Synthesis and some chemical transformations of 3-ferrocenyl-3-phenylcyclopropene

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Crystalline 3-ferrocenyl-3-phenylcyclopropene was obtained by dehydrobromination of 2-bromo-1-ferrocenyl-1-phenylcyclopropane with potassium *tert*-butoxide in dimethyl sulfoxide. The compound synthesized undergoes catalytic hydrogenation to 1-ferrocenyl-1-phenylcyclopropane, reacts with 1,3-diphenylisobenzofuran to give the expected product of stereospecific [4+2]-cycloaddition and 3-ferrocenylindene, and also undegoes opening of the small ring on treatment with superacids to give 3-ferrocenylindene as the major product. The data of single crystal X-ray diffraction analysis of 1-ferrocenyl-1-phenylcyclopropane and the diene adduct of 3-ferrocenyl-3-phenylcyclopropene with 1,3-diphenylisobenzofuran are given.

Key words: ferrocenylcyclopropane, ferrocenylcyclopropene, dehydrobromination, catalytic hydrogenation, [4+2]-cycloaddition, opening of the three-membered ring, carbocations, alkylation, X-ray diffraction analysis.

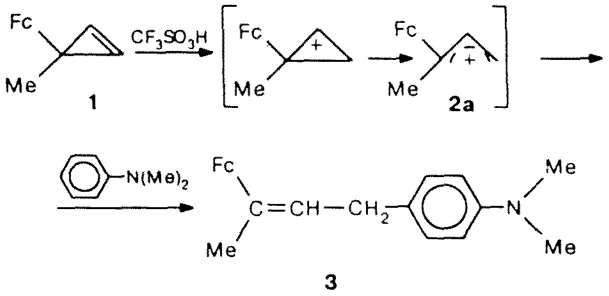
All the data known at this time indicate that introduction of a ferrocenyl substituent into saturated or unsaturated three-membered carbocycles appreciably changes their properties, the change in the properties of ferrocenylcyclopropanes and ferrocenylcyclopropenes being obvious with respect to both the unsaturated carbocyclic compound and the arylcyclopropanes or the arylcyclopropenes having similar structure.[1–5]

In particular, 1,2,3-triferrocenyl-3-*para*-tolylcyclopropene rearranges in a $CHCl_3$ solution in the absence of air already at 50 °C through cleavage of the small ring followed by cyclization at the ferrocenyl and aryl fragments.[3] Judging by the quantitative data published in the literature,[3] the isomerization occurs 10^8—10^9 times more rapidly than isomerization of tetraphenylcyclopropene[6] into an indene derivative. Isomerization of *Z*-1,2-diferrocenylcyclopropanes into the corresponding *E*-isomers proved to be even faster. For example, *Z*-1,2-diferrocenylcyclopropane is quantitatively converted into stable *E*-isomer even under the conditions in which a ^1H NMR spectrum is recorded.[1,2]

Of obvious interest is also the high stabilization of the electron-deficient centers adjacent to the ferrocenyl group. The first long-lived α-ferrocenylcyclopropyl carbocation was observed by Olah and coworkers[7] at −78 °C; this cation still existed at −40 °C without noticeable opening of the small ring.

In view of the fact that the effect of ferrocenyl groups introduced into a small ring is rather high and often highly selective, the elucidation of the characteristic features of the interaction of the ferrocenyl group with the small ring is of great interest both from the theoretical viewpoint and in relation to the search for selective reactions of cyclopropanes and cyclopropenes.

Recently we reported the synthesis of 3-ferrocenyl-3-methylcyclopropene[8,9] (**1**) and characteristic features of its chemical behavior. It was found that the three-membered ring in compound **1** is cleaved through the action of superacids to give the intermediate 1-ferrocenyl-1-methylallyl cation (**2a**) and the product (**3**) formed by alkylation of the *para*-position of *N,N*-dimethylaniline with this cation:



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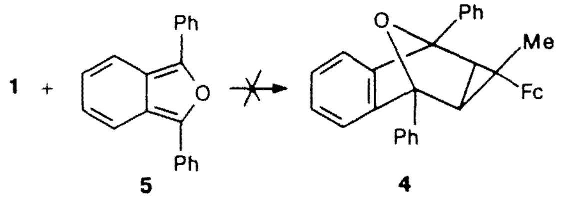
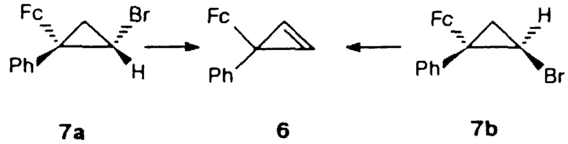
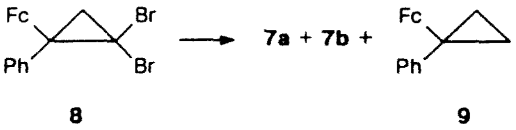
At the same time, compound **1** did not produce the classical adduct (**4**) in the reaction with 1,3-diphenylisobenzofuran (**5**):



In continuation of these studies, we synthesized the second representative of 3-R-3-ferrocenyl-substituted cyclopropenes, *viz.*, 3-ferrocenyl-3-phenylcyclopropene (**6**), by dehydrobromination of isomeric 2-bromo-1-ferrocenyl-1-phenylcyclopropanes (**7a,b**) with Bu^{t}OK in DMSO and studied some of its chemical transformations.



The starting monobromides **7a** and **7b** were obtained in 53 % overall yield by the reduction of 2,2-dibromo-1-ferrocenyl-1-phenylcyclopropane (**8**) with zinc in the presence of Trilon B.[9,10] 1-Ferrocenyl-1-phenylcyclopropane (**9**) was isolated as a minor product; this compound was also obtained in the catalytic hydrogenation of compound **6** over a platinum catalyst.



The structure of compound **9** was determined based on the ^{1}H and ^{13}C NMR spectra (see Tables 1 and 2) and also from an X-ray structural study of single crystals of compound **9**. Fig. 1 shows the general view of molecule **9**; positional parameters of the atoms and their isotropic heat factors are listed in Table 3, and the geometric parameters (interatomic distances and bond angles) are given in Tables 4 and 5, respectively.

Ferrocenylcyclopropene **6**, unlike cyclopropene **1**, is stable in the crystalline state. It reacts with isobenzofuran **5** on prolonged boiling in benzene. This reaction occurs stereospecifically yielding the product of [4+2]-cycloaddition, polycyclic adduct (**10**), and the product of intramolecular transformation of compound **6**, 3-ferrocenylindene (**11**):

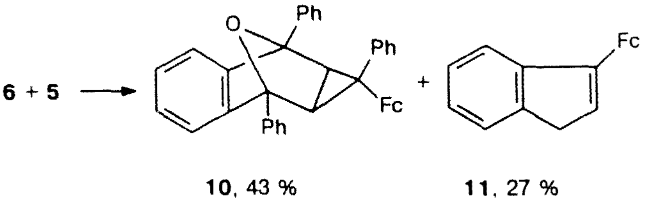


Table 1. Data of ^{1}H NMR spectra of compounds **6**, **7a**, **7b**, and **9—13** (δ, multiplicity, integral intensity, *J*/Hz)

Compound	CH_2	C_5H_5	C_5H_4	CH_3	CH	Ar
6	—	4.16 (s, 5 H)	4.05 (m, 2 H), 3.89 (m, 2 H)	—	7.32 (s, 2 H)	7.20—7.41 (m, 5 H)
7a	1.48 (dd, 1 H), 1.93 (dd, 1 H, J_{gem} = 6.55, J_{trans} = 5.16, J_{cis} = 8.16)	4.0 (s, 5 H)	4.14 (1 H), 4.10 (m, 2 H), 3.88 (m, 1 H)	—	3.44 (dd, 1 H, *J* = 5.15; 8.16)	7.29—7.49 (m, 5 H)
7b	1.73 (dd, 1 H), 1.92 (dd, 1 H, J_{gem} = 6.4, J_{trans} = 5.0, J_{cis} = 8.0)	4.13 (s, 5 H)	4.05 (m, 2 H), 3.80 (m, 2 H)	—	3.37 (dd, 1 H, *J* = 5.0; 8.0)	7.32—7.50 (m, 5 H)
9	1.21 (br.s, 4 H)	4.13 (s, 5 H)	4.02 (m, 2 H), 3.83 (m, 2 H)	—	—	7.20—7.45 (m, 5 H)
10	—	4.07 (s, 5 H)	3.95 (m, 2 H) 3.56 (m, 2 H),	—	2.48 (s, 2 H)	6.6 m, 6.87 m, 7.05 m, 7.6 m, 7.45 m, (19 H)
11	3.38 (d, 2 H, *J* = 2.3)	4.13 (s, 5 H)	4.63 (m, 2 H), 4.33 (m, 2 H)	—	6.52 (m, 1 H, *J* = 2.3)	7.26 (m, 1 H), 7.4 (m, 1 H), 7.5 (m, 1 H), 7.93 (m, 1 H)
12	3.37 (br.s, 2 H), 3.28 (d, 2 H, *J* = 7.4)	4.12 (s, 5 H), 4.10 (s, 5 H)	4.47 (m, 2 H), 4.31 (m, 2 H), 4.17 (m, 4 H)	—	5.99 (m, 1 H, *J* = 7.4)	7.2 (m, 1 H), 7.3—7.5 (m, 7 H), 7.9—8.05 (m, 1 H)
13	3.30 (d, 2 H, *J* = 6.8)	4.08 (s, 5 H)	4.20 (m, 2 H), 3.98 (m, 2 H)	3.02 (s, 6 H)	6.07 (t, 1 H, *J* = 6.8)	7.15—7.61 (m, 9 H)

Table 2. Data of ^{13}C NMR spectra of compounds **6**, **7a**, **7b**, **9**, and **11**, δ

Compound	C_5H_5	C_5H_4		C_s*	CH	CH_2	C_6H_5 and C_6H_4
		CH	C(1)				
6	68.10	67.90, 67.14	97.42	19.81	112.84	—	146.46,** 126.07, 127.92, 125.84
7a	68.70	69.06, 67.97, 66.68	90.96	31.72	32.65	22.85	131.08,** 129.85, 128.21, 127.13
7b	68.70	69.50, 67.61, 67.58, 66.00	92.01	30.98	29.95	25.13	130.81,** 129.71, 128.80, 127.90
9	68.43	66.84, 66.75	97.49	24.47	—	17.91	145.0 128.53, 127.98, 126.1
11	69.18	68.43 67.09	80.73	***	120.94	38.06	*** 128.69, 126.0, 124.55, 123.87

* C_s a carbon atom bearing a substituent. ** C_{ipso}. *** The signals of quaternary carbon atoms 144.94, 144.15, and 141.45 refer to the junction atoms of the indene ring. The signals were not assigned in greater detail.

The structures of compounds **10** and **11** were confirmed by the data of ^1H and ^{13}C NMR spectroscopy (Tables 1 and 2); for adduct **10**, a single-crystal X-ray structural study was also carried out. The general view of the molecule of 3-ferrocenyl-1,3,5-triphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0.^{2,4}]oct-6-ene (**10**) is shown in Fig. 2; positional parameters of the atoms with the corresponding heat factors are listed in Table 3; the geometric parameters are presented in Tables 4 and 5. The data of X-ray diffraction analysis of compound **10** indicate that the adduct obtained has an *exo*-structure with *syn*-arranged phenyl substituents in the molecule.

In our opinion, indene **11** may be formed in the reaction between compounds **6** and **5** similarly to what has been reported for the rearrangement of 1,2,3-triferrocenyl-3-*para*-tolylcyclopropene[3] *via* opening of the small ring in cyclopropene **6** followed by selective cyclization involving exclusively the phenyl fragment, but not the ferrocenyl fragment.

3-Ferrocenylindene was also obtained in a yield of up to 60 % by the protonation of cyclopropene **6** with trifluoromethanesulfonic acid followed by the treatment of the reaction mixture with *N*,*N*-dimethylaniline. In addition to indene **11**, compound **12** formed by alkylation of compound **11** with 1-ferrocenyl-1-phenylallyl cation (**2b**) and the product of alkylation of *N*,*N*-dimethylaniline with the same cation, *viz*., compound **13**, were isolated by the preparative TLC on silica gel.

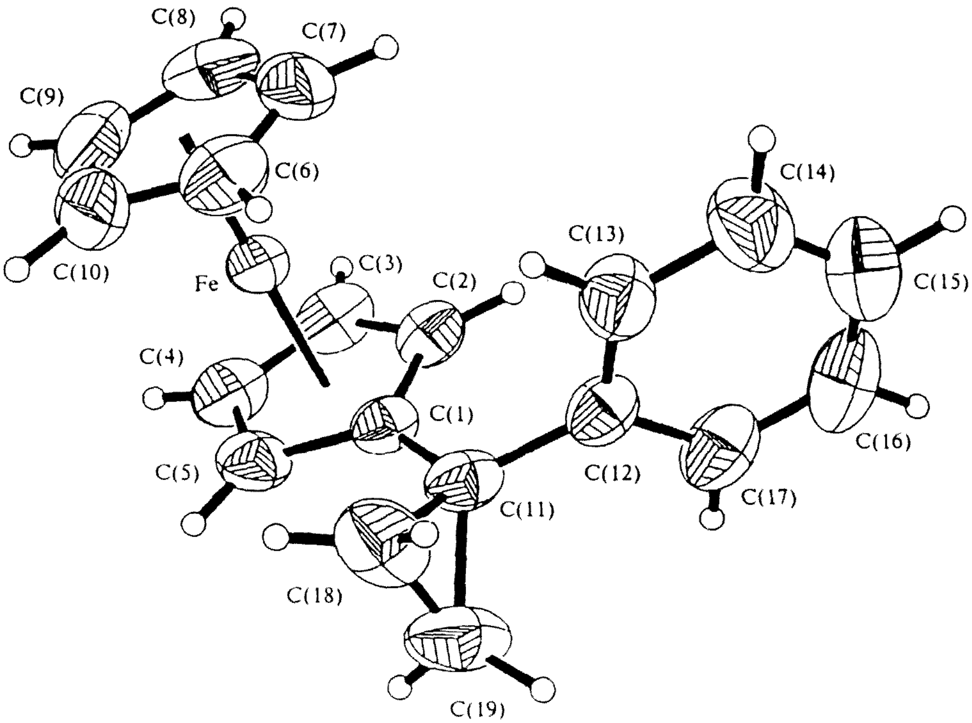
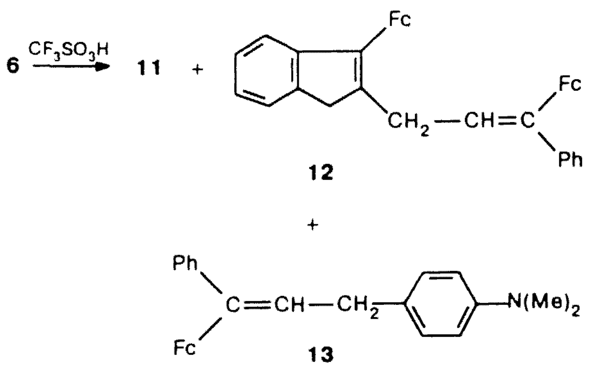


Fig. 1. General view of molecule **9**.



The structures of compounds **11**, **12**, and **13** are consistent with the data of NMR spectra (Tables 1 and 2) and with the results of elemental analysis (Table 6). From the ^1H NMR spectra, it follows that compounds **12** and **13** are formed as single isomers; however, at present, there is no way to find out whether these are *Z*- or *E*-isomers.

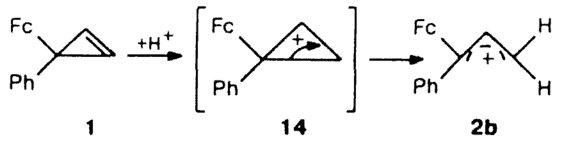
The opening of the small ring in the protonation of compound **6** occurs apparently by the same scheme as that in the protonation of ferrocenylmethylcyclopropene **1** or in the reaction of Ph_3CBF_4 with 1,2-diferrocenylcyclopropane.[2,11]

Table 3. Main atomic coordinates in the structures of compounds **9** and **10** and their equivalent isotropic heat factors ($U_{iso}^{eq} \cdot 10^3$/Å)

9					**10**				
Atom	*x*	*y*	*z*	U_{iso}^{eq}	Atom	*x*	*y*	*z*	U_{iso}^{eq}
Fe	2833(1)	6245(1)	1337(1)	40(1)	Fe	3964(1)	6294(1)	3548(1)	34(1)
C(1)	1364(3)	7644(4)	1790(1)	42(1)	C(40)	3461(1)	4807(1)	3461(2)	29(1)
C(2)	2277(3)	8695(4)	1440(1)	48(1)	C(41)	3375(1)	5182(2)	2334(2)	35(1)
C(3)	3948(4)	8388(4)	1614(2)	58(1)	C(44)	4182(1)	4681(2)	3926(2)	36(1)
C(4)	4075(4)	7154(5)	2069(1)	60(1)	O	1739(1)	3791(1)	4618(1)	31(1)
C(5)	2493(4)	6685(5)	2181(1)	52(1)	C(1)	2905(1)	4421(1)	4011(2)	28(1)
C(6)	1426(5)	4355(4)	874(2)	63(1)	C(2)	2326(1)	3847(2)	3147(2)	31(1)
C(7)	2111(5)	5465(5)	491(1)	62(1)	C(3)	2223(2)	4996(2)	3536(2)	30(1)
C(8)	3799(5)	5336(6)	613(2)	72(1)	C(4)	1776(1)	3196(2)	3577(2)	31(1)
C(9)	4143(5)	4160(5)	1070(2)	73(1)	C(5)	1614(1)	4867(2)	4108(2)	32(1)
C(10)	2688(6)	3536(4)	1231(2)	71(1)	C(6)	1004(1)	4629(2)	3081(2)	39(1)
C(11)	−438(3)	7605(4)	1767(1)	48(1)	C(7)	1098(1)	3565(2)	2749(2)	39(1)
C(12)	−1328(3)	8598(4)	1270(1)	47(1)	C(8)	646(1)	3080(3)	1831(2)	52(1)
C(13)	−1869(4)	7807(5)	747(2)	60(1)	C(11)	454(1)	5238(3)	2490(2)	52(1)
C(14)	−2638(5)	8726(6)	278(2)	75(1)	C(12)	3176(1)	4006(2)	5234(2)	31(1)
C(15)	−2874(5)	10496(6)	324(2)	75(1)	C(13)	3334(1)	4705(2)	6180(2)	40(1)
C(16)	−2349(5)	11293(5)	838(2)	79(2)	C(17)	3343(1)	2917(2)	5420(2)	39(1)
C(17)	−1589(4)	10379(5)	1310(2)	66(1)	C(20)	1859(1)	1998(2)	3788(2)	34(1)
C(18)	−1299(4)	6008(6)	1975(2)	70(1)	C(21)	1705(1)	1528(2)	4757(2)	40(1)
C(19)	−1147(5)	7592(7)	2347(2)	78(2)	C(25)	2069(1)	1336(2)	2990(2)	49(1)
					C(30)	1500(1)	5695(2)	4963(2)	37(1)
					C(31)	958(1)	5563(2)	5494(3)	56(1)
					C(35)	1894(1)	6619(2)	5216(2)	48(1)

Table 4. Main bond lengths in the structures of compounds **9** and **10**

9				**10**			
Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Fe—C(1)	2.050(3)	Fe—C(2)	2.042(3)	Fe—C(40)	2.078(2)	Fe—C(41)	2.046(2)
Fe—C(3)	2.034(3)	Fe—C(4)	2.030(3)	Fe—C(44)	2.054(2)	Fe—C(1)	1.502(3)
Fe—C(5)	2.035(3)	Fe—C(6)	2.033(3)	O—C(4)	1.451(2)	O—C(5)	1.450(2)
Fe—C(7)	2.037(3)	Fe—C(8)	2.026(4)	C(1)—C(2)	1.524(2)	C(1)—C(3)	1.524(2)
Fe—C(9)	2.016(4)	Fe—C(10)	2.032(3)	C(2)—C(3)	1.513(3)	C(2)—C(4)	1.548(3)
C(1)—C(2)	1.421(4)	C(2)—C(3)	1.423(4)	C(1)—C(12)	1.508(2)	C(3)—C(5)	1.546(3)
C(1)—C(11)	1.496(4)	C(1)—C(5)	1.431(4)	C(4)—C(7)	1.541(2)	C(4)—C(20)	1.495(3)
C(3)—C(4)	1.410(5)	C(4)—C(5)	1.417(4)	C(5)—C(6)	1.531(2)	C(5)—C(30)	1.493(3)
C(6)—C(7)	1.395(5)	C(6)—C(10)	1.408(5)	C(6)—C(7)	1.390(3)	C(6)—C(11)	1.377(3)
C(7)—C(8)	1.405(6)	C(8)—C(9)	1.394(6)	C(7)—C(8)	1.374(3)	C(12)—C(13)	1.386(3)
C(9)—C(10)	1.391(6)	C(11)—C(12)	1.500(4)	C(12)—C(17)	1.383(3)	C(20)—C(21)	1.386(3)
C(11)—C(18)	1.501(5)	C(11)—C(19)	1.517(5)	C(20)—C(25)	1.390(3)	C(30)—C(31)	1.395(4)
C(12)—C(13)	1.379(4)	C(12)—C(17)	1.397(5)	C(30)—C(35)	1.374(3)	C(40)—C(41)	1.430(3)
C(13)—C(14)	1.385(5)	C(14)—C(15)	1.365(6)	C(40)—C(44)	1.429(2)	C(41)—C(42)	1.423(3)
C(15)—C(16)	1.371(6)	C(16)—C(17)	1.385(6)	C(42)—C(43)	1.421(3)	C(43)—C(44)	1.408(3)
C(18)—C(19)	1.489(6)						



The intermediate ferrocenylcyclopropyl carbocation (**14**) with a positive charge at the β-carbon atom of the three-membered ring, unlike the α-ferrocenylcyclopropyl cation,[7] readily cleaves to give ferrocenylallyl carbocation,[9] stabilized by the ferrocenyl substituent.

Table 5. Main bond angles in molecules **9** and **10**

9		**10**			
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Fe—C(1)—C(11)	128.5(2)	Fe—C(40)—C(1)	131.4(1)	C(41)—C(40)—C(1)	126.9(1)
C(5)—C(1)—C(11)	126.7(3)	C(44)—C(40)—C(1)	126.3(2)	C(4)—C(7)—C(6)	104.8(2)
C(1)—C(11)—C(18)	118.6(3)	C(4)—O—C(5)	98.2(1)	C(40)—C(1)—C(2)	112.5(2)
C(1)—C(11)—C(19)	117.0(2)	C(40)—C(1)—C(3)	113.1(1)	C(2)—C(1)—C(3)	59.5(1)
C(11)—C(12)—C(17)	121.4(3)	C(40)—C(1)—C(12)	113.0(1)	C(2)—C(1)—C(12)	121.9(2)
C(12)—C(13)—C(14)	121.9(3)	C(3)—C(1)—C(12)	126.5(2)	C(1)—C(2)—C(3)	60.2(1)
C(13)—C(12)—C(17)	117.1(3)	C(1)—C(2)—C(4)	120.5(2)	C(3)—C(2)—C(4)	102.7(2)
C(14)—C(15)—C(16)	119.2(4)	C(1)—C(3)—C(2)	60.2(1)	C(1)—C(3)—C(5)	121.9(2)
C(12)—C(17)—C(16)	120.8(4)	C(2)—C(3)—C(5)	102.7(1)	O—C(4)—C(2)	102.1(1)
C(11)—C(19)—C(18)	59.9(3)	O—C(4)—C(7)	100.0(1)	C(2)—C(4)—C(7)	103.3(1)
C(18)—C(11)—C(19)	59.1(3)	O—C(4)—C(20)	112.3(2)	C(2)—C(4)—C(20)	120.2(2)
C(2)—C(1)—C(11)	126.0(2)	C(7)—C(4)—C(20)	116.2(2)	O—C(5)—C(3)	101.6(1)
C(1)—C(11)—C(12)	115.2(2)	O—C(5)—C(6)	100.5(1)	C(3)—C(5)—C(6)	103.8(2)
C(12)—C(11)—C(18)	117.8(2)	O—C(5)—C(30)	112.1(2)	C(3)—C(5)—C(30)	119.8(2)
C(12)—C(11)—C(19)	117.7(3)	C(6)—C(5)—C(30)	116.4(2)	C(5)—C(6)—C(7)	105.5(2)
C(11)—C(12)—C(13)	121.5(3)	C(5)—C(6)—C(11)	133.6(2)	C(7)—C(6)—C(11)	120.9(2)
C(13)—C(14)—C(15)	120.3(4)	C(4)—C(7)—C(8)	133.6(2)	C(6)—C(7)—C(8)	121.5(2)
C(15)—C(16)—C(17)	120.8(4)	C(7)—C(8)—C(9)	117.5(3)	C(8)—C(9)—C(10)	121.0(2)
C(11)—C(18)—C(19)	61.0(3)	C(9)—C(10)—C(11)	121.2(3)	C(1)—C(12)—C(13)	121.8(2)
		C(1)—C(12)—C(17)	119.8(2)	C(13)—C(12)—C(17)	118.1(2)
		C(4)—C(20)—C(21)	120.7(2)	C(4)—C(20)—C(25)	120.2(2)
		C(21)—C(20)—C(25)	119.1(2)	C(5)—C(30)—C(31)	119.6(2)
		C(5)—C(30)—C(35)	122.3(2)	C(31)—C(30)—C(35)	118.1(2)

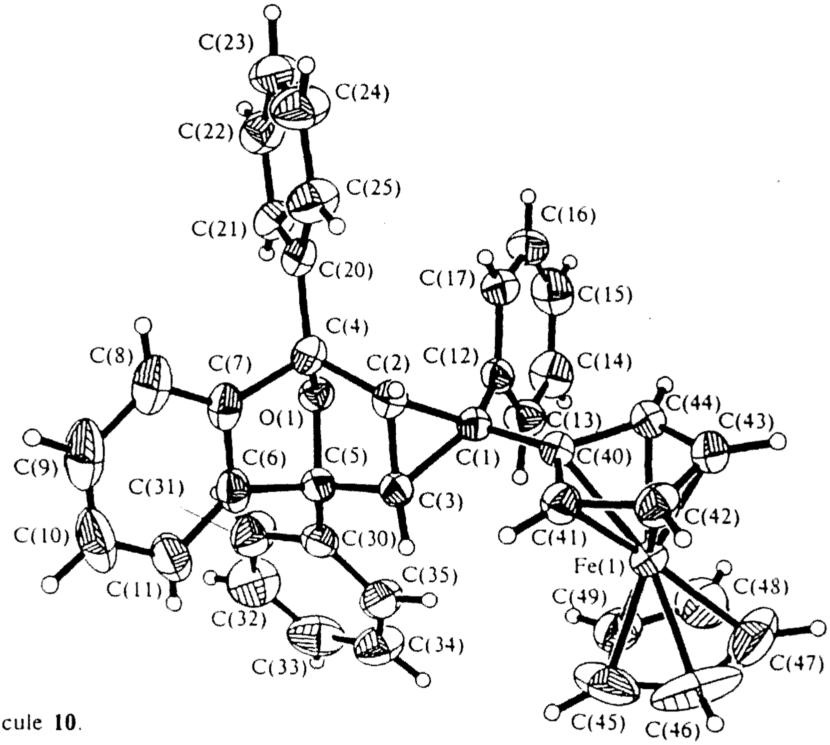


Fig. 2. General view of molecule **10**.

Table 6. Characteristics of the compounds obtained

Compound	M.p./°C	Found/Calculated (%) C	H	Fe	Br/N	Molecular formula
6	68—69	75.89 76.02	5.42 5.37	18.83 18.61	—	$C_{19}H_{16}Fe$
7a	103—104	60.04 59.88	4.27 4.50	14.51 14.66	20.69 20.96	$C_{19}H_{17}BrFe$
7b	86—87	59.65 59.88	4.70 4.50	14.83 14.66	21.24 20.69	$C_{19}H_{17}BrFe$
9	88—89	75.63 75.51	5.84 6.00	18.31 18.49	—	$C_{19}H_{18}Fe$
10	247—248	81.87 82.10	5.32 5.39	9.73 9.80	—	$C_{39}H_{30}FeO$
11	92—93	76.15 76.02	5.28 5.37	18.53 18.61	—	$C_{19}H_{16}Fe$
12	136—138	76.24 76.02	5.53 5.37	18.37 18.61	—	$C_{38}H_{32}Fe_2$
13	Orange oil	77.11 76.96	6.28 6.46	13.34 13.26	3.25 3.32	$C_{27}H_{27}FeN$

After that, ferrocenylallyl cation **2b** participates in alkylation reactions involving as a rule the least substituted carbonium center of the allyl cation.[2,12] Intramolecular alkylation of the ferrocenyl substituent in ferrocenylallyl cations does not occur. No examples of this type of reaction have been reported.

Experimental

The ^1H and ^{13}C spectra were recorded on a Varian Gemini 200 instrument (200 and 50 MHz) using solutions in $CDCl_3$ and tetramethylsilane as the internal standard. Unit cell parameters and the intensities of reflections were measured on a Siemens P3/PC diffractometer at −20 °C (Mo-Kα-radiation, λ = 0.71073 Å, graphite monochromator) using ω-scanning (3° < 2θ < 60°).

X-ray structural study of 1-ferrocenyl-1-phenylcyclopropane (9). The crystals of $C_{19}H_{18}Fe$ are monoclinic, a = 8.323(2), b = 7.722(2), c = 22.976(2), β = 96.41(2)°, V = 1467.51(15) Å^3, Z = 4, space group $P2_{1/n}$ over 7150 reflections (2487 with $F > 4.0\sigma(F)$). The structure was solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation for nonhydrogen atoms. All the hydrogen atoms were placed in the calculated positions and then refined isotropically, except for the atoms bound to the cyclopentadienyl rings, whose positional and heat parameters were fixed. R = 0.0378, R_W = 0.0471. The weighing scheme $W^{-1} = \sigma^2(F) + 0.0008\ F^2$ was used.

X-ray structural study of oxatricyclo[3.2.1.0.^{2,4}]oct-6-ene (10). The crystals of $C_{39}H_{30}FeO$ are monoclinic, a = 20.115(10), b = 12.279(10), c = 11.857(10) Å, β = 104.08(0)°, V = 2840.5(4) Å^3, Z = 4, space group $P2_1/c$ over 10175 reflections (5343 reflections with $F > 6\sigma(F)$). The structure was solved similarly to the structure of compound **9**, R = 0.0402, R_W = 0.0519. The weighing scheme $W^{-1} = \sigma^2(F) + 0.0007\ F^2$ was used.

2,2-Dibromo-1-ferrocenyl-1-phenylcyclopropane (8) was synthesized from 1-ferrocenyl-1-phenylethylene[13] in 73 % yield as orange crystals.[14]

Dibromide **8** was reduced by zinc dust in aqueous ethanol in the presence of Trilon B according to a known procedure.[10] The preparative TLC of the reaction mixture on silica gel (using hexane as the eluent) gave: 1-ferrocenyl-1-phenylcyclopropane (**9**) (yield 28 %), R_f 0.75, orange crystals; *Z*-2-bromo-1-ferrocenyl-1-phenylcyclopropane (**7a**) (30 %), R_f 0.63, orange needles stable during storage at ambient temperature; *E*-2-bromo-1-ferrocenyl-1-phenylcyclopropane (**7b**) (23 %), R_f 0.75, orange crystals that undergo resinification even when stored in the cold. The melting points of the obtained compounds are presented in Table 6.

3-Ferrocenyl-3-phenylcyclopropene (6). Bromide **7a** or **7b** (0.38 g, 1 mmol) was added to a mixture of 20 mL of anhydrous DMSO and Bu^{t}OK (0.34 g, 3 mmol). The reaction mixture was stirred in an argon atmosphere for 12 h at 20 °C, then 100 mL of benzene and 50 mL of water were added. The organic layer was separated and washed with water. The solvent was evaporated *in vacuo*, and the residue was chromatographed on Al_2O_3 (using hexane as the eluent) to give yellow needle crystals stable in air over a period of one month. The yield of compound **6** was 0.22 g (73 %) from **7a** and 0.21 g (70 %) from **7b**.

Reaction of 6 with 1,3-diphenylisobenzofuran 5. Compound **6** (0.15 g, 0.5 mmol) and compound **5** (0.28 g, 1 mmol) were boiled in 50 mL of dry benzene in an inert atmosphere for 18 h. The reaction was monitored by the disappearance of the spot of the starting compound **6** on a Silufol plate. The solvent was evaporated *in vacuo*, and the residue was chromatographed in a thin film on SiO_2 (hexane—benzene, 10:1) to give 0.04 g (27 %) of 3-ferrocenylindene (**11**), R_f 0.82, and 0.185 g (43 %) of adduct **10**, orange crystals, R_f 0.25.

Reaction of 6 with CF_3SO_3H. CF_3SO_3H (2 mL) was added to a solution of compound **6** (0.15 g, 0.5 mmol) in 40 mL of CH_2Cl_2. The nearly black reaction mixture was stirred in an argon flow for 4 h, and then 3 mL of *N,N*-dimethylaniline and, 1 h later, 50 mL of benzene were added. Dimethylaniline was washed with water, with a 1% solution of HCl, and again with water. The solvent was evaporated *in vacuo*, and the residue was chromatographed in a thin film on SiO_2 (hexane—benzene, 10:1) to give 0.09 g (60 %) of 3-ferrocenylindene (**11**), R_f 0.82, yellow lustrous plates; 0.016 g (10 %) of alkylated ferrocenylindene **12**, R_f 0.50; and 0.045 g (21 %) of 3-(*p*-dimethylaminophenyl)-1-ferrocenyl-1-phenylpropene (**13**), R_f 0.21.

References

1. E. I. Klimova, V. N. Postnov, and V. A. Sazonova, *Dokl. Akad. Nauk SSSR*, 1982, **263**, 368 [*Dokl. Chem.*, 1982, **263** (Engl. Transl.)].
2. E. I. Klimova, A. N. Pushin, and V. A. Sazonova, *Zh. Obshch. Khim*, 1987, **57**, 2336 [*J. Gen. Chem. USSR*, 1987, **57** (Engl. Transl.).
3. A. J. Fry, P. S. Jain, and R. L. Krieger, *J. Organomet. Chem.*, 1981, **214**, 381.
4. A. J. Fry, R. L. Krieger, I. Agranat, and E. Aharon-Shalom, *Tetrahedron Lett.*, 1976, **52**, 4803.

5. I. Agranat, E. Aharon-Shalom, A. J. Fry, R. L. Krieger, and W. O. Krug, *Tetrahedron*, 1979, **35**, 733.
6. M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Commun.*, 1967, 907.
7. G. K. Surya Pracash, H. Buchholz, V. Pracash Reddy, A. Meijere, and G. A. Olah, *J. Am. Chem. Soc.*, 1992, **114**, 1097.
8. V. N. Postnov, E. I. Klimova, N. N. Meleshonkova, and I. G. Bolesov, *Dokl. Akad. Nauk*, 1994, **339**, 362 [*Dokl. Chem.*, 1994, **339** (Engl. Transl.).
9. V. N. Postnov, E. I. Klimova, N. N. Meleshonkova, and I. G. Bolesov, *Dokl. Akad. Nauk*, 1994, **339**, 496 [*Dokl. Chem.*, 1994, **339** (Engl. Transl.)].
10. N. I. Yakushkina, and I. G. Bolesov, *Zh. Org. Khim.*, 1979, **15**, 954 [*J. Org. Chem. USSR*, 1979, **15** (Engl. Transl.)].
11. A. N. Nesmeyanov, V. A. Sazonova, V. N. Postnov, A. M. Baran, Ya. A. Angelyuk, and B. A. Surkov, *Dokl. Akad. Nauk SSSR*, 1978, **241**, 1099 [*Dokl. Chem.*, 1978, **241** (Engl. Transl.).
12. A. N. Pushin, and V. A. Sazonova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2769 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 2769 (Engl. Transl.)].
13. N. V. Bovin, L. S. Surmina, N. I. Yakushkina, and I. G. Bolesov, *Zh. Org. Khim.*, 1977, **13**, 1888 [*J. Org. Chem. USSR*, 1977, **13** (Engl. Transl.)].
14. W. M. Horspool, R. G. Sutherland, and B. J. Thomson, *J. Chem. Soc., Perkin. Trans.*, 1971, 1550.

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