraphenylborates **23c** and **23d** were obtained from the alcohols **6** and **17** and $NaBPh_4$ in glacial acetic acid [1].

23c, yield 64%, brown crystals, decomposes on heating. Anal. Calcd. for $C_{46}H_{47}BFe$, %: C, 82.87; H, 7.10; Fe, 8.38. Found: C, 82.63; H, 6.94; Fe, 8.21%.

23d, yield 67%, brown crystals, decomposes on heating. Anal. Found: C, 82.59; H, 7.23; Fe, 8.17%.

3.20. Z- and E-2-ferrocenylmethylene-3-methylenequinuclidines (*3* and *21*)

1. $POCl_3$ (2 ml) was added dropwise to a solution of the alcohol **5** or **19** (1.12 g, 3.3 mmol) in dry pyridine (50 ml), the mixture was stirred for 3 h at ambient temperature and diluted with water. The diene that formed was extracted with benzene. Following concentration of the extract in vacuo, the residue was purified by column chromatography on alumina in hexane.

   3, yield 0.76 g (70%), orange crystals, m.p. 92–93°C (cf. [7]). ^{13}C NMR ($CDCl_3$), δ: 28.08 (CH_2), 34.39 (CH), 47.85 (CH_2), 68.87 (C_5H_5), 68.66, 69.76 (C_5H_4), 80.05 (C_{ipso} Fc), 101.14 (CH_2=), 115.00 (CH=), 144.80, 150.78 (C).

   21, yield 0.78 g (72%), orange crystals, m.p. 63–64°C. ^{1}H NMR ($CDCl_3$), δ: 1.72 (4 H, m), 2.50 (1 H, m), 3.01 (4 H, m), 4.11 (5 H, s, C_5H_5), 4.20 (2 H, m, C_5H_4), 4.45 (2 H, m, C_5H_4), 4.99 (1 H, d, $J = 1.38$ Hz), 5.47 (1 H, d, $J = 1.38$ Hz), 6.22 (1 H, s, CH=); ^{13}C NMR ($CDCl_3$), δ: 28.08 (CH_2), 35.78 (CH), 49.66 (CH_2), 68.36 (C_5H_5), 69.27, 69.54 (C_5H_4), 81.25 (C_{ipso} Fc), 110.02 (CH_2=), 120.60 (CH=), 145.40, 147.65 (C). Anal. Calcd. for $C_{19}H_{21}FeN$, %: C, 71.49; H 6.63; Fe, 17.50; N, 4.38. Found: C, 71.28; H, 6.72; Fe, 17.63; N, 4.61%.

2. Freshly distilled *N*,*N*-dimethylaniline (2 ml) was added dropwise with stirring to a solution of 3.3 mmol of tetrafluoroborate **24a** or **24b** or of the tetraphenylborate **24d** or **24c** in CH_2Cl_2 (20 ml). After 1 h, the mixture was washed with water, 1% aqueous HCl, and again with water. The solvent was distilled off and the residue was chromatographed on alumina to yield 0.74–0.77 g (69–72%) of the diene **21**, m.p. 63–65°C, and 0.75–0.78 g (70–73%) of the diene **3**, m.p. 92–93°C (cf. [7]).

3.21. Methiodide *3a*

A solution of the diene **3** (0.32 g, 1 mmol) and MeI (0.5 ml) in acetonitrile (20 ml) was kept for 7–10 days in darkness at ambient temperature until the starting diene disappeared (TLC, Silufol), and the product was precipitated with dry ether. The precipitate was filtered off and washed with ether to yield 0.37 g (80%) of the salt **3a** as the orange powder, which decomposes on heating. ^{1}H NMR (DMSO-d_6), δ: 1.80–2.28 (4 H, m), 2.57 (1 H, m), 2.95–3.10 (4 H, m), 3.35 (3 H, s, CH_3), 4.34 (5 H, s, C_5H_5), 4.50 (2 H, m, C_5H_4), 4.60 (2 H, m, C_5H_4), 5.47 (1 H, s, CH_2=), 5.60 (1 H, s, CH_2=), 6.90 (1 H, s, CH=). Anal. Calcd. for $C_{20}H_{24}FeIN$, %: C, 52.08; H, 5.25; Fe, 12.11; I, 27.53; N, 3.03. Found: C, 51.83; H, 5.34; Fe, 12.23; I, 27.28; N, 2.87%.

3.22. Methiodide *21a*

MeI (0.5 ml) was added to a solution of the diene **21** (0.32 g, 1 mmol) in chloroform (10 ml), and crystallization began in several min. After 1 h, the crystals that precipitated were filtered off and washed with dry ether to yield 0.36 g (78%) of the salt **21a**, which decomposes on heating. ^{1}H NMR (DMSO-d_6), δ: 1.91–2.20 (4 H, m), 2.50 (1 H, m), 2.80–2.95 (4 H, m), 3.41 (3 H, s, CH_3), 4.28 (5 H, s, C_5H_5), 4.42 (2 H, m, C_5H_4), 4.55 (2 H, m, C_5H_4), 5.45 (1 H, s, CH_2=), 5.53 (1 H, s, CH_2=), 6.81 (1 H, s, CH=). Anal. Found: C, 52.12; H, 5.04; Fe, 11.93; N, 3.20%.

3.23. Z- and E-2-(p-fluorobenzylidene)3-methylenequinuclidines *22a* and *22b*

An ethereal solution of MeLi (30 mmol) was added to a solution of the chalcone **10b** or **11b** (2.32 g, 10 mmol) in dry ether, the mixture was stirred for 1 h at 20°C and quenched with 5% aqueous NaOH (20 ml). The ethereal layer was separated, washed with water, and concentrated to dryness. The residue was dissolved in pyridine (50 ml) and $POCl_3$ (2 ml) was added. The mixture was stirred for 3 h at 40°C and diluted with benzene (100 ml). Pyridine was washed out with water (3 × 50 ml), the solvent was removed in vacuo, and the residue was crystallized from hexane.

22a, yield 1.5 g (65.2%), colorless crystals, m.p. 93–94°C. ^{1}H NMR ($CDCl_3$), δ: 1.72 (4 H, m, CH_2), 2.57 (1 H, m, CH), 2.90 (2 H, m, CH_2), 3.01 (2 H, m, CH_2), 4.80 (1 H, s, CH_2=), 5.28 (1 H, s, CH_2=), 6.42 (1 H, s, CH=), 6.97 (2 H, m, C_6H_4), 7.88 (2 H, m, C_6H_4); ^{13}C NMR ($CDCl_3$), δ: 27.85 (CH_2), 34.25 (CH), 47.41(CH_2), 103.16 (CH_2=), 114.71, 114.99, 115.40, 131.32, 131.41 (CH), 147.38, 150.60, 159.90 (C), 147.88 (d, $^1J_{CF}$ 229.5 Hz, CF). Anal. Calcd. for $C_{15}H_{16}FN$, %: C, 78.57; H 7.04; F, 8.28; N, 6.11. Found: C, 78.69; H, 6.93; F, 8.11; N, 5.98%.

22b, yield 1.61 g (70%), colorless crystals, m.p. 38–39°C. ^{1}H NMR ($CDCl_3$), δ: 1.70 (4 H, m, CH_2), 2.51 (1 H, m, CH), 3.06 (4 H, m, CH_2), 4.85 (1 H, s, CH_2=), 4.98 (1 H, d, J=1.0 Hz, CH_2=), 6.46 (1 H, s, CH=), 6.97 (2 H, m, C_6H_4), 7.31 (2 H, m, C_6H_4); ^{13}C NMR ($CDCl_3$), δ: 29.07 (CH_2), 30.71 (CH), 47.75(CH_2), 102.17 (CH_2=), 114.11, 114.73, 128.84, 130.89, 131.08 (CH), 149.56 (d, $^1J_{CF}$ 272 Hz, CF). Anal. Found: C, 78.41; H, 6.89; F, 8.34; N, 6.23%.

3.24. E- and Z-3-ferrocenylmethylene-2-methylenecamphanes *4* and *18*

E- and *Z*-3-Ferrocenylmethylene-2-methylenecamphanes **4** and **18** were prepared by two methods as described above for the synthesis of the dienes **3** and **21**.

1. The dienes **4** and **18** were obtained from 1.21 g (3.3 mmol) of the alcohols **6** and **17,** respectively: **4**, yield 0.80 g (70%), orange crystals, m.p. 73–74°C [8]; **18**, yield 0.84 g (82%), orange oil, ^{1}H NMR ($CDCl_3$), δ: 0.63 (3 H, s), 0.93 (3 H, s), 1.00 (3 H, s), 1.20–1.95 (4 H, m), 2.77 (1 H, m), 4.10 (5 H, s, C_5H_5), 4.17 (2 H, m, C_5H_4), 4.30 (2 H, m, C_5H_4), 4.53 (1 H, s, CH_2=), 5.00 (1 H, s, CH_2=), 6.17 (1 H, s, CH=). Anal. Calcd. for $C_{22}H_{26}Fe$, %: C, 76.30; H 7.57; Fe 16.13. Found: C, 76.42; H, 7.28; Fe, 16.18%.
2. Starting from 2.22 g (3.3 mmol) of the tetrafluoroborate **23b**, the diene **4**, m.p. 73–75°C (*cf.* [8]), was obtained in a yield of 0.86 g (76%), and the tetrafluoroborate **23a** gave 74% of the diene **18**.

3.25. Mutual Z-/E-isomerization of s-cis-ferrocenyl-1,3-dienes

1. A mixture of the *Z*-diene **3** (0.64 g, 2 mmol) and $NaBPh_4$ (1.7 g, 5 mmol) in glacial acetic acid (50 ml) was stirred in an inert atmosphere for 4 h at 50–60°C. Then it was cooled to room temperature and poured into 10% aqueous Na_2CO_3 (100 ml). The product was extracted with benzene, the extract was concentrated to dryness, and the residue was chromatographed on alumina to give 0.083 g (13%) of the *Z*-diene **3** (eluted with hexane) [6] and 0.52 g (81%) of the *E*-diene **21** (eluted with 2:1 hexane–benzene), m.p. 63–64°C.

Analogous treatment of the *E*-diene **21** (0.64 g, 2 mmol) gave 0.13 g (20%) of **3** and 0.46 g (72%) of the starting **21**.

The treatment of the *E*-diene **4** (0.69 g, 2 mmol) with $NaBPh_4$ (1.02 g, 3 mmol) in glacial acetic acid (50 ml) yielded 0.27 g (33%) of the *Z*-diene **18,** recovery of the starting *E*-diene **4** was 0.3 g (43%) [8].

2. The interaction of the *Z*-alcohol **5** (0.68 g, 2 mmol) with $NaBPh_4$ (1.7 g, 5 mmol) in glacial acetic acid (50 ml) for 5 h at 50°C yielded 0.11 g (17%) of the *Z*-diene **3**, m.p. 92–93°C [7], and 0.48 g (75%) of the *E*-diene **21**, m.p. 63–64°C.

   Analogously, the action of $NaBPh_4$ (1.02 g, 3 mmol) on the *E*-alcohol **6** (0.73 g, 2 mmol) yielded 0.28 g (40%) of the *Z*-diene **18** and 0.31 g (45%) of the *E*-diene **4** [8].

*3.26. Condensation of dienes **21** and **18** with tetrafluoroborates **24a** and **23a***

A solution of the *E*-diene **21** (0.53 g, 1.65 mmol) in CH_2Cl_2 (20 ml) was added with stirring to a solution of the salt **24a** (0.83 g, 1.65 mmol) in CH_2Cl_2 (30 ml). After 15 min, *N*,*N*-dimethylaniline (2 ml) was added dropwise and stirring was continued for an additional 30 min. Then the mixture was diluted with benzene (50 ml) and washed with water, 1% aqueous HCl, and water. Following removal of the solvent, the residue was chromatographed on SiO_2 (hexane–benzene-diethyl ether, 1:1:1) to give 0.64 g (60%) of 3-[2-ferrocenyl-2-(3-methyl-Δ^2-dehydroquinuclid-2-yl)ethylidene]-2-ferrocenylmethylenequinuclidine as a mixture of *Z*- and *E*-isomers **25a**,**b** in a ratio of ~1:2, Rf 0.52, orange crystals, m.p. 146–148°C. The isomer **25b** (0.21 g) was isolated by recrystallization from hexane, m.p. 171–172°C. ^{1}H NMR ($CDCl_3$), δ: 1.30–1.78 (8 H, m), 1.87 (3 H, s, CH_3), 2.38 (1 H, m), 2.56 (1 H, m), 2.75–3.20 (8 H, m), 4.20 (5 H, s, C_5H_5), 4.21 (5 H, s, C_5H_5), 4.02–4.25 (8 H, m, C_5H_4), 4.80 (1 H, m, CH–Fc), 6.67 (1 H, m, CH=), 7.85 (1 H, s, CH&z.rbond3;). Anal. Calcd. for $C_{38}H_{42}Fe_2N_2$, %: C, 71.49; H 6.63; Fe 17.50; N, 4.38. Found: C, 71.53; H, 6.51; Fe, 17.29; N, 4.23%. **25a**, ^{1}H NMR ($CDCl_3$), δ: 1.50 (4 H, m), 1.70 (2 H, m), 1.92 (3H, s, CH_3), 2.30 (1 H, m), 2.32 (2 H, m), 2.60 (1 H, m), 2.80–3.10 (8 H, m), 4.10 (5 H, s, C_5H_5), 4.11 (5 H, s, C_5H_5), 4.10–4.40 (8 H, m, C_5H_4), 4.62 (1 H, m, CH–Fc), 6.58 (1 H, m, CH=), 7.80 (1 H, s, CH=).

The condensation of the *Z*-diene **18** (0.52 g, 1.5 mmol) with the *Z*-tetrafluoroborate **23a** (0.65 g, 1.5 mmol) was carried out analogously to yield 0.75 g (72%) of 2-[2-ferrocenyl-2-(2-methyl-Δ^2-dehydrocamph-3-yl)ethylidene]-3-ferrocenylmethylenecamphane as a mixture of *Z*- and *E*-isomers **26a**,**b** in a ratio of ~1:1, orange powder, m.p. 210–211°C.7 ^{1}H NMR ($CDCl_3$), δ: 0.68 (3 H, s), 0.71 (3 H, s), 0.88 (6 H, s), 0.91 (3 H, s), 0.94 (6 H, s), 0.96 (3 H, s), 0.98 (6 H, s), 1.10 (6 H, s), 1.12–1.60 (8 H, m), 1.53 (3 H, s), 1.64 (3 H, s), 2.80 (1 H, m), 2.82 (1 H, m), 2.88 (1 H, m), 2.91 (1 H, m), 4.06, 4.08, 4.13, 4.14 (20 H, 4 s, 4 C_5H_5), 4.00–4.22 (8 H, m, 2 C_5H_4), 4.30–4.50 (8 H, m, 2 C_5H_4), 5.61 (1 H, d, $J = 6.4$ Hz, CH–Fc), 5.70 (1 H, d, $J = 6.4$ Hz, CH–Fc), 6.36 (1 H, d, $J = 6.4$ Hz, CH=), 6.47 (1 H, s, CH=), 6.58 (1 H, d, $J = 6.4$ Hz, CH=), 7.29 (1 H, s, CH=). Anal. Calcd. for $C_{44}H_{52}Fe_2$, %: C, 76.30; H 7.57; Fe 16.13. Found: C, 76.21; H, 7.64; Fe, 16.27%.

*3.27. Fragmentation of the dimers **25** and **26***

To a solution of the dimer **25** (or **26**) (1 mmol) in dry ether (50 ml), HBF_4 etherate (2 ml) was added with stirring. The corresponding salts sedimented as black precipitates were filtered off and washed with dry ether, the yield was almost quantitative. The ratio of the isomeric salts was determined from the ^{1}H NMR spectra recorded in CD_2Cl_2.

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