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Regioselectivity of alkylation of the naphthalene fragment in the opening of a small ring in 3-ferrocenyl-3-(1-naphthyl)cyclopropene, *Z*-2-bromo-1-ferrocenyl-1-(1-naphthyl)cyclopropane, and 1-ferrocenyl-1-(1-naphthyl)cyclopropane

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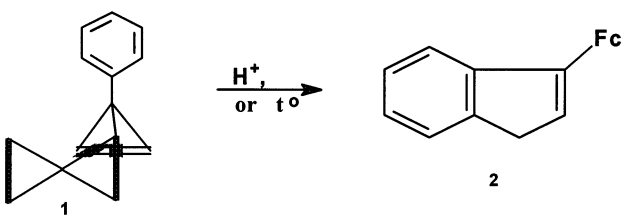
Abstract

The opening of a small ring in 3-ferrocenyl-3-(1-naphthyl)cyclopropene (thermolysis, action of $HBF_4 \cdot Et_2O$ or CF_3SO_3H), *Z*-2-bromo-1-ferrocenyl-1-(1-naphthyl)cyclopropane (action of $AlCl_3$), and in 1-ferrocenyl-1-(1-naphthyl)cyclopropane (action of $Ph_3C^+ BF_4^-$) is accompanied by the alkylation of only the naphthalene fragment giving rise to 1-ferrocenyl-9b*H*-benzo[e]indene or 1-ferrocenyl-3*H*-benzo[e]indene. This is connected with a 'non-bisecting' position of the naphthalene fragment relative to the three-membered cycle in the starting compounds. The compound 1-ferrocenyl-9b*H*-benzo[e]indene gives [4 + 2]-cycloadducts with *N*-phenyl(azodicarboximide) and *N*-phenylmaleimide. X-ray structural data are presented for 3-ferrocenyl-3-(1-naphthyl)cyclopropene and its adduct with 1,3-diphenylisobenzofuran, *Z*-2-bromo-1-ferrocenyl-1-(1-naphthyl)cyclopropane, and 1-ferrocenyl-1-(1-naphthyl)cyclopropane.

Keywords: Ferrocene; Naphthalene; Cyclopropane; Cyclopropene; Alkylation; Opening of a three-membered ring; Carbocations; Carbenoids; X-ray structural analysis; [4 + 2]-Cycloadducts

1. Introduction

The introduction of a ferrocenyl substituent in position 3 of the cyclopropene ring significantly changes the properties of the latter. Some well known examples of changes in the reaction properties of the small carbocycle include the transformations of 1,2,3-triferrocenylcyclopropene [1], 3-ferrocenyl-3-phenylcyclopropene **1** [2–4] and also of 3-*tert*-butyl- and 3-adamantyl-3-ferrocenylcyclopropenes **2a,b** [5]. In particular, 3-*para*-tolyl-1,2,3-triferrocenylcyclopropene, even at 0°C, in a solution of $CHCl_3$, rearranges due to cleavage of the small ring, followed by cyclization at the ferrocenyl and aryl fragments [1]. The compound 3-ferrocenyl-3-phenylcyclopropene **1** at acid or thermal cleavage of the small ring forms 3-ferrocenylindene **2** [2–4].



Fc= $C_5H_5FeC_5H_4$

In our opinion, the high regioselective intramolecular alkylation of the phenyl substituent and not of the ferrocenyl one, as normally observed for other ferrocenyl compounds [1,6–8], should be related to the spatial

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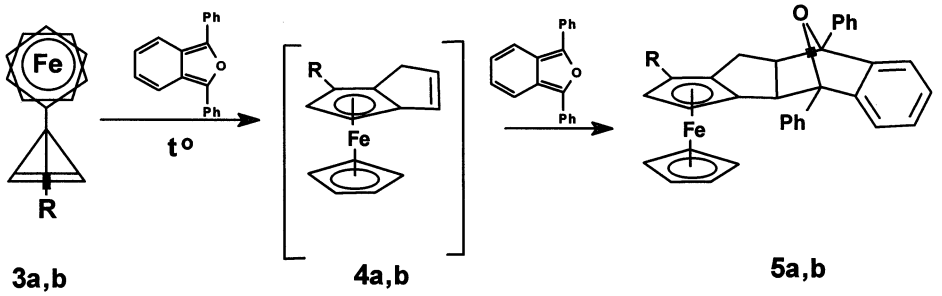
structure of the cyclopropene compound **1** [4]. According to X-ray analysis data, the phenyl subsituent has a 'non-bisecting' position relative to the small ring, while the ferrocenyl fragment has a 'bisecting' spatial orientation. Therefore, during the small ring cleavage, the alkylation should take place at the substituent which has a 'non-bisecting' orientation. However, if the ferrocenyl substituent occupies a 'non-bisecting' position one should expect that the alkylation will take place at the ferrocenyl fragment. In the reaction of 3-alkyl-3-ferrocenylcyclopropenes **3a,b** (the ferrocenyl fragment has a 'non-bisecting' position) with 1,3-diphenylisobenzofuran, the adduct **5a,b** is formed from the intermediate 3-alkyl-1,2-(1-propene-1,3-diyl)ferrocene **4a,b** [5].



3a,b **4a,b** **5a,b**

R= t-Bu- (a); R= 1-Ad- (b)

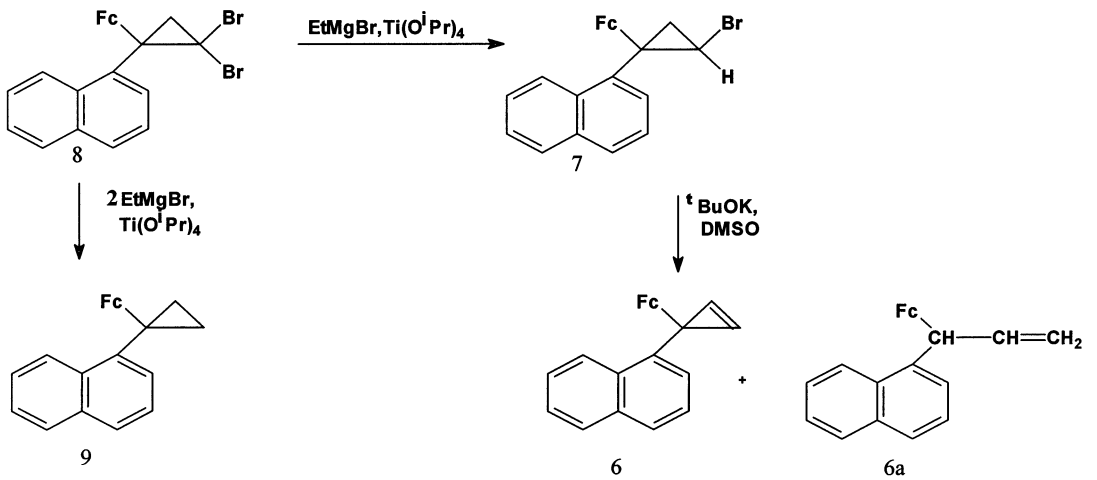
The idea that regioselectivity in similar reactions depends on the spatial orientation of the substituents (the conformational structure of the molecules) is not studied in detail and deserves further investigation.

2. Results and discussion

In a continuation of our investigations, we synthesized crystalline 3-ferrocenyl-3-(1-naphthyl)cyclopropene **6**, *Z*-2-bromo-1-ferrocenyl-1-(1-naphthyl)cyclopropane **7**, and 1-ferrocenyl-1-(1-naphthyl)cyclopropane **9** starting from 2,2-dibromo-1-ferrocenyl-1-(1-naphthyl)cyclopropane **8** and studied their structures and some of their chemical transformations.

Monocrystals of compounds **6**, **7**, and **9** necessary for X-ray structural analysis were obtained by crystallization from hexane. General views of these molecules are shown in Fig. 1(Fig. 2a) and Fig. 3, respectively. The X-ray analysis data indicate that all studied compounds (cyclopropene **6**, monobromide **7** and cyclopropane **9**) have identical conformations. This is probably caused by sterical restrictions imposed on the rotation of the geminal ferrocenyl and aryl substituents arround the simple C–C bonds.

The principal elements in the structures of **6**, **7**, and **9** are the three-membered rings. The three-membered ring in compound **6** is a triangle with an acute angle extended towards C(11). The length of the CH=CH double bond ($d = 1.272(6)$ Å) and the angle ω at C(11) is equal to 50.0(2)°. In compounds **7** and **9**, the angles at the carbon atoms C(1) and C(21), respectively, are smaller than 60° (56.4 and 59.0°), C(2)–C(3) and C(22)–C(23) bond lengths are shorter than the lengths of the lateral bonds C(1)–C(2), C(1)–C(3), C(21)–C(22), and C(21)–C(23). The angles of rotation of the ferrocene and naphthalene fragments in the molecules under consideration correspond to the 'bisecting' position of the former and 'non-bisecting' position of the latter relative to the small ring (Figs. 1, 2a and 3). X-ray analysis of monobromide **7** revealed that the unit cell of monoclinic



8 7 9 6 6a

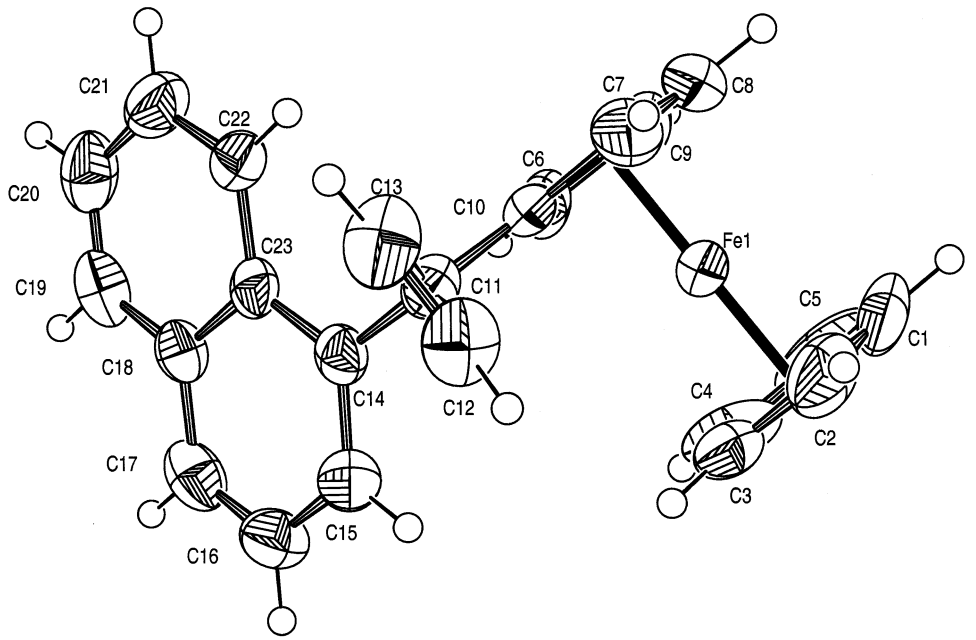
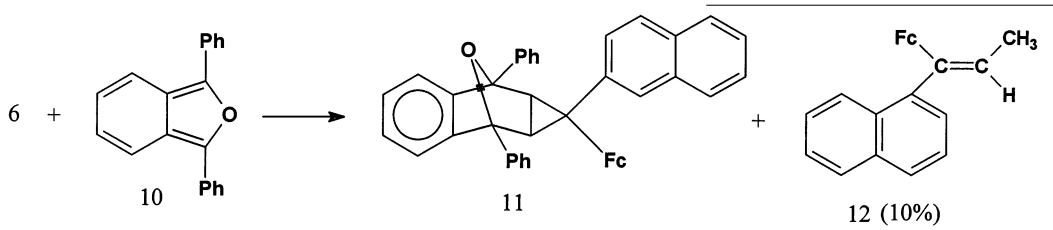


Fig. 1. Crystal structure of **6**. Selected bond lengths (Å): C_{11}–C_{12} = 1.498(5); C_{11}–C_{13} = 1.509(5); C_{12}–C_{13} = 1.272(6); and selected bond angles (°): C_{12}–C_{11}–C_{13} = 50.0(2); C_{13}–C_{12}–C_{11} = 65.4(3); C_{12}–C_{13}–C_{11} = 64.5(3).

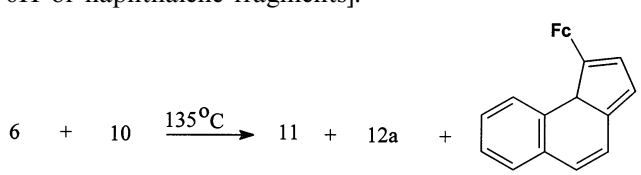
crystals of this compound contains two molecules with the bromine atoms close to each other (Fig. 2b). In all the three compounds **6**, **7**, and **9**, the Fe–C and C–C bonds as well as the geometry of the ferrocene sandwich have normal parameters.

We found that in the Diels–Alder adduct **11** the conformation of the fragment containing the small ring is preserved: ferrocene occupies a 'bisecting' position and naphthalene a 'non-bisecting' position.



^{1}H- and ^{13}C-NMR spectra of the adduct **11** correspond to only one structural isomer, which attests to a stereospecific [4 + 2]-cycloaddition. The structure of compound **11** is established on the basis of X-ray data. General view of this molecule is shown in Fig. 4. X-ray data show that compound **11** has the structure of *exo*-3-ferrocenyl-3-(1-naphthyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene with a *syn*-orientation of the naphthalene substituent. The non-equivalence of the hydrogen atoms H(2) and H(4) in the ^{1}H-NMR spectrum and of the carbon atoms C(1) and C(5) in the ^{13}C-NMR spectrum (see Section 4) can easily be explained by a mutual 'anti'-orientation of the naphthalene and ferrocene fragments in the adduct **11** (Fig. 4).

Not only was the adduct **11** isolated from the reaction mixture but also *Z*-1-ferrocenyl-1-(1-naphthyl)propene-1. The fact that propene **12a** is formed in the reaction of **6** with **10** points to a possible opening of the small ring in the thermal process. When the reaction was carried out at a higher temperature (in boiling *m*-xylene), the yields of both the adduct **11** and propene **12a** were lower. A product isolated from the reaction mixture was identified as 1-ferrocenyl-9b*H*-benzo[e]indene **13** on the basis of ^{1}H-NMR spectral data [δ 2.49 (s, 1 H, CH), 6.48 (d, 1 H, J = 5.55 Hz), 6.80 (d, 1 H, J = 5.55 Hz), plus signals for 9H of ferrocene and 6H of naphthalene fragments].



13 (20 %)

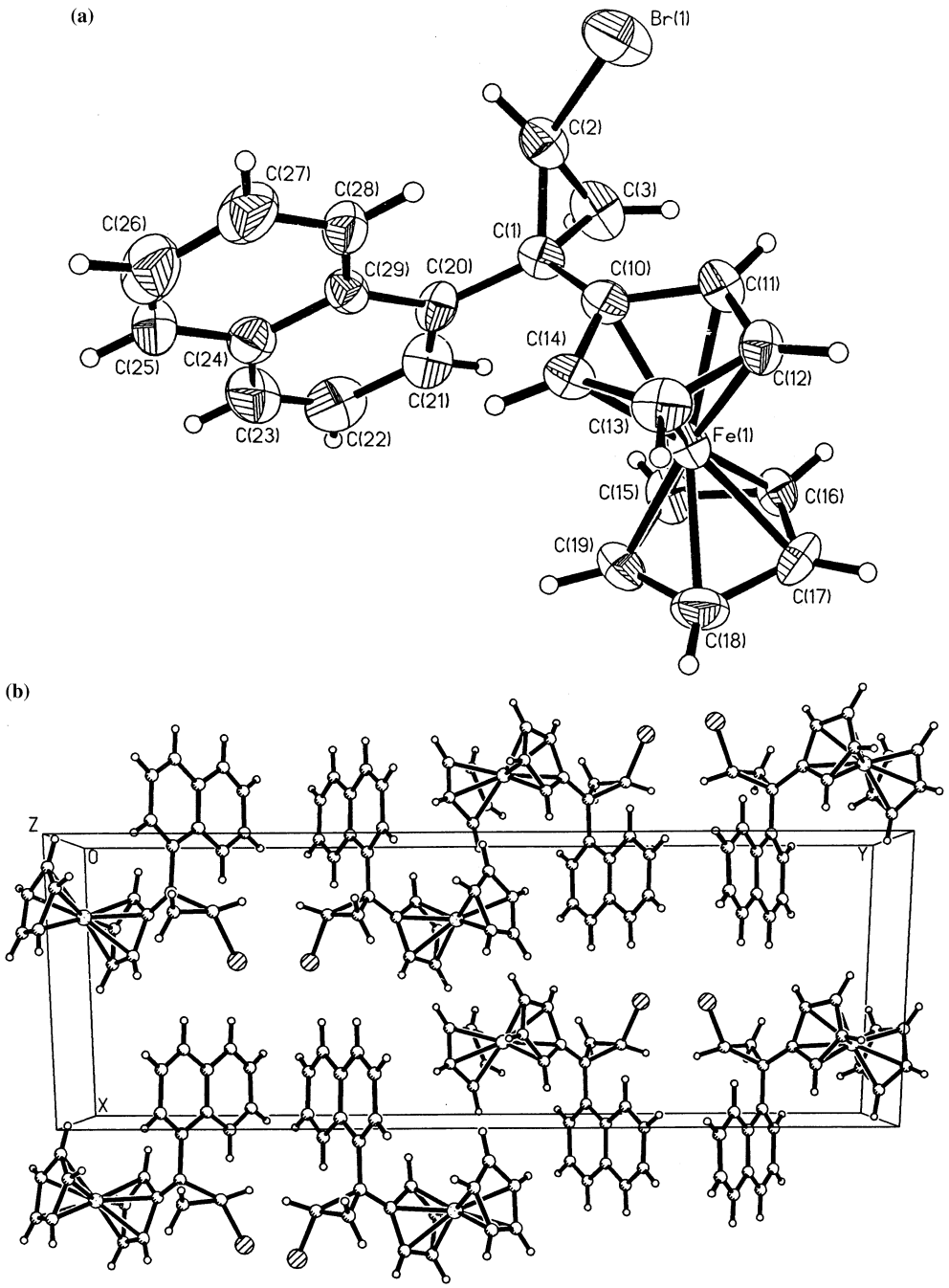
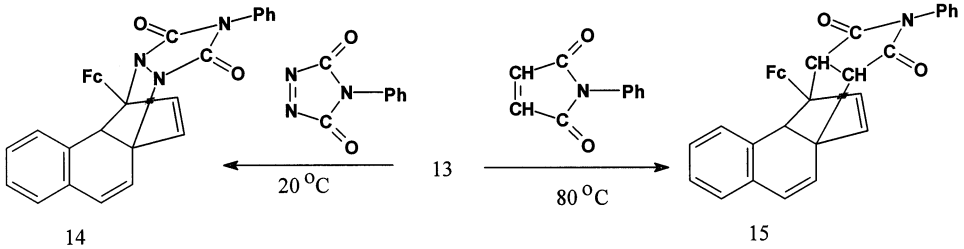


Fig. 2. (a) Crystal structure of **7**. Selected bond lengths (Å): C_1–C_2 = 1.513(17); C_1–C_3 = 1.510(15); C_2–C_3 = 1.429(19); and selected bond angles (°): C_2–C_1–C_3 = 56.4(8); C_1–C_2–C_3 = 61.7(8); C_1–C_3–C_2 = 61.9(8). (b) Crystal packing of **7**.

Benzoindene **13** was also obtained in a 63% yield when cyclopropene **6** was boiled in *m*-xylene for 8 h: **6** $\xrightarrow{135^{\circ}C}$ **13** + **12a** (14%)

Compound **13** forms [4 + 2]-cycloadducts **14** and **15** with *N*-phenyl(azodicarboximide) and *N*-phenylmaleimide, respectively.



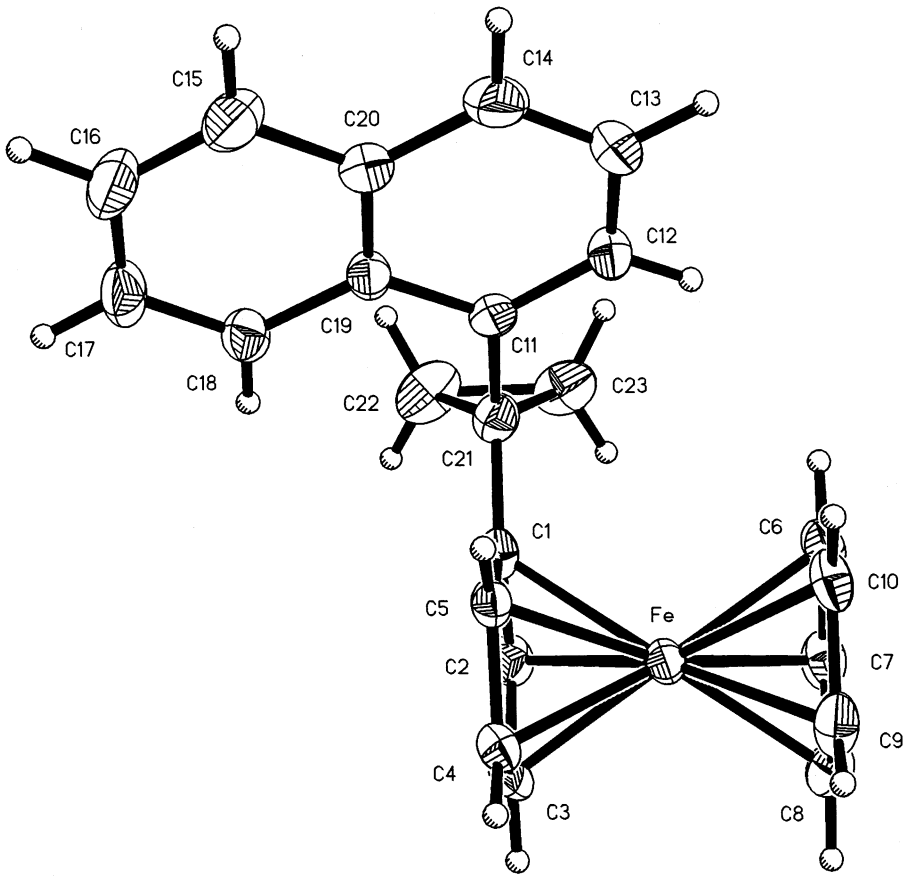


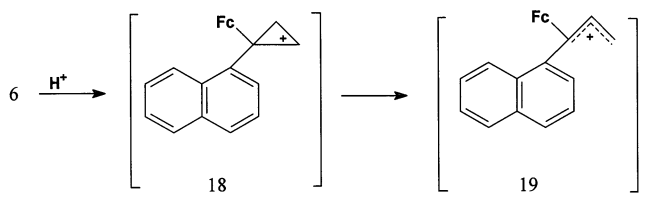
Fig. 3. Crystal structure of **9**. Selected bond lengths (Å): $C_{21}-C_{22} = 1.517(6)$; $C_{21}-C_{23} = 1.513(6)$; $C_{22}-C_{23} = 1.492(8)$; and selected bond angles (°): $C_{22}-C_{21}-C_{23} = 59.0(3)$; $C_{21}-C_{22}-C_{23} = 60.4(3)$; $C_{22}-C_{23}-C_{21} = 60.6(3)$.

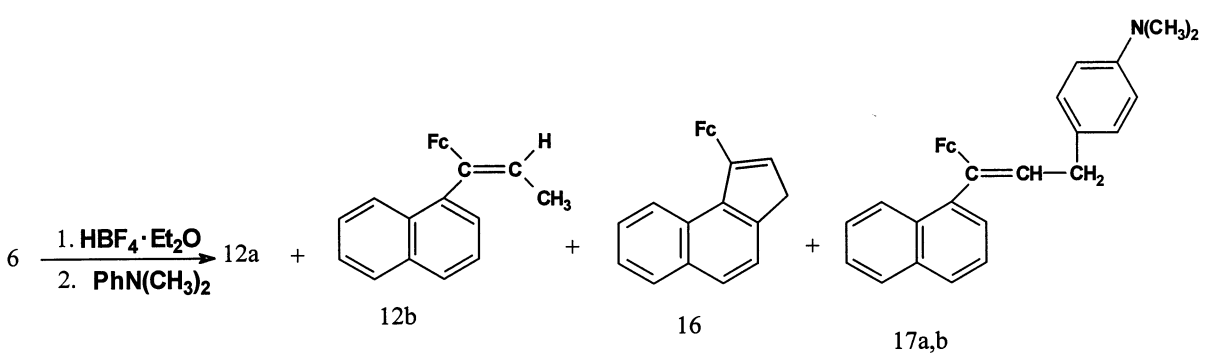
The structures of the adducts **14** and **15** were established on the basis of ^{1}H- and ^{13}C-NMR spectral data (see Section 4). The fact that the signals for the protons of the C_5H_4 group of the ferrocene fragment are shifted downfield relative to the singlet for the protons of the non-substituted cyclopentadienyl ring of ferrocene made it possible to attribute **15** to the *exo*-type structure [2,6].

It has also been discovered that the three-membered ring in cyclopropene **6** undergoes smooth opening under the action of $HBF_4 \cdot Et_2O$. Following treatment of the reaction mixture with *N*,*N*-dimethylaniline, *Z*- and *E*-1-ferrocenyl-1-(1-naphthyl)prop-1-enes **12a** and **12b** (ca. 5:1, ^{1}H-NMR data), 1-ferrocenyl-3*H*-benzo[e]indene **16**, and *Z*- and *E*-3-(*p*-dimethylaminophenyl)-1-ferrocenyl-1-(1-naphthyl)prop-1-enes **17a** and **17b** (ca. 4:1, ^{1}H-NMR data) were isolated by TLC.

The opening of a small ring in cyclopropene **6** with superacid CF_3SO_3H gave mainly benzoindene **16** (ca. 64%) and the products of *p*-alkylation of *N*,*N*-dimethylaniline, **17a,b** (ca. 11%).

It is believed that in this case the protonation of cyclopropene **6** results in an intermediate cyclopropyl cation **18**, which undergoes smooth opening to give a ferrocenylallylic cation **19** [2–4] stabilized by the ferrocene substituent.





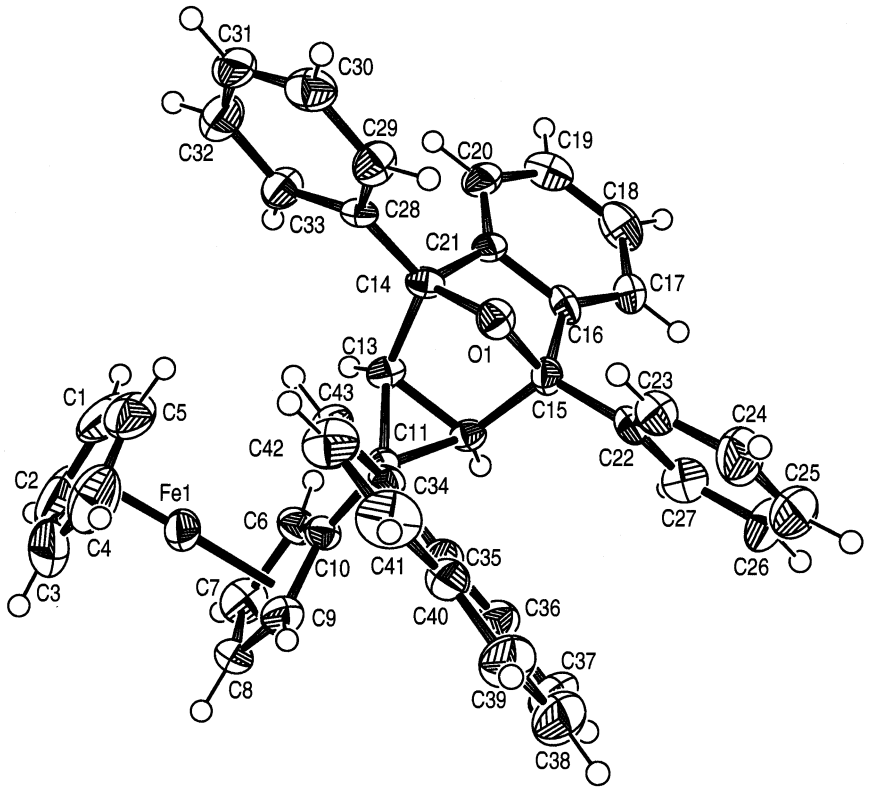


Fig. 4. Crystal structure of **11**. Selected bond lengths (Å): C_{11}–C_{12} = 1.519(6); C_{11}–C_{13} = 1.532(6); C_{12}–C_{13} = 1.513(6); and selected bond angles (°): C_{12}–C_{11}–C_{13} = 59.5(3); C_{13}–C_{12}–C_{11} = 60.7(3); C_{12}–C_{13}–C_{11} = 59.8(3); C_{34}–C_{11}–C_{10} = 113.9(4); C_{34}–C_{11}–C_{12} = 121.7(4); C_{34}–C_{11}–C_{13} = 125.7(4).

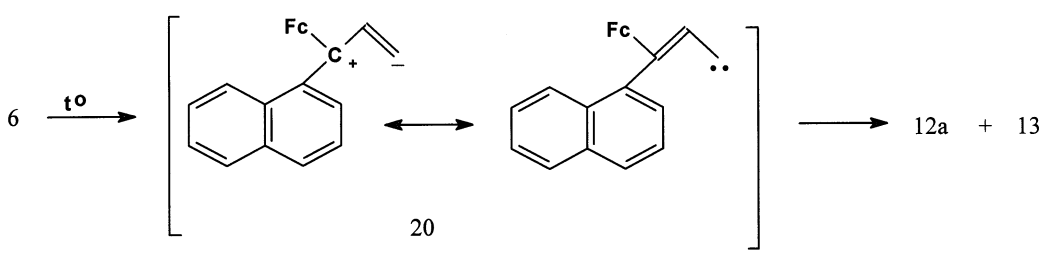
The cation **19** then enters into intramolecular transformations and alkylates the naphthalene ('non-bisecting') substituent, it also alkylates *N*,*N*-dimethylaniline by the less substituted carbenium center [9,10], and undergoes reduction. Reduction of this type of ferrocenylallylic cations has previously been observed for 1-ferrocenyl-1-phenylallyl cation [4] and 3-ferrocenylmethylene-1,2,7,7-tetramethylbicyclo[2.2.1]hept-2-yl cation [11,12], which is associated, in our opinion, with the participation of the iron atom [13].

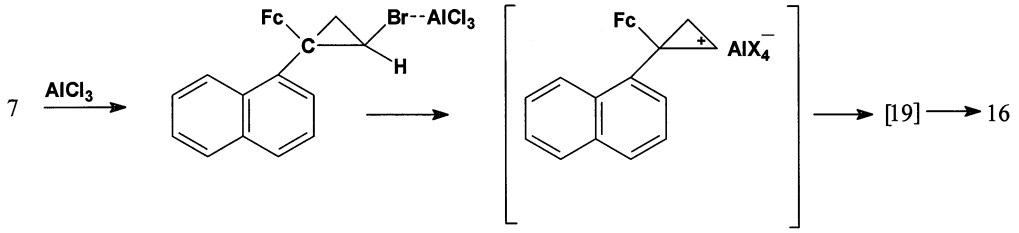
The formation of compounds **12a** and **13** in thermal processes might occur due to heterolysis of one of the σ-bonds of the small ring [3,5]. The intermediate carbenoid **20** is involved in intramolecular alkylation and reduction analogous to those of the ferrocenylallylic cation **19**.

However, the reduction of **20**, unlike that of cation **19**, is stereospecific, this results in the *Z*-alkene **12a**; the intramolecular transformation of **20** gives 9b*H*-benzo[e]indene **13**, which differs in structure from 3*H*-benzo[e]indene **16**.

It has also been demonstrated that the small ring is easily opened upon treatment of monobromocyclopropane **7** with $AlCl_3$ [4] and of cyclopropane **9** with triphenylcarbenium tetrafluoroborate [14,15].

The opening of a small ring in **7** occurs as a result of detachment of a halide anion and generation of a cationic center in the cyclopropane ring with subsequent (or simultaneous) opening of the small ring and formation of an allylic cation **19**.

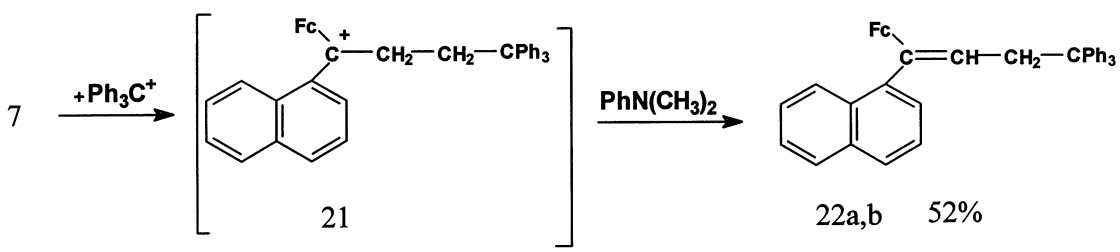




Thus, 1-ferrocenyl-3*H*-benzo[e]indene **16** was isolated as the main reaction product (ca. 67%). The reaction of cyclopropane **9** with triphenylcarbenium tetrafluoroborate occurs in a more complex way. Ring-opening in **9** due to hydride detachment [14,15] and the formation of the allylic cation **19** is only one of the processes that occur:

$$\mathbf{7} \xrightarrow[-Ph_3CH]{+Ph_3C^+BF_4^-} [\mathbf{18}] \rightarrow [\mathbf{19}] \xrightarrow{PhN(CH_3)_2} \mathbf{16}\ (23\%) + \mathbf{17a,b}\ (5\%)$$

In addition, competitive opening of the three-membered ring occurs predominantly due to electrophilic addition of Ph_3C^+ leading to cation **21**. Its deprotonation with *N*,*N*-dimethylaniline results in 1-ferrocenyl-4,4,4-triphenyl-1-(1-naphthyl)but-1-ene **22** as a mixture of two isomers **22a** and **22b** in a ratio of ca. 2:1 according to ^{1}H-NMR data.



The major isomer **22a** was isolated individually. However, the configuration of compounds **22a** and **22b** (*Z*- or -*E*) has not been established yet.

3. Conclusion

Thus, the results of this study support our previous conclusion [4] that the regioselectivity of intramolecular transformations of 3-aryl-3-ferrocenylcyclopropenes **1** and **6** and 1-aryl-1-ferrocenylcyclopropanes **7** and **9** is determined by spatial orientation of substituents in the starting compounds. Aryl substituents that occupy a 'non-bisecting' position relative to the three-membered ring undergo alkylation upon opening of the small ring under various conditions. We did not observe intramolecular cyclization involving the ferrocene fragment, although such an intramolecular alkylation of a γ-ferrocenyl group (relative to the cationic or carbenoid center) is well known. This seems to be connected with the 'bisecting' orientation of the ferrocene fragment in compounds under study.

4. Experimental

The solvents were dried by standard methods and distilled prior to use. Column chromatography was carried out on Al_2O_3 (activity III according to Brockmann). Elemental analyses were carried out by the Microanalytical laboratory of the Department of Chemistry of the Moscow State University. ^{1}H- and ^{13}C-NMR spectra were registered in $CDCl_3$ on a Gemini 200 Varian spectrometer at 200 and 50 MHz using Me_4Si as the internal standard. The parameters of the unit cell and the X-ray diffraction intensities were recorded on Siemens P4/PC (compounds **6**, **9** and **11**) and Siemens P4 (compound **7**) spectrometers (Table 1).

4.1. 2,2-Dibromo-1-ferrocenyl-1-(1-naphthyl)cyclopropane ***8***

Cyclopropane **8** was obtained by a standard procedure [16] from 1-ferrocenyl-1-(1-naphthyl)ethylene in a yield of 75%; orange crystals, m.p. 141–142°C. ^{1}H-NMR: δ 2.46 (d, 1 H, CH_2, $J = 8.0$ Hz), 2.55 (d, 1H, CH_2, $J = 8.0$ Hz), 3.95 (s, 5 H, C_5H_5), 3.63 (m, 1H), 3.98 (m, 1 H), 4.15 (m, 1H), 4.27 (m, 1H) (C_5H_4), 7.98, 8.05 (m, 7H, $C_{10}H_7$). ^{13}C-NMR: δ 35.63 (CH_2), 38.60 (C), 66.10 (C), 68.79 (C_5H_5), 67.04, 68.09, 68.99, 71.16 (C_5H_4), 89.72 (C_{ipso} Fc), 125.11, 125.84, 125.98, 127.39, 127.53, 128.26, 128.41 (CH), 129.44, 133.73, 138.75 (C_{ipso}). Anal. Found: C, 54.25; H, 3.49; Br, 31.60; Fe, 11.04. $C_{23}H_{18}Br_2Fe$. Calc.: C, 54.16; H, 3.56; Br, 31.33; Fe, 10.95%.

4.2. Z-2-Bromo-1-ferrocenyl-1-(1-naphthyl)cyclopropane ***7***

A solution of EtMgCl (3.2 mmol) in ether and several drops of $(^i$PrO$)_4$Ti were added to a solution of

Table 1
Crystal data, data collection and refinement parameters for **6**, **7**, **9** and **11**

Data	**6**	**7**	**9**	**11**
Molecular formula	$C_{23}H_{18}Fe$	$C_{23}H_{19}BrFe$	$C_{23}H_{20}Fe$	$C_{43}H_{32}FeO$
Formula weight (g mol^{-1})	350.23	431.10	352.24	620.54
Crystal size (mm)	$0.70\times0.15\times0.15$	$0.75\times0.70\times0.15$	$0.70\times0.24\times0.16$	$0.15\times0.10\times0.10$
Color, habit	Orange, needle	Yellow, plate	Orange, prism	Orange, regular
Temperature (K)	298	293	293	298
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	7.508(1)	9.668(3)	7.404(2)	7.765(2)
b (Å)	14.563(2)	27.143(4)	18.980(3)	10.909(2)
c (Å)	15.995(2)	6.9920(10)	12.418(2)	18.967(3)
α (°)	92.14(1)	—	90	89.73(1)
β (°)	102.95(1)	102.45(2)	98.30(2)	85.47(1)
γ (°)	94.40(1)	—	90	78.22(2)
V (Å^3)	1696.62(42)	1790.1(7)	1726.8(6)	1567.8(6)
Z	2	4	4	2
D_{calc} (g cm^{-3})	1.355	1.600	1.355	1.314
μ (mm^{-1})	0.887	3.076	0.873	0.515
$F(000)$	712	872	736	648
Radiation	Mo–K_α	Mo–K_α	Mo–K_α	Mo–K_α
λ (Å)	0.71073	0.71073	0.71073	0.71073
Monochromator	Highly oriented graphite crystal			
2θ range (°)	$3.0<2\theta<50.0$	$2.0<2\theta<50.0$	$3.97<2\theta<50.0$	$3.0<2\theta<46.0$
Scan type	$\theta/2\theta$	2θ-ω	2θ-ω	$\theta/2\theta$
Reflections collected	7445	4351	3281	5490
Unique reflections	5954	3158	3034	4354
R_{int}	0.0236	0.0494	0.0425	0.0672
Reflections with $I>2\sigma(I)$	$R_1=0.0474$, $wR_2=0.0798$	$R_1=0.0657$, $wR_2=0.0849$	$R_1=0.0475$, $wR_2=0.0928$	$R_1=0.0637$, $wR_2=0.0757$
R indices (all data)	$R_1=0.0990$, $wR_2=0.0905$	$R_1=0.1420$, $wR_2=0.1621$	$R_1=0.0879$, $wR_2=0.1093$	$R_1=0.1707$, $wR_2=0.0932$
Data/restraints/parameters	5904/0/469	3158/0/226	3034/0/217	4304/0/438
Refinement method	Full-matrix least-squares on F^2			
Weighting scheme	$w^{-1}=\sigma^2(F)+0.0008F^2$	$w^{-1}=\sigma^2(F)+0.0050F^2$	$w^{-1}=\sigma^2(F_o^2)+(0.0334P)^2+0.4027P$; where $P=(F_o^2+2F_c^2)/3$	$w^{-1}=\sigma^2(F)+0.0008F^2$
Goodness-of-fit	0.944	0.95	1.027	0.895
Min./max. residual electron density (e Å^{-3})	−0.253/0.261	−1.28/0.95	−0.269/0.318	−0.293/0.284
Hydrogen atoms	Riding	Riding	Riding	Riding
R (observed data)	0.0474	0.0657	0.0475	0.0637
Solution	SHELX-97	Direct methods	Direct methods (SIR92)	SHELX-97

dibromide **8** (1.53 g, 3 mmol) in dry ether (50 ml). The mixture was stirred at room temperature (r.t.) until the dark brown color turned yellow, and then water (50 ml) was added dropwise. The organic layer was separated, the solvent was distilled off and the residue was chromatographed on Al_2O_3 (hexane as the eluent) to yield 1.04 g (80%) of monobromide **7**, yellow crystals, m.p. 108–109°C. ^{1}H-NMR: δ 1.76 (dd, 1H, CH_2, $J=5.7$, 6.6 Hz), 2.15 (dd, 1H, CH_2, $J=6.6$, 8.4 Hz), 3.53 (dd, 1H, CH_2, $J=5.7$, 8.4 Hz), 4.08 (s, 5H, C_5H_5), 3.55 (m, 1H), 3.98 (m, 1H), 4.20 (m, 1H), 4.35 (m, 1H) (C_5H_4), 7.46–8.02 (m, 7H, $C_{10}H_7$). Anal. Found: C, 63.85; H, 4.58; Br, 18.68; Fe, 13.07. $C_{23}H_{19}BrFe$. Calc.: C, 64.07; H, 4.44; Br, 18.54; Fe, 12.95%.

4.3. 1-Ferrocenyl-1(1-naphthyl)cyclopropane **9**

The compound 1-ferrocenyl-1(1-naphthyl)cyclopropane **9** was obtained analogously from dibromide **8** (1.53 g) and EtMgCl (6.2 mmol) in ether and (^{i}PrO)$_4$Ti (1 ml). Yield 0.95 g (73%), yellow crystals, m.p. 118–119°C. ^{1}H-NMR: δ 1.35 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 3.71 (m, 2H), 3.93 (m, 2H) (C_5H_4), 4.11 (s, 5H, C_5H_5), 7.40–8.26 (m, 7H, $C_{10}H_7$). ^{13}C-NMR: δ 19.40 (CH_2), 19.44 (CH_2), 37.15 (C), 66.60 (C_5H_4), 68.48 (C_5H_5), 69.56 (C_{ipso} Fc), 125.34, 125.41, 125.43, 125.94, 127.37, 127.94, 128.42 (CH), 133.10, 133.82, 140.78 (C_{ipso}). Anal. Found: C, 78.35; H, 5.94; Fe, 15.63. $C_{23}H_{20}Fe$. Calc.: C, 78.42; H, 5.72; Fe, 15.85%.

4.4. 3-Ferrocenyl-3-(1-naphthyl)cyclopropene **6**

A mixture of *Z*-**7** (1.3 g, 3 mmol) and ^{t}BuOK (4 mmol) in DMSO (30 ml) was stirred for 10 h at 20°C in an atmosphere of dry argon. Benzene (100 ml) and water (50 ml) was then added, the organic layer was separated and washed with water. The solvent was distilled in vacuo and the residue was chromatographed on Al_2O_3 (hexane as the eluent). Eluted first was 3-ferrocenyl-3-(1-naphthyl)prop-1-ene (**6a**), (0.21 g, 20%), m.p. 103–104°C. ^{1}H-NMR: δ 4.11 (s, 5H, C_5H_5), 4.12 (d, 1H, $J = 5.8$ Hz), 3.75 (m, 2 H), 4.27 (m, 1H), 4.53 (m, 1H) (C_5H_4), 4.80 (dd, 1H, CH_2, $J = 1.20$, 5.8 Hz), 5.28 (dd, 1H, CH_2, $J = 1.20$, 8.0 Hz), 5.96 (m, 1H, CH=), 6.85, 7.30–7.60, 7.72–7.90 (m, 7H, $C_{10}H_7$). Anal. Found: C, 78.19; H, 5.93; Fe, 16.06. $C_{23}H_{20}Fe$. Calc.: C, 78.42; H, 5.72; Fe, 15.85%. Eluted second was cyclopropene **6**, yield 0.63 g (60%), yellow needles, m.p. 123–124°C. ^{1}H-NMR: δ 3.74 (m, 2 H), 3.96 (m, 2H) (C_5H_4), 4.15 (s, 5H, C_5H_5), 7.51 (s, 2H, CH=CH), 7.38–7.58, 7.70–7.80, 8.10–8.20 (m, 7H, $C_{10}H_7$). ^{13}C-NMR: δ 26.33 (C), 67.12, 67.94 (C_5H_4), 68.05 (C_5H_5), 98.73 (C_{ipso} Fc), 113.48 (CH=CH), 125.42, 125.46, 125.49, 125.63, 125.92, 126.99, 128.51 (CH), 132.04, 133.99, 143.08 (C_{ipso}). Anal. Found: C, 78.98; H, 5.26; Fe, 15.73. $C_{23}H_{18}Fe$. Calc.: C, 78.87; H, 5.18; Fe, 15.95%.

4.5. Reaction of cyclopropene **6** with 1,3-diphenylisobenzofuran **10**

(a) A mixture of cyclopropene **6** (0.35 g, 1 mmol) and compound **10** (0.56 g, 2 mmol) in toluene (50 ml) was refluxed until the starting compound **6** disappeared (TLC control on Silufol plates in hexane). The solvent was evaporated in vacuo and the residue was chromatographed (TLC on silica gel, hexane–benzene, 2:1) to give compounds **12a** and **11**.

Z-1-Ferrocenyl-1-(1-naphthyl)prop-1-ene (**12a**), R_f 0.78, yield 0.042 g (10.2%), yellow crystals, m.p. 118–119°C. ^{1}H-NMR: δ 1.42 (d, 3H, CH_3, $J = 6.92$ Hz), 4.08 (s, 5H, C_5H_5), 3.74 (m, 1H), 4.02 (m, 1H), 4.19 (m, 1H), 4.41 (m, 1H) (C_5H_4), 6.32 (q, 1H, CH=, $J = 6.92$ Hz), 7.31–7.60, 7.75–7.90 (m, 7H, $C_{10}H_7$). ^{13}C-NMR: δ 29.69 (CH_3), 69.26 (C_5H_5), 64.79, 67.94, 68.05 (C_5H_4), 87.12 (C_{ipso} Fc), 122.08 (CH=), 125.35, 125.62, 125.66, 126.20, 126.74, 127.12, 128.15 (CH), 128.05 (C), 133.63, 137.01, 140.05 (C_{ipso}). Anal. Found: C, 78.23; H, 5.88; Fe, 15.69. $C_{23}H_{20}Fe$. Calc.: C, 78.43 (compound**6a** 78.42%); H, 5.72; Fe, 15.85%.

Adduct **11**, R_f 0.36, yield 0.41 g (65%), yellow needles, m.p. 266–267°C. ^{1}H-NMR: δ 2.55 (d, 1H, CH, $J = 7.2$ Hz), 2.75 (d, 1H, CH, $J = 7.2$ Hz), 3.12 (br.s, 1H), 3.74 (br.s, 1H), 3.96 (br.s, 1H), 4.01 (br.s, 1H) (C_5H_4), 4.05 (s, 5H, C_5H_5), 6.45, 6.80, 6.92–7.15, 7.31–7.40, 7.46–7.65 (m, 21H, arom.). ^{13}C-NMR: δ 41.86 (CH), 45.36 (C), 47.82 (CH), 68.77 (C_5H_5), 63.86, 66.59, 67.25, 69.58 (C_5H_4), 88.52, 88.54 (C-1, C-5), 95.86 (C_{ipso} Fc), 118.98, 119.04, 123.39, 124.38, 125.03, 126.10, 126.27, 126.66, 126.85, 127.63, 127.74, 128.34 (CH), 132.05, 132.98, 134.78. 136.24, 138.08, 149.63, 150.35 (C_{ipso}). Anal. Found: C, 83.36; H, 5.04; Fe, 8.74. $C_{43}H_{32}FeO$. Calc.: C, 83.22; H, 5.20; Fe, 9.00%.

(b) Analogously, compounds **6** (0.35 g) and **10** (0.56 g) were refluxed in *m*-xylene to give 0.024 g (7%) of *Z*-**12a**, m.p. 119°C, 0.32 g (50%) of adduct **11**, m.p. 265–267°C, and 0.07 g (20%) of indene **13**, R_f 0.29, pale-yellow crystals, m.p. 121–122°C. ^{1}H-NMR: δ 2.48 (s, 1H, CH), 4.18 (s, 5H, C_5H_5), 4.01 (m, 1H), 4.06 (m, 1H), 4.20 (m, 1H), 4.72 (m, 1H) (C_5H_4), 6.75 (d, 1H, $J = 5.7$ Hz), 6.81 (d, 1H, $J = 5.7$ Hz), 7.33–7.46, 7.75–7.81, 8.31–8.34 (m, 6H, $C_{10}H_6$). Anal. Found: C, 78.71; H, 5.27; Fe, 16.23. $C_{23}H_{18}Fe$. Calc.: C, 78.87; H, 5.18; Fe, 15.95%.

4.6. Thermolysis of 3-ferrocenyl-3-(1-naphthyl)cyclopropene **6**

A solution of cyclopropene **6** (0.35 g, 1 mmol) in *m*-xylene (50 ml) was refluxed for 6 h under dry argon. The solvent was evaporated in vacuo and the residue was chromatographed (TLC on silica gel, hexane–benzene, 2:1) to yield 0.05 g (14%) of alkene **12a**, m.p. 118–119°C, R_f 0.75, and 0.22 g (63%) of indene **13**, m.p. 121–122°C, R_f 0.3.

4.7. Reaction of 1-ferrocenyl-9bH-benzo[e]indene **13** with N-phenyl(azodicarboximide)

Portions of *N*-phenyl(azodicarboximide) (0.058 g) were added at 20°C to a solution of indene **13** (0.12 g, 0.33 mmol) in dry benzene (10 ml) as the bright-red color disappeared. Heptane (10 ml) was added to the pale-yellow solution and it was left for 12 h at r.t. The residue that precipitated was filtered off and washed with pentane to give adduct **14**, yield 0.14 g (78%), yellow crystals, m.p. 278–279°C. ^{1}H-NMR: δ 3.95 (s, 1H, CH), 4.29 (s, 5H, C_5H_5), 3.52 (m, 1H), 4.08 (m, 1H), 4.23 (m, 1H), 4.79 (m, 1H) (C_5H_4), 5.94 (d, 2H, $J = 1.08$ Hz), 7.40–7.60, 7.80–8.00, 8.65–8.78 (m, 11H, arom.). ^{13}C-NMR: δ 30.93 (C), 69.08 (C_5H_5), 67.06, 67.59, 68.51, 69.88 (C_5H_4), 65.73 (CH), 81.97 (C), 93.52 (C_{ipso} Fc), 122.22, 125.07, 125.51, 126.75, 127.11, 128.78, 129.38, 129.70, 131.58, 135.37 (CH), 142.71, 161.20, 162.91 (C_{ipso}), 206.10, 208.01 (C=O). Anal. Found: C, 70.64; H, 4.57; Fe, 10.82; N, 7.73. $C_{31}H_{23}FeN_3O_2$. Calc. C, 70.87; H, 4.41; Fe, 10.63; N, 8.00%.

4.8. Reaction of indene **13** with N-phenylmaleimide

A solution of indene **13** (0.12 g, 0.33 mmol) and *N*-phenylmaleimide (0.057 g) in benzene (50 ml) was refluxed for 5 h. The solvent was distilled off in vacuo

and the residue was chromatographed (TLC on silica gel, hexane–benzene, 2:1) to give 0.12 g of the adduct **15**, yellow crystals, m.p. 259–260°C. ^{1}H-NMR: δ 3.95 (d, 1H, $J = 9.1$ Hz), 4.23 (d, 1H, $J = 9.1$ Hz), 4.25 (s, 5H, C_5H_5), 4.56 (m, 1H), 4.59 (m, 1H), 4.81 (m, 1H), 4.92 (m, 1H) (C_5H_4), 4.67 (d, 1H, $J = 1.25$ Hz), 5.352 (d, 1H, $J = 4.9$ Hz), 5.376 (d, 1H, $J = 4.9$ Hz), 7.11–7.15, 7.29–7.82, 8.40–8.44 (m, 11H, arom.). ^{13}C-NMR: δ 30.35 (C), 39.43, 39.68 (CH), 52.14 (CH), 70.31 (C_5H_5), 69.71, 69.93, 72.08, 73.13 (C_5H_4), 73.05 (C), 96.10 (C_{ipso} Fc), 125.32, 125.77, 126.43, 126.53, 126.74, 127.37, 128.33, 128.44, 128.53, 128.82, 129.02, 129.10, 132.39 (CH), 132.58, 134.62, 161.50 (C_{ipso}), 176.43, 179.55 (C=O). Anal. Found: C, 75.83; H, 4.65; Fe, 10.74; N, 2.78. $C_{33}H_{25}FeNO_2$. Calc.: C, 75.72; H, 4.82; Fe, 10.67; N, 2.67%.

4.9. Reaction of cyclopropene 6 with $HBF_4 \cdot Et_2O$

A solution of **6** (0.175 g, 0.5 mmol) in dry ether (25 ml) was treated with $HBF_4 \cdot Et_2O$ (2 ml). The brown mixture was stirred in an atmosphere of argon for 1 h and *N*,*N*-dimethylaniline (2 ml) was then added. Stirring continued for an additional 30 min and the mixture was partitioned between benzene (50 ml) and water (100 ml). The organic layer was separated, washed several times with 1% HCl and water, and the solvents were distilled off in vacuo. The residue was chromatographed (TLC on silica gel, hexane–benzene, 2:1) to give the following products.

The compound propene **12** (0.09 g, 50%) was recovered as a ca. 5:1 mixture of *Z*-(**12a**) and *E*-(**12b**) isomers, R_f 0.75, yellow crystals, m.p. 84–86°C. ^{1}H-NMR for **12b**: δ 2.17 (d, 3H, CH_3, $J = 7.22$ Hz), 4.07 (s, 5H, C_5H_5), 3.85 (m, 1H), 4.03 (m, 1H), 4.09 (m, 1H), 4.40 (m, 1H) (C_5H_4), 5.74 (q, 1H, CH=, $J = 7.22$ Hz), 7.34–7.98 (m, 7H, $C_{10}H_7$). Anal. Found: C, 78.59; H, 5.61; Fe, 15.58. $C_{23}H_{20}Fe$. Calc.: C, 78.43 (compound **6a**—78.42%); H, 5.72; Fe, 15.85%.

The compound 3-(*p*-dimethylaminophenyl)-1-ferrocenyl-1-(1-naphthyl)prop-1-ene (0.041 g, 17%) was recovered as a ca. 1:1 mixture of *Z*-(**17a**) and *E*-(**17b**) isomers, R_f 0.42, brown oil. ^{1}H-NMR: δ 2.84 (s, 6H, CH_3), 2.89 (s, 6H, CH_3), 2.94 (d, 2H, $J = 6.7$ Hz), 2.98 (d, 2H, $J = 6.62$ Hz), 4.06 (s, 5H, C_5H_5), 4.08 (s, 5H, C_5H_5), 4.19 (m, 2H), 4.23 (m, 2H) (C_5H_4), 4.17 (m, 1H), 4.26 (m, 1H), 4.31 (m, 2H) (C_5H_4), 6.68 (d, 1H, $J = 6.62$ Hz), 6.92 (m, 1H, $J = 6.7$ Hz), 7.35–7.60, 7.68–7.75, 7.82–7.90 (m, 11H, arom.). Anal. Found: C, 79.11, H, 6.29, Fe, 11.64; N, 2.83. $C_{31}H_{29}FeN$. Calc.: C, 78.98; H, 6.20; Fe, 11.85%; N, 2.97%.

Indene **16**, (0.027 g, 15%), R_f 0.35, yellow crystals, m.p. 136–137°C. ^{1}H-NMR: δ 3.85 (dd, 2H, $J = 1.2$, 6.92 Hz), 4.09 (s, 5H, C_5H_5), 3.72 (m, 1H), 4.08 (m, 1H), 4.25 (m, 1H), 4.52 (m, 1H) (C_5H_4), 6.43 (t, 1H, $J = 6.95$ Hz), 7.15–7.60, 7.75–7.93 (m, 6H, $C_{10}H_6$). Anal. Found: C, 78.93, H, 4.98, Fe, 15.72. $C_{23}H_{18}Fe$. Calc.: C, 78.87; H, 5.18; Fe, 15.95%.

4.10. Reaction of cyclopropene 6 with CF_3SO_3H

Trifluoromethanesulfonic acid (0.5 ml) was added to a solution of **6** (0.175 g) in CH_2Cl_2 (20 ml). The mixture was stirred for 30 min at 20°C under dry argon and then *N*,*N*-dimethylaniline (0.5 ml) was added. Following conventional work-up and TLC on silica gel, compounds **17a,b** (0.026 g, 11%), R_f 0.42, and **16** (0.112 g, 64%), R_f 0.36, m.p. 137°C, were obtained.

4.11. Opening of a small ring in monobromide 7

Aluminum chloride (0.1 g) was added to a solution of monobromocyclopropane **7** (0.22 g, 0.5 mmol) in CH_2Cl_2 (50 ml). The mixture was stirred for 2 h at 20°C under dry argon and then *N*,*N*-dimethylaniline (1 ml) was added. The organic layer was separated and washed with 1% HCl and water. Following removal of the solvent and TLC on silica gel, indene **16** (0.13 g, 68%), R_f 0.35, m.p. 136–137°C, was obtained.

4.12. Reaction of cyclopropane 9 with triphenylmethylium tetrafluoroborate

Triphenylmethylium tetrafluoroborate (0.4 g) was added to a solution of cyclopropane **9** (0.35 g, 1 mmol) in CH_2Cl_2 (50 ml) at 20°C under dry argon. The mixture was stirred for 2 h and then worked up as described above. Following TLC on silica gel (hexane–benzene, 2:1), the following products were isolated: **17a,b** (0.025 g, 5%), R_f 0.43; indene **16** (0.081 g, 23%), R_f 0.36, m.p. 136–137°C; and a mixture of two isomeric butenes **21a** and **21b** (ca. 2:1), R_f 0.27, yellow powder, m.p. 186–188°C. Anal. Found: C, 85.11, H, 5.49, Fe, 9.68. $C_{42}H_{34}Fe$. Calc.: C, 84.84; H, 5.76; Fe, 9.40%. Recrystallization from benzene afforded the individual isomer **22a**, m.p. 213–214°C. ^{1}H-NMR: δ 3.56 (d, 2H, $J = 5.28$ Hz), 4.19 (s, 5H, C_5H_5), 3.89 (m, 1H), 3.98 (m, 1H), 4.26 (m, 1H), 4.81 (m, 1H) (C_5H_4), 6.93 (t, 1H, $J = 5.3$ Hz), 7.01–8.20 (m, 22H, arom.). Anal. Found: C, 84.72; H, 5.89; Fe, 9.21. Isomer **22b**, ^{1}H-NMR: δ 3.50 (d, 2H, $J = 5.4$ Hz), 3.87 (s, 5H, C_5H_5), 3.43 (m, 1H), 3.75 (m, 1H), 3.99 (m, 2H) (C_5H_4), 6.92 (t, 1H, $J = 5.4$ Hz), 7.10–8.20 (m, 22H, arom.).

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