Behavior of *Z*- and *E*-*s*-*cis*-ferrocenyl-1,3-dienes in cycloaddition and dimerization reactions

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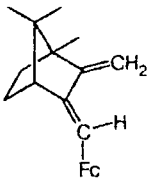
Z-3-Ferrocenylmethylene-2-methylenecamphane and *E*-2-ferrocenylmethylene-3-methylenequinuclidine were synthesized by isomerization of the corresponding isomeric *E*- and *Z*-1,3-dienes in an acidic medium. The dienes obtained form [4+2]-cycloaddition *endo*-adducts with *N*-phenylmaleimide, do not form cyclodimers upon thermal or acid-catalyzed [4+2]-cyclodimerization, and add *Z*-3-ferrocenylmethylene-1,2,7,7-tetramethylbicyclo[2.2.1]hept-2-ylium and *E*-2-ferrocenylmethylene-3-methyl-1-azoniabicyclo[2.2.1]oct-3-ylium salts, respectively, at the terminal methylene group to give linear addition products. The latter undergo fragmentation on treatment with HBF_4 to form the corresponding carbocation tetrafluroborates.

Key words: ferrocene, camphane, quinuclidine, isomerization, *s*-*cis*-1,3-dienes, cycloaddition, dimerization, fragmentation, carbocations.

Recently we reported on the syntheses of stable *E*-3-ferrocenylmethylene-2-methylenecamphane (**1**)[1] and *Z*-2-ferrocenylmethylene-3-methylenequinuclidine (**2**)[2], which are *s*-*cis*-1,3-dienes in whose molecules the bulky ferrocenyl substituent occupies an "external" position in relation to the *s*-*cis*-1,3-diene system.



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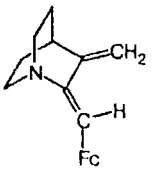


2

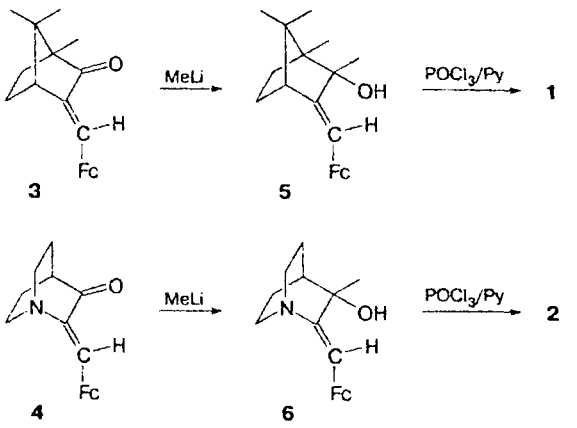
Dienes **1** and **2** were prepared from chalcones **3** and **4**, respectively, according to Scheme 1.

Like the initial chalcones, alcohols **5** and **6**, as well as dienes **1** and **2**, are characterized by *E*- and *Z*-configurations of the double bonds, respectively.[3,4]

However, no approaches to the synthesis of *s*-*cis*-1,3-dienes with "internal" arrangement of bulky substituents in the molecule or chemical properties of these compounds have been reported.

While investigating the possibility of preparing structures of this type for ferrocenyl-containing compounds, we showed that *Z*-3-ferrocenylmethylene-2-methylenecamphane (**7**) and *E*-2-ferrocenylmethylene-3-methylenequiniclidine (**8**) can be obtained in good yields from the corresponding alcohols **5** and **6** or

Scheme 1



1,3-dienes **1** and **2** on treatment with strong acids (HBF_4, $HBPh_4$) (Scheme 2). Dienes **7** and **8** are evidently formed *via* the intermediate participation of methyl(ferrocenyl)allylic carbocations **9a,b** and **10a,b**, which can isomerize to give carbocations **11a,b** and **12a,b**, respectively, through a rotation around the delocalized C(α)=C(β) bond (α and β atoms in relation to Fc), despite the fact that this rotation is restricted and is associated with a fairly high energy barrier.[5–8]

This conclusion is confirmed by the results of examination of the ^1H NMR spectra of tetrafluoroborates **9a–12a** in CD_2Cl_2 at room temperature. It was found

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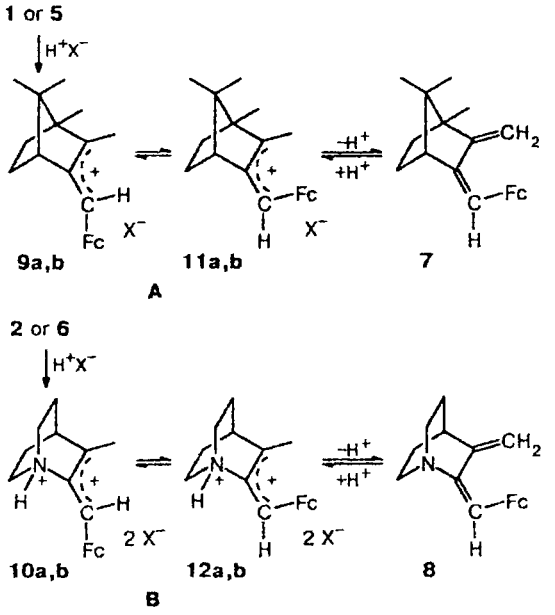
Scheme 2

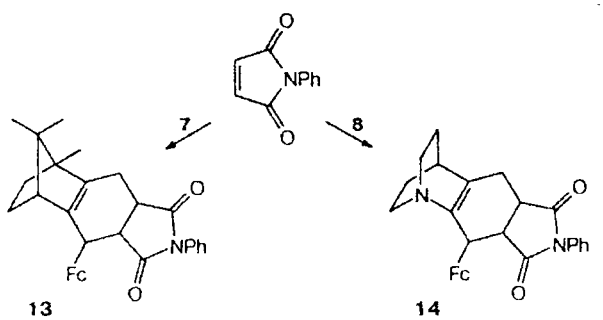


that solid tetrafluoroborates **9a** or **10a**, isolated as single diastereomers upon treatment of alcohols **5** or **6** with HBF_4, gradually isomerize in solutions which is manifested as doubling of all the ^1H NMR signals. When the equilibrium is attained, the integral intensities of the signals of the corresponding protons point to a ~1.5-fold predominance of the initial compound **9a** (after 8 h) and a 4-fold predominance of isomer **12a** (after 14 h) in the corresponding mixtures **A** and **B**. Treatment of the equilibrium solutions of the salts with bases ($PhNMe_2$, Py) followed by chromatography on Al_2O_3 yields isomeric 1,3-dienes **1** and **7** (~3 : 2) or **2** and **8** (~1 : 4).

The preparative isomerization is conveniently carried out by using sodium tetraphenylborate in glacial acetic acid (~5 h at 50—60 °C) (see Experimental).

Despite the "internal" arrangement of the ferrocene fragment, on heating with *N*-phenylmaleimide, dienes **7** and **8** form [4+2]-cycloadducts **13** and **14**, respectively (Scheme 3).

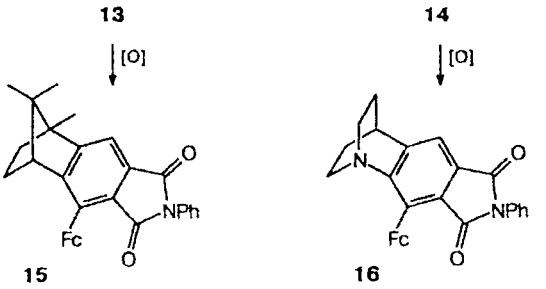
Scheme 3



These reactions are stereospecific; compounds **13** and **14** are formed as single *endo*-isomers. The identification of these compounds as *endo*-forms was based on the ^1H NMR spectra and criteria proposed previously,[9,10] namely, the signals for all the protons of the C_5H_4 groups and the signals of one of the protons of the phenyl group in adducts **13** and **14** are located in a higher field than the singlets for the protons of unsubstituted cyclopentadienyl rings in ferrocene and the multiplets for the four protons of the phenyl groups, which is typical of *endo*-isomers.

We found that compounds **13** and **14** are readily oxidized by atmospheric oxygen to the *N*-phenylimides of phthalic acid derivatives **15** and **16**, respectively (Scheme 4).

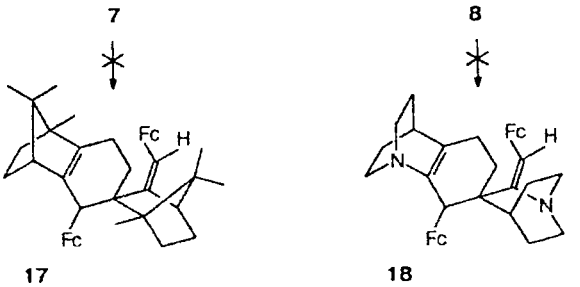
Scheme 4



A similar type of oxidation by atmospheric oxygen has been observed previously for carbocyclic adducts of *N*-arylmaleimides with ferrocenylbuta-1,3-dienes.[9]

Unlike *s-cis*-ferrocenyl-1,3-dienes **1** and **2** with the "external" arrangement of the ferrocene substituent,[1,2] dienes **7** and **8** do not undergo cyclodimerization according to the [4+2]-cycloaddition pattern. Spirane cyclodimers **17** and **18** are not formed even on refluxing in xylene, apparently, because of steric hindrance (Scheme 5).

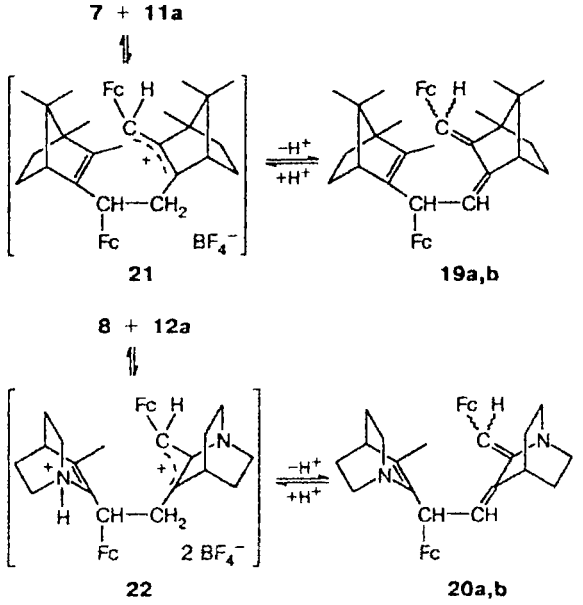
Scheme 5



Dienes **7** and **8** do not form linear or cyclic dimers in acidic media according to the acid-catalyzed dimerization scheme characteristic of many ferrocenyl-1,3-dienes.[9—12]

We synthesized linear dimers **19** and **20** by the reactions of dienes **7** and **8** with the corresponding tetrafluoroborates **11a** and **12a** (Scheme 6).

Scheme 6



Compounds **19** and **20** were isolated as mixtures of two isomers **19a** and **19b** (~1 : 1) and **20a** and **20b** (~1 : 2, ^{1}H NMR data). One of the isomers, **20b**, was isolated in a pure state. However, the configuration of the dimers (*Z* or *E*) has not yet been determined.

Evidently, linear dimers **19** and **20** are formed upon deprotonation (induced by bases[11,12]) of salts of the intermediate allylic carbocations **21** and **22**, respectively, resulting from the addition of cations **11a** and **12a** through their secondary cationic centers to the methylene groups of dienes **7** and **8**.

We found that on treatment with HBF_4 etherate, dimers **19** and **20** undergo fragmentation, as has been found previously for ferrocenylcyclodimers with the terpenoid structures.[13] According to ^{1}H NMR spectroscopy, fragmentation of dimers **19a,b** and **20a,b** yields mixtures of isomeric tetrafluoroborates **9a** and **11a** (~3 : 2) and **10a** and **12a** (~1 : 3), respectively.

In our opinion, fragmentation is the process opposite to dimerization, which occurs in the presence of a large excess of a strong acid as a result of protonation of the C(3)=C(4) bond in the linear dimers.

The formation of mixtures of isomeric linear dimers **19a,b** and **20a,b** from homoisomeric compounds introduced in the reaction indicates that the dimerization is accompanied by isomerization. Apparently, both the initial methyl(ferrocenyl)allylic cations **11a** and **12a** and the intermediate allylic cations **21** and **22** are able to isomerize in solutions.

Thus, *s*-*cis*-1,3-dienes readily isomerize into compounds **7** and **8** with the "internal" arrangement of the bulky substituent. The latter do not form cyclodimers according to a scheme typical of ferrocenyl-1,3-dienes; they give only linear dimers in reactions with the corresponding salts of ferrocenylcarbocations **11a** and **12a**.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Gemini 200 Varian spectrometer (200 and 50 MHz, respectively) for solutions in $CDCl_3$ and CD_2Cl_2, using tetramethylsilane as the internal standard (Tables 1 and 2). The data of elemental analysis are listed in Table 3. Chromatography was carried out on a column with Al_2O_3 (Brockmann activity III).

***E*-3-Ferrocenylmethylenecamphor (3).** Dry benzene (100 mL), ferrocenecarbaldehyde (2.1 g, 10 mmol), and camphor (2.3 g, 15 mmol) were added to a solution of Bu^{t}OK (from 0.1 g of K metal) in Bu^{t}OH (20 mL), and the mixture was refluxed for 6 h. After evaporation of the solvent, the residue was chromatographed on Al_2O_3 (using a 3 : 1 hexane—benzene mixture as the eluent) to give 2.34 g (67%) of chalcone **3** as orange crystals, m.p. 130—131 °C.[1]

***Z*-2-Ferrocenylmethylenequinuclidone (4)** was prepared by the standard procedure from ferrocenecarbaldehyde and quinuclidone hydrochloride in water-alcoholic alkali, yield 79%, dark red crystals, m.p. 122—123 °C.[2]

***E*-3-Ferrocenylmethylene-2-methylborneol (5)** was prepared from chalcone **3** and methyllithium by the standard procedure;[11] yield 45%, yellow crystals, m.p. 97—98 °C.[1]

***Z*-2-Ferrocenylmethylene-3-methylquinuclidin-3-ol (6)** was prepared in a similar way from chalcone **4** and methyllithium, yield 72%, orange crystals, m.p. 161—162.5 °C.[2]

***E*-3-Ferrocenylmethylene-1,2,7,7-tetramethylbicyclo[2.2.1]hept-2-ylium tetrafluoroborate (9a)** was synthesized by adding HBF_4 etherate to alcohol **5** in anhydrous ether, yield 72%, dark brown powder decomposing on heating. **Tetraphenylborate (9b)** was prepared from alcohol **5** by the standard procedure involving treatment with $NaBPh_4$ in glacial AcOH.[1,2] The solid salt was quickly filtered off and washed on the filter with anhydrous ether, yield 68%. All operations with solid salts **9a** and **9b** were carried out in an atmosphere of dry argon.

***Z*-2-Ferrocenylmethylene-3-methyl-1-azoniabicyclo[2.2.2]oct-3-ylium bis(tetrafluoroborate) (10a) and bis(tetraphenylborate) (10b)** were prepared in a similar way. Salt **10a**, yield 75%, black powder decomposing on heating; the yield of salt **10b** was 73%.

***E*-3-Ferrocenylmethylene-2-methylenecamphane (1).** $POCl_3$ (2 mL) was added dropwise to a solution of alcohol **5** (1.21 g, 3.3 mmol) in dry Py (50 mL), and the mixture was stirred for 3 h at 20 °C and diluted with water. Diene **1** was extracted with benzene. After evaporation of the solvent, the residue was chromatographed on Al_2O_3 (elution with hexane) to give 0.80 g (70%) of diene **1** as orange crystals, m.p. 73—74 °C.[1]

***Z*-2-Ferrocenylmethylene-3-methylenequinuclidine (2)** was prepared in a similar way, yield 73%, orange powder, m.p. 92—93 °C.[2]

Z-/*E*-*Isomerization of s*-*cis*-*ferrocenyl*-*1,3*-*dienes*

1. *Z*-3-Ferrocenylmethylene-2-methylenecamphane (7). *A.* A mixture of alcohol **5** (1.21 g, 3.3 mmol) and $NaBPh_4$ (1.7 g, 5 mmol) in glacial AcOH (100 mL) was stirred under argon for 4 h at 50 °C, cooled to 20 °C, and diluted with water. The diene was extracted with benzene. After evaporation of the solvent, the residue was chromatographed on Al_2O_3 (hexane as

Table 1. Data of the ^1H NMR spectra ($CDCl_3$) of the compounds synthesized (δ, *J*/Hz)

Compound	C_5H_5 (s)	C_5H_4	CH_2	CH	CH_3, OH, Ar, NH^+
7	4.10	4.17 (m, 2 H); 4.30 (m, 2 H)	1.20—1.95 (m, 4 H); 4.53 (s, 1 H); 5.00 (s, 1 H)	2.77 (m, 1 H); 6.17 (s, 1 H)	0.63 (s, 3 H); 0.93 (s, 3 H); 1.00 (s, 3 H)
8	4.11	4.20 (m, 2 H); 4.45 (m, 2 H)	1.72 (m, 4 H); 3.01 (m, 4 H); 4.99 (d, 1 H, *J* = 1.4); 5.47 (d, 1 H, *J* = 1.4)	2.50 (m, 1 H); 6.22 (s, 1 H)	—
10a*	5.29	4.98 (m, 1 H); 5.34 (m, 1 H); 6.52 (m, 2 H)	2.08 (m, 2 H); 2.32 (m, 2 H); 3.46 (m, 2 H); 3.98 (m, 2 H)	3.30 (m, 1 H); 7.84 (s, 1 H)	2.42 (s, 3 H); 9.01 (s, 1 H)
11a*	4.85	4.96 (m, 1 H); 5.38 (m, 1 H); 6.07 (m, 1 H); 6.20 (m, 1 H)	1.65 (m, 2 H); 1.72—1.83 (m, 2 H)	3.46 (m, 1 H); 8.42 (s, 1 H)	0.79 (s, 3 H); 0.92 (s, 3 H); 1.13 (s, 3 H); 1.81 (s, 3 H)
12a*	5.26	4.97 (m, 1 H); 5.30 (m, 1 H); 6.47 (m, 1 H); 6.50 (m, 1 H)	2.06 (m, 2 H); 2.25 (m, 2 H); 3.44 (m, 2 H); 3.96 (m, 2 H)	3.25 (m, 1 H); 7.80 (s, 1 H)	2.37 (s, 3 H); 8.80 (s, 1 H)
13	4.17	4.01 (m, 2 H); 4.05 (m, 2 H)	1.23—1.60 (m, 4 H); 2.00—2.20 (m, 2 H)	2.50 (m, 1 H); 3.4—3.8 (m, 3 H)	0.60 (s, 3 H); 0.70 (s, 3 H); 0.87 (s, 3 H); 6.78 (m, 1 H); 7.38 (m, 4 H)
14	4.21	4.10 (m, 1 H); 4.30 (m, 3 H)	1.40—1.90 (m, 2 H); 2.60 (m, 2 H); 3.02 (m, 4 H); 3.20 (m, 2 H)	2.50 (m, 1 H); 2.90 (m, 1 H); 3.72 (d, 1 H, *J* = 1.8); 3.92 (m, 1 H)	6.90—7.00 (m, 1 H); 7.32 (m, 4 H)
15	4.14	4.25 (m, 2 H); 4.37 (m, 2 H)	1.42—1.95 (m, 4 H)	2.82 (m 1 H); 7.61 (s, 1 H)	0.94 (s, 3 H); 1.15 (s, 3 H); 1.31 (s, 3 H); 7.20—7.40 (m, 5 H)
16	4.11	4.44 (m, 2 H); 5.36 (m, 2 H)	1.5—2.0 (m, 4 H); 3.2—3.4 (m, 4 H)	2.70 (m, 1 H); 7.69 (s, 1 H)	7.35—7.56 (m, 5 H)
19a,b	4.06, 4.08, 4.13, 4.14	4.02—4.22 (m, 8 H); 4.30—4.50 (m, 8 H)	1.12—1.60 (m, 8 H); 1.90—2.30 (m, 8 H)	2.80 (m, 1 H); 2.82 (m, 1 H); 2.88 (m, 1 H); 2.91 (m, 1 H); 6.28 (d, 1 H, *J* = 6.4); 6.36 (d, 1 H, *J* = 6.4); 6.58 (d, 1 H, *J* = 6.4); 6.67 (d, 1 H, *J* = 6.4); 7.18 (s, 1 H); 7.29 (s, 1 H)	0.68 (s, 3 H); 0.71 (s, 3 H); 0.88 (s, 6 H); 0.91 (s, 3 H); 0.94 (s, 6 H); 0.96 (s, 3 H); 0.98 (s, 3 H); 1.10 (s, 6 H); 1.53 (s, 3 H); 1.64 (s, 3 H)
20a	4.10, 4.11	4.10—4.40 (m, 8 H)	1.50 (m, 4 H); 1.70 (m, 2 H); 2.32 (m, 2 H); 2.80—3.10 (m, 8 H)	2.30 (m, 1 H); 2.60 (m, 1 H); 4.62 (m, 1 H); 6.58 (m, 1 H); 7.80 (s, 1 H)	1.92 (s, 3 H)
20b	4.20, 4.21	4.02—4.25 (m, 8 H)	1.30—1.78 (m, 8 H); 2.75—3.20 (m, 8 H)	2.38 (m, 1 H); 2.56 (m, 1 H); 4.80 (m, 1 H); 6.67 (m, 1 H) 7.85 (s, 1 H)	1.87 (s, 3 H)

* In CD_2Cl_2.

Table 2. Data of the ^{13}C NMR spectra of compounds **7**, **8**, and **14** (δ)

Compound	C_5H_5	C_5H_4	C_5Fc	CH_2=, CH=	CH_2	CH	Ar	C_q	C_{ipso}
7	68.9	68.7, 69.8	80.0	101.1, 115.0	28.1, 47.9	34.4	—	144.8, 150.8	—
8	68.7	69.3, 69.5	81.3	110.0, 120.6	28.1, 49.7	35.8	—	145.4, 147.7	—
14	69.2	67.0, 67.8, 68.2, 68.9	84.5	—	23.5, 28.5, 29.6, 32.6, 39.3	40.5, 49.7, 50.1, 50.3	126.6, 128.8, 128.7	138.9, 145.8, 176.9, 178.5	138.8

Table 3. Data of elemental analysis of the compounds synthesized

Compound	Found / Calculated (%) C	H	Fe	N	Molecular formula
7	76.42 / 76.30	7.28 / 7.57	16.18 / 16.13	—	$C_{22}H_{26}Fe$
8	71.28 / 71.49	6.72 / 6.63	17.63 / 17.50	4.61 / 4.38	$C_{19}H_{21}FeN$
10a	46.12 / 46.08	4.77 / 4.68	11.31 / 11.28	3.07 / 2.82	$C_{19}H_{23}B_2F_8FeN$
11a	60.59 / 60.87	6.32 / 6.27	13.01 / 12.86	—	$C_{22}H_{27}BF_4Fe$
12a	45.84 / 46.08	4.33 / 4.68	11.12 / 11.28	3.01 / 2.82	$C_{19}H_{23}B_2F_8FeN$
13	74.07 / 74.00	6.58 / 6.40	10.63 / 10.75	2.91 / 2.70	$C_{32}H_{33}FeNO_2$
14	70.81 / 70.74	5.63 / 5.73	11.27 / 11.34	5.74 / 5.69	$C_{29}H_{28}FeN_2O_2$
15	74.38 / 74.57	5.54 / 5.67	10.97 / 10.83	2.85 / 2.72	$C_{32}H_{29}FeNO_2$
16	71.48 / 71.32	5.07 / 4.96	11.53 / 11.44	5.52 / 5.73	$C_{29}H_{24}FeN_2O_2$
19a,b	76.21 / 76.30	7.64 / 7.57	16.27 / 16.13	—	$C_{44}H_{52}Fe_2$
20b	71.53 / 71.49	6.51 / 6.63	17.29 / 17.50	4.23 / 4.38	$C_{38}H_{42}Fe_2N_2$

the eluent) to give 0.33 g (42%) of diene **7** as an orange oil and 0.24 g (30%) of diene **1** as an orange powder, m.p. 73—74 °C.[1]

B. A similar procedure starting from diene **1** (0.69 g, 2 mmol) and $NaBPh_4$ (1.02 g, 3 mmol) in 50 mL of AcOH gave 0.27 g (33%) of diene **7** and 0.32 g (40%) of diene **1**.[1]

C. A solution of tetrafluoroborate **9a** (1.3 g, 3 mmol) in 50 mL of CH_2Cl_2 was stirred under argon for 18 h at 20 °C, and $PhNMe_2$ or Py (1 mL) was added dropwise. The reaction mixture was washed with water, the organic layer was separated, the solvent was evaporated, and the residue was chromatographed on Al_2O_3 (elution with hexane) to give 0.42 g (40%) of diene **7** and 0.52 g (51%) of diene **1**. A similar procedure starting from salt **9b** (2.0 g, 3 mmol) gave 0.44 g (41%) of compound **7** and 0.50 g (49.5%) of diene **1**.

2. *E*-2-Ferrocenylmethylene-3-methylenequinuclidine (8). *A.* The reaction of alcohol **6** (1.12 g, 3.3 mmol) and $NaBPh_4$ (3.0 g) in glacial AcOH (100 mL) under conditions similar to those described for the preparation of diene **7** gave 0.12 g (11%) of diene **2** (elution with hexane) and 0.78 g (72%) of diene **8** (elution with a 2 : 1 hexane—benzene mixture) as orange crystals, m.p. 63—64 °C.

B. A similar procedure starting from diene **2** (0.64 g, 2 mmol) and $NaBPh_4$ (1.7 g, 5 mmol) in 50 mL of AcOH gave 0.109 g (17%) of recovered diene **2** and 0.46 g (71%) of diene **8**, m.p. 64 °C.

C. The reaction of tetrafluoroborate **10a** (0.99 g, 2 mmol) in CH_2Cl_2 (50 mL) gave 0.09 g (15%) of diene **2** and 0.40 g (61%) of diene **8**. A similar procedure starting from salt **10b** (1.9 g, 2 mmol) in CH_2Cl_2 (100 mL) gave 0.068 g (11%) of diene **2** and 0.48 g (78%) of diene **8**.

Reaction of dienes 7 and 8 with *N*-phenylmaleimide. A mixture of diene **7** (0.69 g, 2 mmol) and *N*-phenylmaleimide (0.5 g) in dry toluene (50 mL) was refluxed for 8 h. After evaporation of the solvent *in vacuo*, the residue was chromatographed on Al_2O_3 (elution with benzene) to give 0.8 g (76%) of *endo*-3-ferrocenyl-8,11,11-trimethyl-*N*-phenyltricyclo[6.2.1.$0^{2,7}$]undec-2(7)-ene-4,5-dicarboximide (**13**) as yellow crystals, m.p. 209—210 °C.

A similar procedure starting from 0.64 g (2 mmol) of diene **8** and 0.5 g of *N*-phenylmaleimide gave 0.74 g (75%) of *endo*-3-ferrocenyl-*N*-phenyl-1-azatricyclo[6.2.2.$0^{2,7}$]dodec-2(7)-ene-4,5-dicarboximide (**14**) as yellow crystals, m.p. 158—159 °C.

Oxidation of adducts 13 and 14. At 20 °C, dry air was passed through a solution of adduct **13** (0.52 g, 1 mmol) in $CHCl_3$ (50 mL) for 6 h. After evaporation of the solvent, the residue was chromatographed in a thin SiO_2 film (hexane—benzene, 1 : 1) to give 0.34 g (66%) of 3-ferrocenyl-8,11,11-trimethyl-*N*-phenyltricyclo[6.2.1.$0^{2,7}$]undeca-2(7),3,5-triene-4,5-dicarboximide (**15**) as red crystals, m.p. 261—263 °C, R_f 0.56.

A similar procedure starting from adduct **14** (0.49 g, 1 mmol) gave 0.35 g (72%) of 3-ferrocenyl-*N*-phenyl-1-azatricyclo[6.2.2.$0^{2,7}$]dodeca-2(7),3,5-triene-4,5-dicarboximide (**16**) as red crystals, m.p. 232—233 °C.

Reaction of diene 8 with tetrafluoroborate 12a. A solution of diene **8** (0.53 g, 1.65 mmol) in CH_2Cl_2 (20 mL) was added with stirring to a solution of salt **12a** (0.83 g, 1.65 mmol) in CH_2Cl_2 (50 mL). After 20 min, $PhNMe_2$ (2 mL) was added dropwise, and the mixture was stirred for an additional 3 min. Then the mixture was diluted with 50 mL of benzene and washed with water, with 1% HCl, and again with water. After evaporation of the solvent, the residue was chromatographed on SiO_2 (hexane—benzene—Et_2O, 1 : 1 : 1) to give 0.64 g (60%) of *Z*- and *E*-isomers of 3-[2-ferrocenyl-2-(3-methyl-Δ^2-dehydroquinuclidin-2-yl)ethylidene]-2-ferrocenylmethylenequinuclidine (**20a,b**) in a ratio of ~1 : 2, R_f 0.50, orange crystals, m.p. 147—150 °C. Recrystallization from hexane gave isomer **20b** (0.21 g), m.p. 171—172 °C.

Reaction of diene 7 with tetrafluoroborate 11a was carried out in a similar way. Diene **7** (0.52 g, 1.5 mmol) and salt **11a** (0.65 g, 1.5 mmol) gave 0.75 g (72%) of a mixture of *Z*- and *E*-isomers of 3-[2-ferrocenyl-2-(2-methyl-Δ^2-dehydrocamphan-3-yl)ethylidene]-2-ferrocenylmethylenecamphane (**19a,b**) in a ratio of ~1 : 1 as an orange powder, m.p. 210—211 °C, R_f 0.53.

Fragmentation of dimers 19 and 20. HBF_4 etherate (2 mL) was added with stirring to a mixture of dimer **19** or **20** (1 mmol) in anhydrous ether (50 mL). The black precipitate of the salts was filtered off and washed with anhydrous ether. The yields of the salts were nearly quantitative. The ratio of isomeric tetrafluoroborates was found from the data of the ^1H NMR spectra of the samples in CD_2Cl_2.

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