Synthesis, structures, and selected chemical properties of 2-chloro- and 2-bromo-1,1-diferrocenylcyclopropanes

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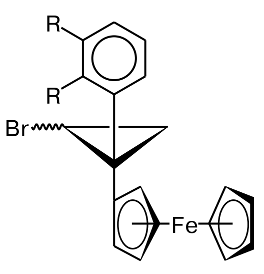
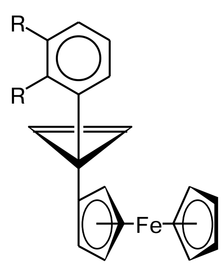
2-Chloro- and 2-bromo-1,1-diferrocenylcyclopropanes were synthesized as *Z*- and *E*-isomers with respect to the ferrocenyl substituent having a bisector orientation. The structure of *Z*-2-chloro-1,1-diferrocenylcyclopropane was confirmed by X-ray diffraction analysis. Treatment of the resulting monohalides with potassium *tert*-butoxide in dimethyl sulfoxide afforded 3,3-diferrocenylcyclopropene in 20% yield. The small ring in halogen-substituted diferrocenylcyclopropanes and diferrocenylcyclopropene is readily cleaved to give predominantly 3-ferrocenyl-1*H*-cyclopentaferrocene.

Key words: 3,3-diferrocenylcyclopropene, 1,1-diferrocenyl-2-halocyclopropanes, X-ray diffraction analysis, dehydrohalogenation, opening of the three-carbon ring.

Earlier,[1—3] we have synthesized the *Z*- and *E*-isomers of 2-bromo-1-ferrocenyl-1-phenyl-, 2-bromo-1-ferrocenyl-1-naphthylcyclopropanes (**1a,b**), and the corresponding 3-aryl-3-ferrocenylcyclopropenes **2a,b**, studied their three-dimensional structures, and examined selected chemical transformations.



1a,b

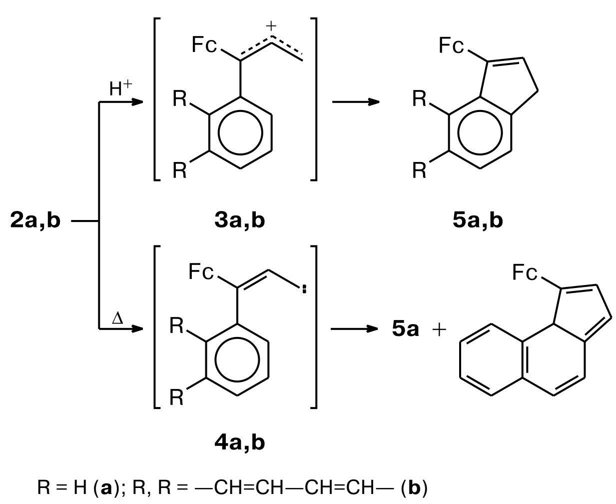


2a,b

R = H (**a**); R, R = —CH=CH—CH=CH— (**b**)

The conformations of monobromo(aryl)ferrocenylcyclopropanes **1a,b** and arylferrocenylcyclopropenes **2a,b** were established by X-ray diffraction analysis. It was found that the ferrocenyl substituent in all these compounds has a bisector orientation with respect to the plane of the three-membered ring, whereas the aryl groups have non-bisector orientations. In the cyclopropene compounds adopting these conformations, MOs of the ethylene and aryl fragments interact through space, like in 3-alkyl-3-phenylcyclopropenes,[4] which is, apparently, responsible for stereoselectivity of the addition reactions and intramolecular transformations of 3-aryl-substituted cyclo-

Scheme 1



R = H (**a**); R, R = —CH=CH—CH=CH— (**b**)

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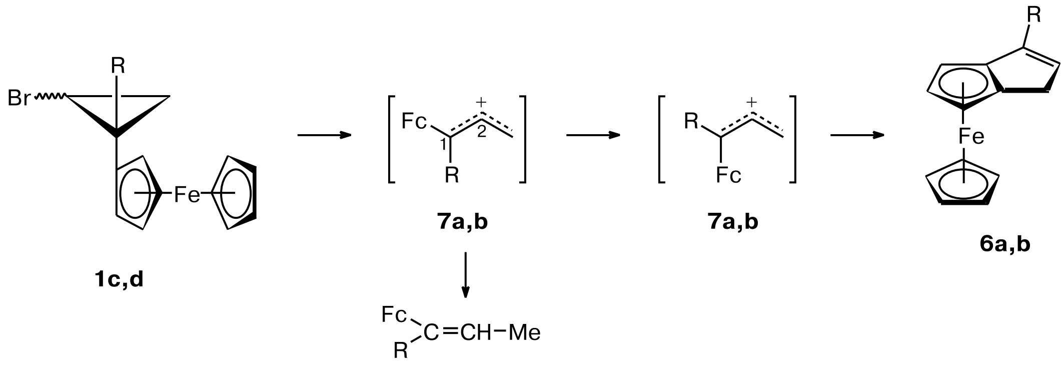
Scheme 2



1c,d **7a,b** **7a,b** **6a,b**

R = Pr[i] (**a**, **c**), C_4H_7 (**b**, **d**)

propenes.[1–3,5–9] Thus, the small ring in cyclopropenes **2a,b** is readily cleaved to give ferrocenylallylic cations **3a,b** [1–3] (under the action of acids) or carbenoid intermediates **4a,b** [1–3] (on heating), which undergo subsequent recyclization exclusively at the aryl fragment, the ferrocenyl substituent remaining intact (Scheme 1).

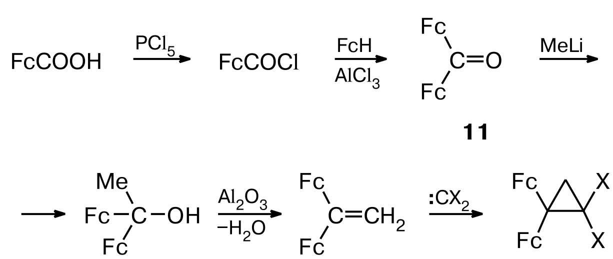
The small ring in monobromo(aryl)ferrocenylcyclopropanes **1a,b** is cleaved under the action of $AlCl_3$ to form analogous allylic cations **3a,b** [1–3] and products of their recyclization **5a,b**.[1–3]

Earlier, products of alkylation of the ferrocene fragment in **6a,b** have been obtained in low yields (4 and 11%, respectively) upon the small-ring opening in 2-bromo-1-isopropyl-[10] and 2-bromo-1-cyclobutylcyclopropanes[11] **1c,d**, which could be indicative of a non-bisector orientation of the ferrocenyl substituent in monobromo(alkyl)ferrocenylcyclopropanes by analogy with the orientation of the aryl fragments in 1-aryl-1-ferrocenylcyclopropane monobromides. However, X-ray diffraction study of the structure of 3-ferrocenyl-3-isopropylcyclopropene demonstrated that the ferrocene group in monobromides **1c,d** also has a bisector orientation.[1,10] Apparently, the small-ring opening in compounds **1c,d** gave rise to 3-alkyl-1*H*-cyclopentaferrocenes **6a,b** due to a change in the spatial arrangement of the ferrocenyl fragment in intermediate alkyl(ferrocenyl)allylic cations **7a,b** as a result of rotation about the one-and-a-half order C(1)—C(2) bond in spite of a rather high energy barrier[12–16] (Scheme 2).

Therefore, a non-bisector orientation of the ferrocenyl substituent in cyclopropane compounds remained an open question. It was reasonable to assume that this substituent could have a non-bisector orientation, in particular, in the case of the simultaneous presence of two ferrocene groups (Fc^1 and Fc^2) at one of the C atoms of the small ring. In our opinion, this conformation would be expected to facilitate diastereoselectivity of intramolecular transformations of the three-carbon ring in diferrocenylcyclopropane- and diferrocenylcyclopropene-containing compounds to form predominantly products of alkylation of the ferrocenyl substituent, which has, apparently, a non-bisector orientation with respect to the plane of the three-membered ring.

As part of our continuing studies in this field, we synthesized *gem*-diferrocenyl-substituted monochloro- and monobromocyclopropanes **8** and **9** starting from 2,2-dichloro- and 2,2-dibromo-1,1-diferrocenylcyclopropanes (**10a,b**), respectively, which were prepared according to Scheme 3.[17,18]

Scheme 3



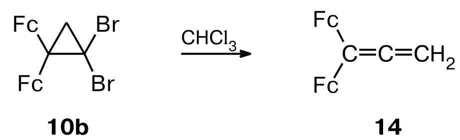
11 **12** **13** **10a,b**

X = Cl (**a**), Br (**b**)

Compounds **10a** and **11—13** were formed without complications in 50—70% yields (see the Experimental section). Dibromide **10b** was isolated in 32% yield. Dichloro- and dibromo(diferrocenyl)cyclopropanes **10a,b** are yellow crystalline compounds, which rapidly decompose on heating. Compound **10a** is more stable than dibromide **10b**. In the crystalline state, compound **10a** remains unchanged upon storage under standard conditions for several months. Crystalline dibromide **10b** turns black after storage even at low temperature during several days.

In solutions (MeCN, C_6H_6, or $CHCl_3$ + Py), dibromide **10b**, unlike dichloride **10a**, undergoes solvolysis accompanied by the small-ring opening to give 1,1-diferrocenylallene **14** (Scheme 4).

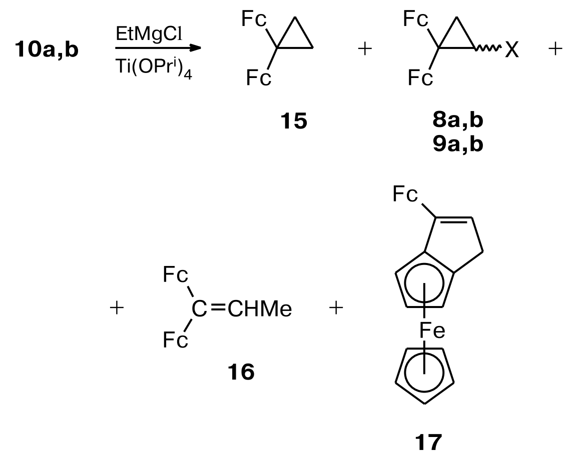
Scheme 4



The structure of compound **14** was confirmed by the ^{1}H and ^{13}C NMR spectroscopic data (Table 1) and results of elemental analysis (see the Experimental section).

Dihalides **10a,b** were reduced with a mixture of EtMgCl and Ti(OPr^i)$_4$.[19] It was found that 2-chloro- and 2-bromo-1,1-diferrocenylcyclopropanes **8** and **9** were generated as mixtures of the *Z* and *E* isomers in a ratio of ~1 : 1 in low total yields (20—25%) (Scheme 5). In addition to monohalides, products of complete reduction (1,1-diferrocenylcyclopropane (**15**)) and opening of the three-carbon ring (1,1-diferrocenylpropene (**16**) and 3-ferrocenyl-1*H*-cyclopentaferrocene (**17**)) were isolated from the reaction mixture.

Scheme 5



X = Cl (**8**), Br (**9**)

Variations in the reduction conditions did not lead to an increase in the yields of monohalides **8** and **9**. Never-

Table 1. ^{1}H NMR spectra of the resulting compounds

Compound	δ (*J*/Hz)			
	C_5H_5 (s)	C_5H_4 (m), C_5H_3 (m)	CH_2	Other protons
8a	4.05 (5 H); 4.16 (5 H)	3.83 (1 H); 4.01 (1 H); 4.04 (1 H); 4.07 (1 H); 4.18 (1 H); 4.21 (3 H)	1.33 (dd, 1 H, *J* = 4.8, *J* = 5.7); 1.90 (dd, 1 H, *J* = 5.7, *J* = 7.5)	3.94 (dd, 1 H, CH, *J* = 4.8, *J* = 7.5)
8b	4.08 (5 H); 4.12 (5 H)	4.03 (2 H); 4.06 (2 H); 4.16 (2 H); 4.23 (2 H)	1.50 (dd, 1 H, *J* = 2.7, *J* = 7.3); 1.69 (dd, 1 H, *J* = 4.2, *J* = 7.3)	3.92 (dd, 1 H, CH, *J* = 2.7, *J* = 7.3)
9a	4.03 (5 H); 4.17 (5 H)	3.82 (1 H); 4.00 (1 H); 4.02 (1 H); 4.06 (1 H); 4.19 (1 H); 4.20 (3 H)	1.34 (dd, 1 H, *J* = 4.8, *J* = 5.9); 1.94 (dd, 1 H, *J* = 5.9, *J* = 7.6)	3.92 (dd, 1 H, CH, *J* = 4.8, *J* = 7.6)
9b	4.10 (5 H); 4.14 (5 H)	4.00 (2 H); 4.04 (2 H); 4.16 (2 H); 4.22 (2 H)	1.49 (dd, 1 H, *J* = 3.5, *J* = 6.0); 1.70 (dd, 1 H, *J* = 6.0, *J* = 7.5)	3.90 (dd, 1 H, CH, *J* = 3.5, *J* = 7.5)
10a	4.13 (5 H); 4.14 (5 H)	4.00 (2 H); 4.16 (2 H); 4.17 (2 H); 4.19 (2 H)	2.24 (s, 2 H)	—
10b	4.11 (5 H); 4.12 (5 H)	4.05 (2 H); 4.18 (4 H); 4.25 (2 H)	2.37 (s, 2 H)	—
11	4.20 (10 H)	4.53 (4 H); 4.99 (4 H)	—	—
12	4.19 (10 H)	4.09 (4 H); 4.11 (4 H)	—	1.88 (s, 3 H, Me); 2.59 (s, 1 H, OH)
13	4.14 (10 H)	4.26 (4 H); 4.62 (4 H)	5.41 (s, 2 H)	—
14	3.96 (5 H); 4.03 (5 H)	4.29 (6 H); 4.97 (2 H)	4.10 (s, 2 H)	—
15	4.10 (5 H); 4.11 (5 H)	3.94 (4 H); 4.05 (4 H)	1.20 (s, 4 H)	—
16	4.09 (5 H); 4.13 (5 H)	4.18 (1 H); 4.23 (1 H); 4.49 (3 H); 4.51 (3 H)	—	1.98 (d, 3 H, Me, *J* = 7.5); 6.23 (q, 1 H, CH, *J* = 7.5)
17	4.11 (5 H); 4.15 (5 H)	4.20 (2 H); 4.24 (2 H); 4.26 (1 H); 4.55 (2 H)	2.80 (d, 2 H, *J* = 7.3)	6.20 (t, 1 H, CH, *J* = 7.3)
18	4.06 (5 H); 4.07 (5 H)	3.80 (4 H); 3.94 (4 H)	—	6.78 (s, 2 H, 2 CH)

theless, in spite of the formation of a mixture of compounds, reaction products **8a,b** (or **9a,b**), **15**, **16**, and **17** were isolated by chromatography on Al_2O_3. The structures of the resulting compounds were unambiguously established by ^1H and ^{13}C NMR spectroscopy (Tables 1 and 2). The assignment of isomeric monohalides **8a**, **9a** and **8b**, **9b** to the *Z* or *E* isomers was made based on the ^1H NMR spectra taking into account the NMR criteria, which have been proposed earlier for determining the *Z*- and *E*-geometric isomers of monobromo(ferrocenyl)cyclopropanes containing the ferrocenyl substituents in a bisector orientation.[1—3,20—22] Thus, the ^1H NMR spectra of compounds **8a** and **9a** each have two doublets of doublets (δ 1.33 and 1.90; δ 1.36 and 1.94, respectively) belonging to the protons of the methylene group (AB portion of the ABM spin system) with $|\Delta\delta| = \delta_A - \delta_B = 0.57$ and 0.58, which is characteristic of *Z*-monobromo(ferrocenyl)cyclopropanes. In the ^1H NMR spectra of isomeric halocyclopropanes **8b** and **9b**, analogous signals are observed at δ 1.50 and 1.69 ($|\Delta\delta| = 0.19$) and at δ 1.49 and 1.70 ($|\Delta\delta| = 0.21$), respectively, like those in the spectra of the *E* isomers of alkyl- and arylferrocenylbromocyclopropanes studied earlier. In the present study, we discovered for the first time the geometric isomerism in compounds containing pairs of identical substituents at the adjacent C atoms, two bulky ferrocenyl substituents being in different spatial orientations.

No isomerization of *Z*-monohalides (**8a**, **9a**) into the *E* isomers (**8b**, **9b**) and conversely was revealed by measuring the ^1H NMR spectra of isomeric monohalides **8a**, **9a** and **8b**, **9b** at equal intervals (6 measurements at 12-hour intervals). Only accumulation of the product of the small-ring opening, *viz*., of compound **17**, was observed in solutions of compounds **8a**, **9a** and **8b**, **9b**. In our opinion, this fact indicates that free rotation about the exocyclic Fc—C(cyclopropyl) bonds is substantially hindered or, conceivably, absent, which is the probable reason for the geometric isomerism because two ferrocenyl substituents (Fc^1 and Fc^2) become nonequivalent.

The *Z* configuration of one of the monohalides synthesized, *viz*., 2-chloro-1,1-diferrocenylcyclopropane (**8a**), was confirmed not only by spectroscopic data but also by X-ray diffraction analysis (Tables 3 and 4). The overall view of molecule **8a** is shown in Fig. 1. The molecular packing in the crystal is presented in Fig. 2. An interesting characteristic feature of the crystal structure of compound **8a** is that the unit cell is composed of closely-spaced pairs of the monochlorocyclopropane molecules containing the Cl atoms in opposite orientations (see Fig. 2). The three-membered ring in molecule **8a** is a scalene triangle. The C(11)—C(13) and C(34)—C(35) bond lengths are somewhat larger (1.540 and 1.520 Å, respectively), whereas the C(12)—C(13) and C(34)—C(36) bond lengths are slightly smaller (1.48 and 1.478 Å, respectively) than the standard values (the typical C—C bond length in cyclopropanes is ~1.51 Å).[23,24] In compound **8a**, the angles of rotation of the cyclopentadienyl rings of the Fc^1 and Fc^3 fragments correspond to the bisector orientations with respect to the three-membered ring, whereas the angles of rotation of the cyclopentadienyl rings of the Fc^2 and Fc^4 fragments correspond to nonbisector orientations. The ferrocenyl substituents Fc^1 and Fc^3 having the bisector orientations and the Cl(1) and Cl(3) atoms are in *cis* positions. The Fe—C bond lengths have standard values, and the ferrocene sandwiches show a typical geometry.[10]

Table 2. ^{13}C NMR spectra of compounds **8a**, **10b**, and **13—17**

Compound	δ					
	C_5H_5	C_5H_4, C_5H_3	CH_2	Me, CH	C	C_{ipso} (Fc)
8a	68.5, 68.7	66.5, 67.0, 67.2, 67.4, 67.8, 68.0, 68.9, 69.0	24.5	43.7	25.3	90.3, 95.0
10b	69.4, 69.5	66.1 (2 C); 66.7 (2 C); 69.6; 70.0; 70.6; 71.5	36.2	—	32.5, 37.5	94.2, 94.4
13	69.5	67.8, 68.1	109.4	—	143.0	85.7
14	69.5, 69.7	66.9, 67.3, 70.7, 71.0	112.6	—	116.6, 124.7	87.8, 88.7
15	68.4	66.7, 67.5	19.2	—	17.8	96.8
16	69.2, 69.3	67.2, 67.4, 68.2, 69.7	—	19.2, 123.3	133.5	84.4, 90.4
17	69.3, 69.4	67.3, 67.6, 68.3, 68.5, 69.2, 69.5, 69.9	30.6	128.9	133.4	84.5, 90.3, 98.7

Table 3. Selected bond lengths (*d*) and bond angles (ω) in molecule **8a**

Bond	*d*/Å	Angle	ω/deg
C(11)—C(12)	1.513(16)	C(12)—C(13)—C(11)	60.0(7)
C(11)—C(13)	1.540(15)	C(12)—C(11)—C(13)	58.2(9)
C(12)—C(13)	1.48(2)	C(13)—C(12)—C(11)	61.8(8)
C(1)—C(11)	1.466(17)	C(13)—C(12)—Cl(1)	119.1(11)
C(11)—C(14)	1.519(16)	C(11)—C(12)—Cl(1)	122.5(10)
Cl(20)—C(12)	1.753(15)	C(1)—C(11)—C(14)	113.4(9)
C(34)—C(35)	1.520(19)	C(1)—C(11)—C(13)	120.9(11)
C(35)—C(36)	1.50(2)	C(12)—C(11)—C(14)	113.9(10)
C(34)—C(36)	1.478(18)	C(36)—C(34)—C(35)	60.1(9)
C(34)—C(37)	1.539(16)	C(36)—C(35)—C(34)	58.6(9)
C(24)—C(34)	1.472(19)	C(34)—C(36)—C(35)	61.3(9)
C(11)—C(10)	1.558(11)	C(24)—C(34)—C(36)	118.8(11)
Cl(3)—C(35)	1.752(14)	C(36)—C(35)—Cl(3)	119.2(11)
C(24)—C(25)	1.479(18)	C(34)—C(35)—Cl(3)	121.3(12)
C(1)—C(2)	1.424(17)	C(24)—C(34)—C(37)	113.7(11)
C(1)—Fe(1)	2.058(11)	C(41)—C(37)—C(34)	127.2(11)

Table 4. Crystallographic characteristics and details of X-ray diffraction study of compound **8a**

Parameter	**8a**
Molecular formula	$C_{46}H_{42}Cl_2Fe_4$
Molecular weight/g mol^{-1}	889.10
T/K	293
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	17.209(3)
b/Å	12.611(3)
c/Å	17.320(3)
α/deg	90.0
β/deg	94.23(2)
γ/deg	90.0
V/Å^3	3748.6(13)
Z	4
d_{calc}/g cm^{-3}	1.575
Absorption coefficient/mm^{-1}	1.694
F(000)	1824
Radiation	Mo-Kα
λ/Å	0.71073
Monochromator	Graphite
θ/deg	1.61—25.00
Total number of reflections	6819
Number of independent reflections with $R(I > 2\sigma(I))$	6585
R_1	0.1093
WR_2	0.2958
R_{int}	0.1779
Number of parameters in the refinement	470
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.1693P)^2 + 10.77P]$, where $P = (F_0^2 + 2F_c)/3$
Goodness-of-fit (full-matrix least-squares based on F^2)	1.033
Residual electron density (ρ_{min}/ρ_{max})/e $\cdot$ Å^{-3}	−0.912/1.219

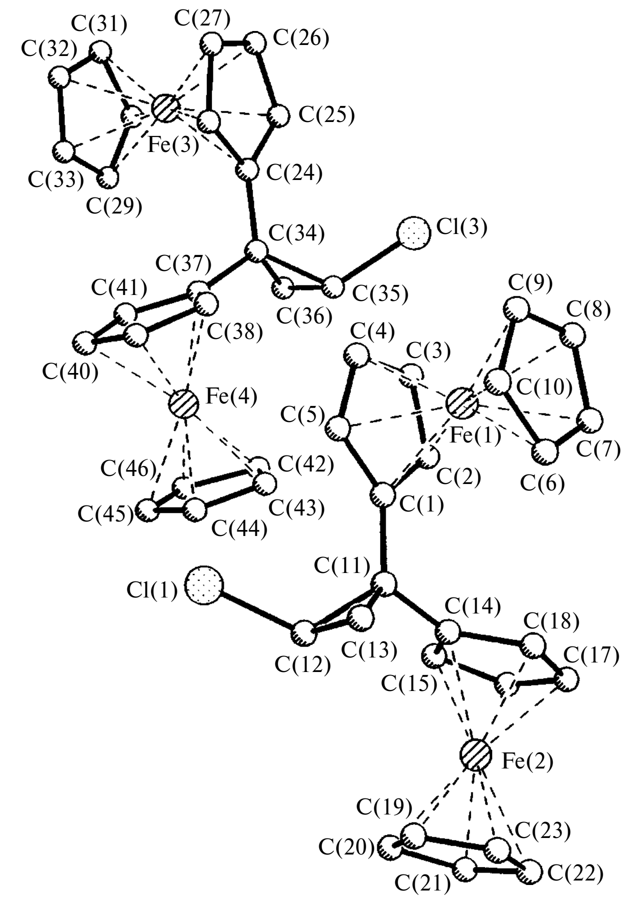
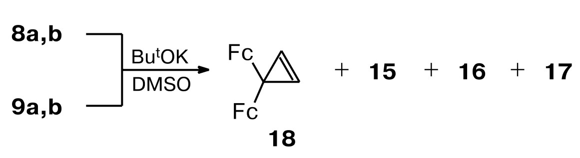


Fig. 1. Molecular structure of compound **8a**.

Dehydrohalogenation of monohalo(diferrocenyl)cyclopropanes **8a,b** and **9a,b** with Bu^{t}OK in DMSO[1—3,10,17] afforded 3,3-diferrocenylcyclopropene (**18**) in low yield (~20%) (Scheme 6). In addition, 3-ferrocenyl-1*H*-cyclopentaferrocene **17** (30—40%), diferrocenylcyclopropane **15** (~20%), and diferrocenylpropene **16** (~10%) were isolated.

Scheme 6



Cyclopropene **18** was obtained as a pale-yellow crystalline compound, which rapidly decomposed on storage under standard conditions. In solutions, compound **18** was isomerized to give compound **17** (~55%) and alkene **16** (~15%) even in the cold (0 °C). We failed to grow crystals of cyclopropene **18** and study its three-dimensional structure by X-ray diffraction analysis. However, based on comparison of the results of X-ray diffraction analysis of the crystal structures of arylferrocenylcyclopropane monobromides prepared from arylferrocenylcyclopropenes and arylferrocenylcyclopropanes[1—3,10] and taking into account evidence for the essential steric effects of the substituents at the C(3) atom of the cyclopropene nucleus,[7—9] we believe that the ferrocenyl substituents in 3,3-diferrocenylcyclopropene (**18**) has a spatial orientation identical to that observed in the starting monohalides **8a,b** and **9a,b**.

Apparently, compounds **16** and **17** are generated through the opening of the three-membered ring in monohalides **8** and **9** giving rise to 1,1-diferrocenylallylic cation **7c** (in the presence of magnesium salts, *viz.*, Lewis acids) and through the cleavage of cyclopropene **18** to form diferrocenylcarbenoid **7d**, species **7c** and **7d** being

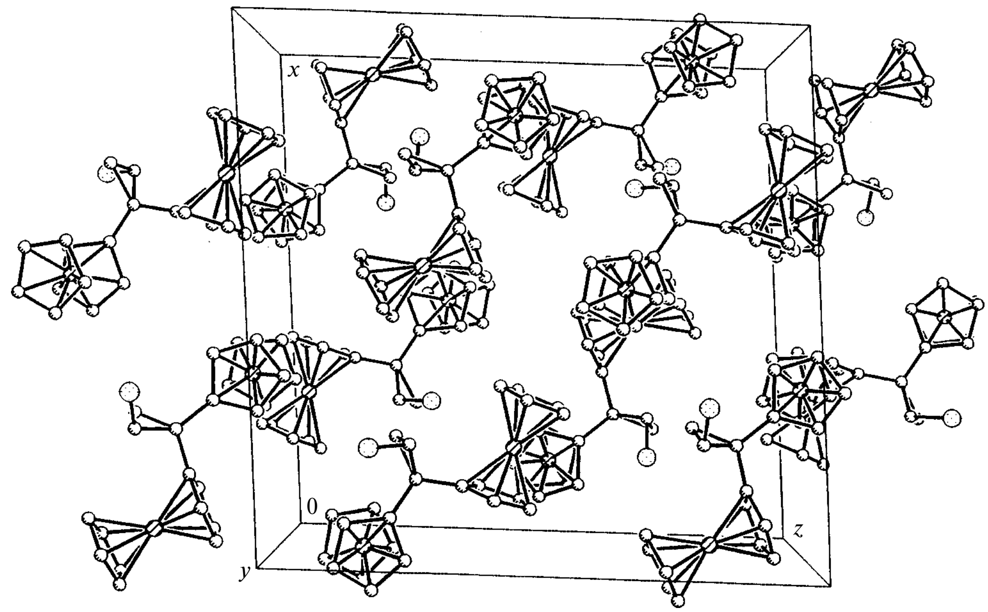
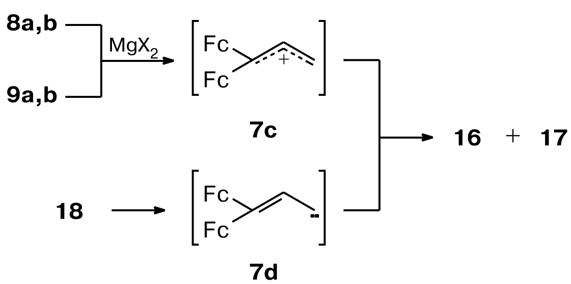


Fig. 2. Molecular packing in the crystal of compound **8a**.

intermediates stabilized by two ferrocenyl substituents (Scheme 7).

Scheme 7



Then one of the ferrocenyl substituents (in a non-bisector orientation) in intermediates **7c,d** undergoes intramolecular alkylation or these substituents are reduced. Apparently, the latter process, which has been observed by us earlier,[1—3,18—22] takes place with the involvement of the Fe atom.

To summarize, the results of the present study are indicative of rather high regioselectivity of the intramolecular transformations of monohalo(diferrocenyl)cyclopropanes **8a,b** and **9a,b** and diferrocenylcyclopropene **18**. The small-ring opening in all the compounds under consideration, unlike that in alkyl(ferrocenyl)- and aryl(ferrocenyl)-substituted analogs studied earlier,[1—3,10] affords predominantly a product of alkylation of the ferrocene fragment. Apparently, the latter fact is associated with a non-bisector orientation of the ferrocenyl substituent with respect to the three-carbon ring.

Experimental

All solvents were dried according to standard procedures and distilled before use. Column chromatography was carried out with the use of Al_2O_3 (Brockmann activity III) and plates with a fixed layer of SiO_2. The ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Inova instrument (300 and 75 MHz, respectively) in $CDCl_3$ with Me_4Si as the internal standard.

The unit cell parameters and intensities of reflections were measured on a Siemens P4/PC diffractometer at 293 K.

Ferrocenylcarboxylic acid (97%), ferrocene (98%), cycloheptanone (99%), a 1.4 *M* MeLi solution in Et_2O, a 2.0 *M* EtMgCl solution in Et_2O, $Ti(OPr^i)_4$ (97%), Bu^tOK (95%), and PCl_5 (95%) were purchased from Aldrich.

Diferrocenyl ketone (11) (see Ref. 25). Phosphorus pentachloride (6.9 g) was added portionwise to a suspension of FcCOOH (6.9 g, 0.03 mol) in dry benzene (80 mL). The reaction mixture was stirred at ~20 °C for 20 min and the solvent was distilled off *in vacuo*. The residue (orange oil) was dissolved in CH_2Cl_2 (200 mL) containing ferrocene (6.6 g, 0.035 mol). Then this solution was added dropwise with stirring to a mixture of $AlCl_3$ (4.0 g, 0.03 mol) in CH_2Cl_2 (200 mL) during ~1 h. The reaction mixture was stirred at 20 °C for 1 h and then poured into ice water (500 mL). The organic layer was separated from the aqueous layer and washed with water. The solvent was distilled off *in vacuo*. The residue was purified by recrystallization from propan-1-ol. Ketone **11** was obtained as orange crystals in a yield of 5.2 g (50%), m.p. 203—204 °C (*cf.* lit data[25]: m.p. 204 °C).

1,1-Diferrocenylethanol (12). A solution of MeLi in Et_2O (0.03 mol) was added with stirring to a solution of ketone **11** (4.0 g, 0.01 mol) in anhydrous THF (100 mL). The reaction mixture was stirred for 1 h and then treated with a 5% NaOH solution. The organic layer was separated from the aqueous layer, washed with water, and dried over Na_2SO_4. The solvent was distilled off *in vacuo* and the residue was recrystallized from propan-1-ol. Alcohol **12** was obtained as yellow crystals in a yield of 2.92 g (70%), m.p. 221—223 °C. Found (%): C, 63.67; H, 5.48; Fe, 27.11. $C_{22}H_{22}Fe_2O$. Calculated (%): C, 63.80; H, 5.36; Fe, 26.98.

1,1-Diferrocenylethylene (13). Alcohol **12** (4.14 g, 0.01 mol) was dissolved in $CHCl_3$ (50 mL). The resulting solution was mixed with Al_2O_3 (Brockmann activity I, 50 g). The reaction mixture was dried in air and chromatographed on a 30-cm column with a layer of pure Al_2O_3 (Brockmann activity III) using hexane as the eluent. Alkene **13** was obtained as red crystals in a yield 2.8 g (70%), m.p. 163—164 °C. Found (%): C, 66.54; H, 5.27; Fe, 28.41. $C_{22}H_{20}Fe_2$. Calculated (%): C, 66.71; H, 5.09; Fe, 28.20.

2,2-Dichloro-1,1-diferrocenylcyclopropane (10a) was synthesized according to a procedure described previously.[26] Alkene **13** (3.96 g, 0.01 mol), $CHCl_3$ (50 mL), a 50% NaOH solution (40 mL), CH_2Cl_2 (100 mL), and $BnNEt_3Cl$ (1 g) were placed in a round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction mixture, which immediately warmed up, was stirred at ~20 °C for 2 h and poured into ice water (200 mL). The organic layer was separated from the aqueous layer, washed with water, and dried over Na_2SO_4. The solvent was distilled off *in vacuo* and the residue was chromatographed on Al_2O_3 (hexane as the eluent). Dichlorocyclopropane **10a** was obtained as a yellow powder in a yield of 3.21 g (67%), t.decomp. ~178 °C. Found (%): C, 57.87; H, 4.08; Cl, 14.73; Fe, 23.49. $C_{23}H_{20}Cl_2Fe_2$. Calculated (%): C, 57.66; H, 4.20; Cl, 14.82; Fe, 23.32.

2,2-Dibromo-1,1-diferrocenylcyclopropane (10b). Dibromide **10b** was prepared according to a known procedure[22] from alkene **13** (3.96 g, 0.01 mol) in a yield of 1.82 g (32%) as yellow crystals, t.decomp. 163 °C. Found (%): C, 48.49; H, 3.71; Br, 28.23; Fe, 19.51. $C_{23}H_{20}Br_2Fe_2$. Calculated (%): C, 48.64; H, 3.55; Br, 28.14; Fe, 19.67.

Solvolysis of 2,2-dibromo-1,1-diferrocenylcyclopropane 10b. Dibromocyclopropane **10b** (0.57 g, 0.001 mol) was dissolved in a mixture of $CHCl_3$ (10 mL) and Py (0.5 mL). The solution was kept at ~20 °C for 7 days. Then the solvent was distilled off *in vacuo* and the residue was chromatographed in a thin layer on Al_2O_3 (hexane as the eluent). 1,1-Diferrocenylallene (**14**) was obtained as yellow crystals in a yield of 0.17 g (41%), m.p. 128—129 °C, R_f 0.78. Found (%): C, 67.56; H, 5.08; Fe, 27.54. $C_{23}H_{20}Fe_2$. Calculated (%): C, 67.70; H, 4.93; Fe, 27.37.

Reduction of dihalides 10a,b. A solution of EtMgCl in Et_2O and several drops of $Ti(OPr^i)_4$ were added to a solution of dihalide **10a,b** (0.005 mol) in anhydrous THF (100 mL). The reaction mixture was stirred at ~20 °C for 3 h and then water (50 mL) was added. The organic layer was separated from the aqueous layer, washed with water, and dried over Na_2SO_4. The solvent was distilled off *in vacuo* and the residue was chromatographed on a plate with a fixed layer of SiO_2 (hexane—ether, 10 : 1).

Products **15**, **16**, **8a,b**, and **17** were obtained from dichloride **10a**.

1,1-Diferrocenylcyclopropane (15). The yield was 0.26 g (13%), yellow crystals, m.p. 141—142 °C, R_f 0.75. Found (%): C, 67.49; H, 5.27; Fe, 27.38. $C_{23}H_{22}Fe_2$. Calculated (%): C, 67.36; H, 5.40; Fe, 27.24.

1,1-Diferrocenylpropene (16). The yield was 0.2 g (11%), yellow crystals, m.p. 136—138 °C, R_f 0.68. Found (%): C, 67.54; H, 5.18; Fe, 27.43. $C_{23}H_{22}Fe_2$. Calculated (%): C, 67.36; H, 5.40; Fe, 27.24.

***Z*-2-Chloro-1,1-diferrocenylcyclopropane (8a).** The yield was 0.25 g (11%), yellow crystals, t.decomp. ~162 °C, R_f 0.60. Found (%): C, 62.24; H, 4.58; Cl, 8.12; Fe, 25.21. $C_{23}H_{21}ClFe_2$. Calculated (%): C, 62.13; H, 4.76; Cl, 7.99; Fe, 25.12.

***E*-2-Chloro-1,1-diferrocenylcyclopropane (8b).** The yield was 0.21 g (9%), yellow crystals, t.decomp. ~170 °C, R_f 0.54. Found (%): C, 61.97; H, 4.99; Cl, 7.84; Fe, 25.27. $C_{23}H_{21}ClFe_2$. Calculated (%): C, 62.13; H, 4.76; Cl, 7.99; Fe, 25.12.

3-Ferrocenyl-1*H*-cyclopentaferrocene (17). The yield was 0.7 g (33%), yellow crystals, m.p. 153—154 °C, R_f 0.36. Found (%): C, 67.82; H, 4.79; Fe, 27.49. $C_{23}H_{20}Fe_2$. Calculated (%): C, 67.69; H, 4.94; Fe, 27.37.

The reaction of dibromide **10b** gave rise to compound **15** (0.37 g, 18%; m.p. 142 °C), compound **16** (0.24 g, 12%; m.p. 137—138 °C), monobromide *Z*-**9a** (0.4 g, 16%; t.decomp. 163 °C), monobromide *E*-**9b** (0.34 g, 14%; t.decomp. 169 °C), and compound **17** (0.61 g, 30%; m.p. 154 °C).

Dehydrohalogenation of diferrocenylcyclopropane monohalides 8a,b and 9a,b (general procedure). Monohalide **8a,b** or **9a,b** (0.003 mol) was added to a solution of Bu^tOK (0.004 mol) in DMSO (30 mL), and the reaction mixture was stirred at ~35—45 °C for 7 h. Then benzene (100 mL) and water (50 mL) were added. The organic layer was separated from the aqueous layer and washed with water. The solvent was distilled off *in vacuo*. The residue was chromatographed in a thin layer on Al_2O_3 (hexane as the eluent). Products **15—18** were obtained.

Compound 15. The yield was 0.18—0.25 g (15—20%), m.p. 141—142 °C, R_f 0.78.

3,3-Diferrocenylcyclopropene (18). The yield was 0.20—0.24 g (18—21%), m.p. 130—131 °C, R_f 0.78. Found (%): C, 67.86; H, 5.04; Fe, 27.13. $C_{23}H_{20}Fe_2$. Calculated (%): C, 67.69; H, 4.94; Fe, 27.37.

Alkene 16. The yield was 0.12—0.24 g (10—20%), m.p. 137 °C, R_f 0.65.

Compound 17. The yield was 0.36—0.48 g (30—40%), m.p. 153—154 °C, R_f 0.53.

Opening of the three-carbon ring in 3,3-diferrocenylcyclopropene (18). A solution of cyclopropene **18** (0.4 g, 0.001 mol) in benzene (50 mL) was stirred at ~20 °C for 1 h. The solvent was distilled off *in vacuo* and the residue was chromatographed in a thin layer on SiO_2 (hexane—ether, 10 : 1). Alkene **16** was obtained as yellow crystals in a yield of 0.06 g (15%), m.p. (136—138 °C), R_f 0.68. Compound **17** was obtained in a yield of 0.23 g (55%), m.p. 154 °C, R_f 0.39.

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