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Journal of Organometallic Chemistry 598 (2000) 254–261

Journal of Organometallic Chemistry

Synthesis and some chemical properties of 3-ferrocenyl-3-isopropylcyclopropene: 3-ferrocenyl-3-isopropylstructures of cyclopropene and its adducts with 1,3-diphenylisobenzofuran

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Received 9 September 1999; received in revised form 13 November 1999

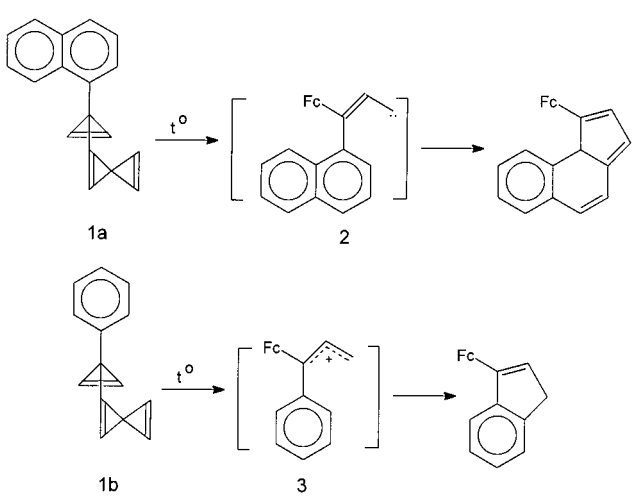
Abstract

X-ray structural analysis allowed the molecular conformation of 3-ferrocenyl-3-isopropylcyclopropene to be established, where the ferrocenyl fragment occupies a bisecting position relative to the three-membered ring. Some heterolytic cleavage of a σ C–C bond in cyclopropene was observed. As a result, predominantly linear products are formed: 1,1-dimethyl-2-ferrocenyl-1,3-butadiene, 3-ferrocenyl-4-methyl-2-pentene, 3-ferrocenyl-4-methyl-3-pentenine and also 3-isopropyl-1H-cyclopentaferrocene. Cyclopropene forms a classical Diels–Alder adduct with 1,3-diphenylisobenzofuran and an adduct with the intermediate 3-isopropyl-1,2-(1-propene-1,3-diyl)ferrocene. X-ray structural data of *exo*-1,5-diphenyl-3-*anti*-ferrocenyl-3-*syn*-isopropyl-6,7-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene are presented. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopropene; Cyclopropane; Carbenoid intermediate; Carbocation; Rearrangement; Intramolecular transformation; Alkylation; Deprotonation; Recyclization; Molecular conformation; Diene adduct; Ferrocene

1. Introduction

A quantum-chemical study [1] revealed that the most probable position of the phenyl fragment in the molecule of 3-methyl-3-phenylcyclopropene is the nonbisecting one, relative to the plane of the three-membered ring. The interaction between the molecular orbitals of the ethylene and benzene fragments in this conformation determines the stereoselectivity of the addition reactions [2–6]. These results are in agreement with our conclusions concerning the chemical properties of 3-aryl-3-ferrocenylcyclopropenes **1a**,**b** [7,8]. The small ring in these compounds is opened easily on thermal treatment or in the presence of acids, forming the intermediate carbenoids of type **2** or the ferrocenylallylic cations of type **3**. Then recyclization in the aryl fragment occurs, without the participation of the ferrocenyl substituent.



The X-ray structural study of monocrystals of 3-(1-naphthyl) and of 3-phenyl-3-ferrocenylcyclopropenes (**1a** and **1b**) [7,8] revealed that the aryl substituents have a non-bisecting orientation, which determines the regioselectivity of the recyclization reaction.

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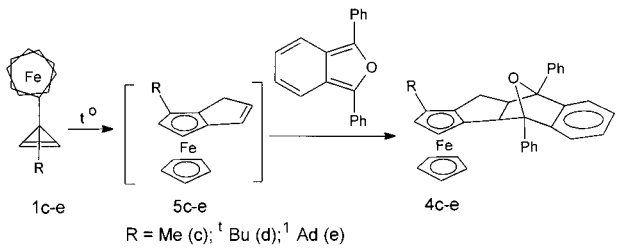
PII: S0022-328X(99)00721-4

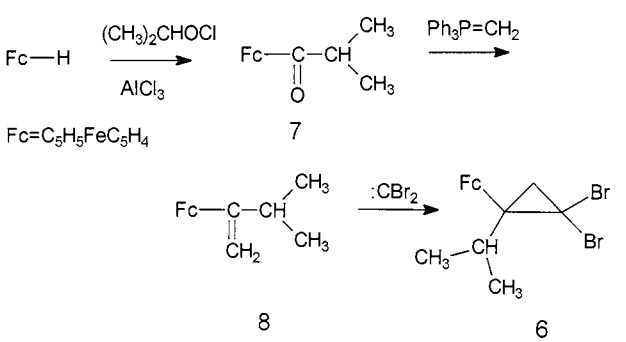
The spatial structure of the earlier synthesized 3-alkyl-3-ferrocenylcyclopropenes (**1c–e**) [9,10] has not been established up to now. The separation of the Diels–Alder adducts **4c–e**, which are derivatives of the intermediate 3-alkyl-1H-cyclopentaferrocenes (**5c–e**), suggested that the ferrocene fragment in compounds **1c–e** might occupy a non-bisecting position in analogy to the position of the aryl fragments in **1a** and **1b**.



However, this assumption was debatable because the reaction of intramolecular transformations in compounds **1c–e**, contrary to that in the cyclopropenes **1a** and **1b**, resulted in the formation of a large amount of linear and polymeric products, together with the expected products of alkylation of the ferrocene substituent.

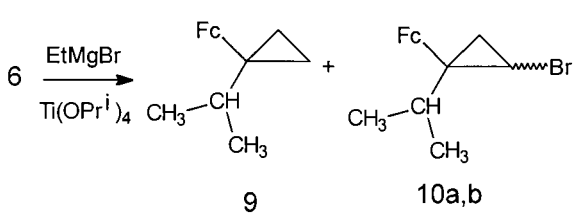
2. Results and discussion

In a continuation of our previous studies, we synthesized the crystal 3-ferrocenyl-3-isopropylcyclopropene (**1f**) from 2,2-dibromo-1-ferrocenyl-1-isopropylcyclopropane (**6**). The dibromide **6** was prepared according to the following reaction scheme [11–13]:



Compounds **6**, **7** and **8** are synthesized easily with a yield of about 70–75%.

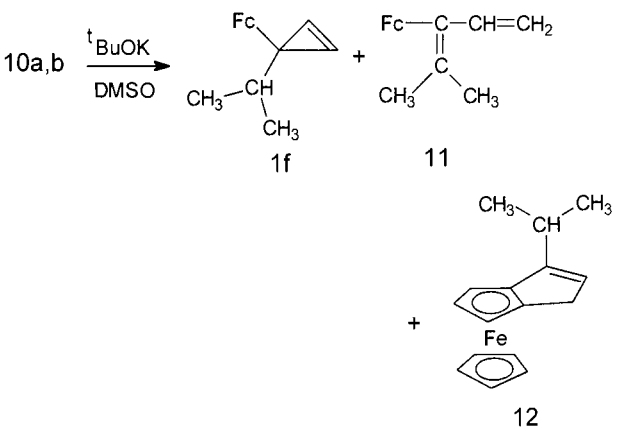
Further we established that the dibromide **6** is easily reduced in a mixture of EtMgBr and $Ti(O^iPr)_4$ [14].



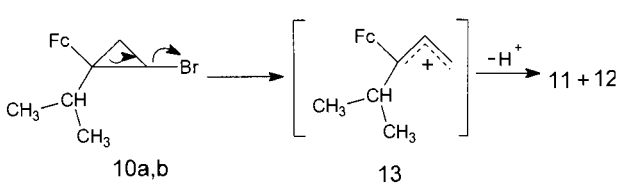
Besides, we found that even for an equimolar mixture of the reagents, it is difficult to avoid the formation of small amounts of completely reduced 1-ferrocenyl-1-isopropylcyclopropane (**9**):

2-Bromo-1-ferrocenyl-1-isopropylcyclopropane (**10**) was separated as a mixture of *Z* and *E* isomers with ratio 3:1 (yield approximately 62%). The assigment of the isomer monobromides to *Z* and *E* geometry was carried out by ^{1}H-NMR spectroscopy (Table 1) taking into account the earlier established [7–10,14] NMR criteria for distinguishing *Z*- and *E*-geometric isomers of monobromoferrocenylcyclopropanes.

Cyclopropene (**1f**) was synthesized by dehydrobromation of the monobromide (*Z*-/*E*-**10**) in the presence of 5% excess of ^{t}BuOK in DMSO:



We separated compounds **11** and **12** as reaction side products, which are obviously related to opening of the three-membered ring in monobromocyclopropane **10** in the presence of ^{t}BuOK in DMSO. One of the possible reaction paths is via solvolysis of the monobromide **10**, resulting in the intermediate alkylferrocenylallyl cation **13** followed by further transformations (deprotonation and intramolecular alkylation) to form products **11** and **12**:

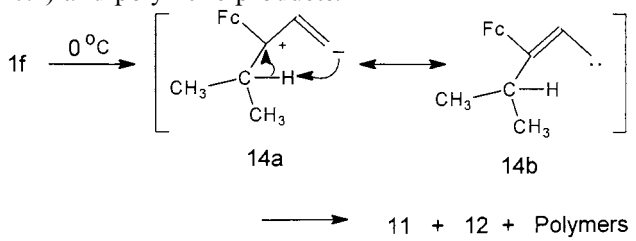


Cyclopropene (**1f**) is easily crystallized in *n*-heptane forming orange crystals with m.p. 62–63°C. Freshly prepared crystals of **1f** were studied by X-ray analysis. Fig. 1 shows a general view of the **1f** molecule and Fig. 2 shows one of its projections.

The basic element in the structure of **1f** is the three-membered ring. It is an acute-angled isosceles triangle distorted in the direction of atom C(13). The length of the C(11)=C(12) double bond is $\delta = 1.27$ Å and the acute angle at C(13) has a value of $\omega = 50.0°$. The position of the ferrocenyl fragment in **1f** corresponds to

a bisecting orientation relative to the small ring (Fig. 2). The bond lengths Fe–C and C–C in the ferrocenyl fragment, as well as the geometry of the ferrocenyl sandwich, are the usual ones. Therefore, it appears that the molecules of 3-aryl-3-ferrocenylcyclopropenes (**1a**,**b**) and of 3-alkyl-3-ferrocenylcyclopropenes (**1c**–**f**) have a similar conformation with a bisecting orientation of the ferrocenyl substituent and a non-bisecting position of the aryl and alkyl groups.

Further we established that the chemical properties of 3-ferrocenyl-3-isopropylcyclopropene correspond to its conformational structure. For example, cyclopropene **1f** is unstable both in solution and in its crystal state. It gradually isomerizes in cold solutions (0°C) of hexane, benzene or chloroform to form 1,1-dimethyl-2-ferrocenyl-1,3-butadiene (**11**) (yield 42%), 3-isopropyl-1H-cyclopentaferrocene (**12**) (yield 4%) and polymeric products of unknown structure and composition. These results are obviously related to the easy opening of the cyclopropene ring even at low temperatures. The formed intermediate carbenoid compound **14** is then isomerized to give the diene **11**, compound **12** (ratio 10:1) and polymeric products:



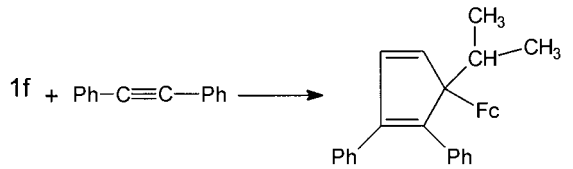
The crystals of the cyclopropene **1f** are gradually converted into an orange oil on prolonged storage (0°C, 1–2 months). The chromatographic analysis of the oil indicated the presence of compounds **11**, **12** and of polymers.

We managed to trap the carbenoid intermediate **14**, formed initially at the heterolytic cleavage of the C–C bond in the three-membered ring using diphenylacetylene. 5-Ferrocenyl-5-isopropyl-1,2-diphenylcyclopentadiene (**15**) was formed (yield 54%) according to the following scheme:

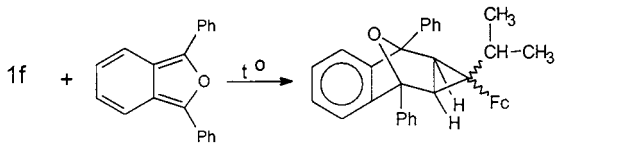
Table 1
^{1}H-NMR spectroscopy data for the obtained compounds (300 MHz, $CDCl_3$, TMS) [a]

Compounds	C_5H_5	C_5H_4	CH_2	CH	CH_3, Ar
1f	4.12 s, 5H	4.02 s, 4H		2.41 m, 1H, $J = 6.76$; 6.95 s, 2H	0.79 d, 6H, $J = 6.76$
6	4.16 s, 5H	4.21 m, 2H, 4.25 m, 2H	1.75 d, 1H, $J = 7.2$; 2.11 d, 1H, $J = 7.2$	2.17 m, 1H, $J = 6.8$	0.98 d, 3H, $J = 6.8$; 1.15 d, 3H, $J = 6.8$
7	4.15 s, 5H	4.45 m, 2H, 4.75 m, 2H		3.07 m, 1H, $J = 6.88$	1.17 d, 6H, $J = 6.88$
8	4.06 s, 5H	4.19 m, 2H, 4.38 m, 2H	4.90 bs, 1H, 5.21 d, 1H, $J = 1.06$	2.64 m, 1H, $J = 6.88$, 1.06	1.18 d, 6H, $J = 6.88$
9	4.10 s, 5H	4.12 m, 2H, 4.14 m, 2H	0.66 m, 2H, 0.75 m, 2H	2.80 m, 1H, $J = 6.7$	0.93 d, 6H, $J = 6.7$
***Z*-10**	4.14 s, 5H	4.07 m, 1H, 4.12 m, 2H, 4.18 m, 1H	1.45 dd, 1H, 2.05 dd, 1H, $J_{gem} = 6.50$, $J_{trans} = 5.20$, $J_{cis} = 8.10$	1.93 m, 1H, $J = 6.0$; 3.47 dd, 1H, $J = 5.20$, 8.10	0.83 d, 3H, $J = 6.0$; 0.91 d, 3H, $J = 6.0$
***E*-10**	4.10 s, 5H	3.98 m, 2H, 4.05 m, 2H	1.64 dd, 1H, 1.89 dd, 1H, $J_{gem} = 5.12$, $J_{trans} = 6.10$, $J_{cis} = 7.6$	1.72 m, 1H, $J = 6.9$; 3.67 dd, 1H, $J = 6.10$, 7.6	0.80 d, 3H, $J = 6.9$; 0.85 d, 3H, $J = 6.9$
11	4.13 s, 5H	3.90 m, 2H, 4.22 m, 2H	5.05 dd, 1H, $J = 0.7$, 17.5; 5.14 dd, 1H, $J = 0.7$, 10.6	6.01 dd, 1H, $J = 10.6$, 17.5	1.75 s, 3H, 1.79 s, 3H,
12	4.12 s, 5H	4.20 m, 1H, 4.31 m, 2H	4.28 d, 2H, $J = 6.69$	2.94 m, 1H, $J = 7.15$	1.20 d, 6H, $J = 7.15$
15	4.09 s, 5H	3.62 m, 1H, 4.01 m, 1H, 4.12 m, 1H, 4.14 m, 1H		2.23 m, 1H, $J = 6.6$; 6.70 d, 1H, 6.78 d, 1H, $J = 5.61$	0.85 d, 3H, 1.30 d, 3H, $J = 6.6$; 6.90 m, 2H, 7.16 m, 8H
16a	4.07 s, 5H	3.91 s, 4H		2.45 s, 2H, 2.95 m, 1H, $J = 6.66$	0.39 d, 6H, $J = 6.66$; 6.95–7.12 m, 4H, 7.40–7.60 m, 6H, 7.75–7.83 m, 4H
16b	3.98 s, 5H	4.10 s, 4H		2.40 s, 2H, 2.72 m, 1H, $J = 6.7$	0.42 d, 6H, $J = 6.7$; 7.05 m, 7.15 m, 7.46 m, 7.70 m, 7.81 m, 14H
17	4.12 s, 5H	4.15 m, 2H, 4.19 m, 2H		2.98 s, 1H	1.85 s, 3H, 2.02 s, 3H
18a	4.05 s, 5H	4.00 m, 1H, 4.20 m, 2H, 4.27 m, 1H		2.40 m, 1H, $J = 6.8$: 5.51 q, 1H, $J = 6.6$	1.17 d, 6H, $J = 6.8$; 1.81 d, 3H, $J = 6.6$
18b	4.03 s, 5H	3.75 m, 1H, 4.01 m, 1H, 4.18 m, 1H, 4.43 m, 1H		2.75 m, 1H, $J = 6.78$; 5.83 q, 1H, $J = 6.62$	1.19 d, 6H, $J = 6.78$; 1.70 d, 3H, $J = 6.62$
19	4.00 s, 5H	3.71 d, 1H, 3.90 d, 1H, $J = 2.10$	2.15 dd, 1H, $J = 15.0$, 2.8; 2.90 dd, 1H, $J = 15.0$, 8.9	2.63 m, 1H; 4.12 td, 1H, $J = 8.9$, 2.8; 4.35 d, 1H, $J = 8.9$	0.89 d, 6H, $J = 6.2$; 6.70–6.90 m, 7.30–7.70 m, 14H

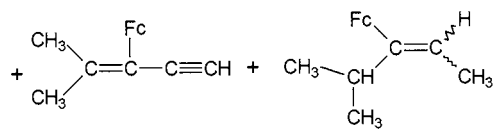
[a] δ (ppm), J (Hz).



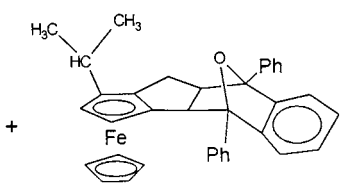
Freshly prepared cyclopropene **1f** interacts with 1,3-diphenylisobenzofuran at boiling in benzene forming a Diels–Alder adduct **16** and compounds **17**, **18a**,**b** and **19**:



16 a,b



17 18 a,b



19

The classical Diels–Alder adduct was formed as a mixture of two structural isomers **16a** and **16b** (3:1) as revealed by ^{1}H-NMR (Table 1). The isomers were separated by TLC on SiO_2. The monocrystals of isomer **16a** (formed with a higher yield from a solution of *n*-heptane) were studied by X-ray structural analysis (Fig. 3). The X-ray results indicate that the three-membered ring is practically an equilateral triangle. The three-membered ring is condensed with the six-membered ring in a rigid boat conformation. The adduct **16a** has an *exo* structure. The isopropyl group has a *syn* position relative to the bridge oxygen atom and a non-bisecting position relative to the small ring. The ferrocenyl fragment occupies the *anti* position relative to the oxygen atom. Contrary to the adduct **16a**, an *exo*-1,5-diphenyl-3-*syn*-ferrocenyl-3-*anti*-isopropyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene structure is assigned to isomer **16b**.

Without doubt, the formation of compounds **17**, *Z*-**18a** and of *E*-**18b** (according to ^{1}H-NMR data, Table 1), as well as **19**, is possible only if small ring opening takes place during the reaction and the further transformations of the intermediates **14a**,**b**. For example, the intermolecular disproportionation of **14a**,**b** leads to the formation of **17** and of **18a**,**b**. In our opinion the intramolecular transformations in **14a**,**b**

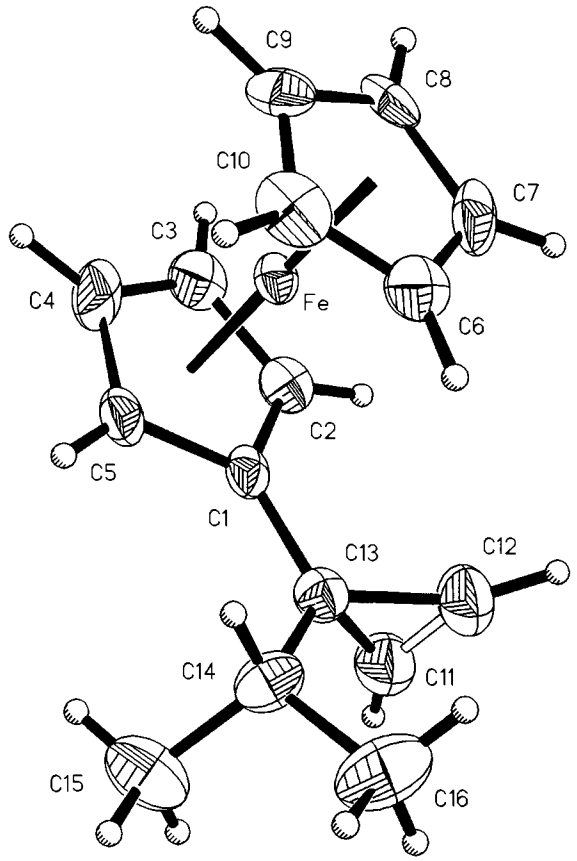
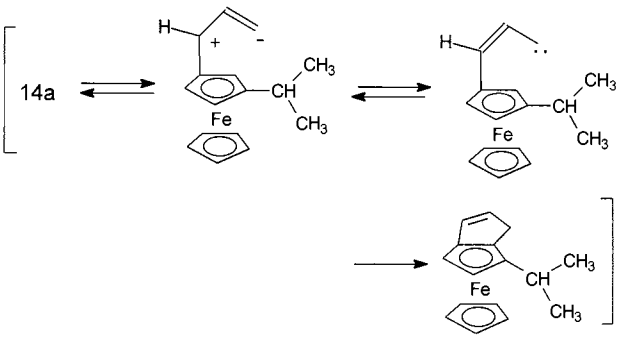


Fig. 1. Crystal structure of **1f**. Selected bond lengths (Å): C_{11}–C_{12} = 1.274(6); C_{11}–C_{13} = 1.510(5); C_{12}–C_{13} = 1.507(6); C_{13}–C_{14} = 1.542(6); C_1–C_{13} = 1.487(5). Selected bond angles (°): C_{11}–C_{13}–C_{12} = 50.0(3); C_{11}–C_{12}–C_{13} = 65.1(3); C_{12}–C_{11}–C_{13} = 64.9(3).

result in the formation of the intermediate 3-isopropyl-1,2-(1-propene-1,3-diyl)ferrocene (**20**). Then it is transformed into the adduct **19**. These transformations are well described for α-ferrocenylcarbocations having bulky substituents [10,15–17]. They include migration of the isopropyl substituent from the α-ferrocenylcarbocationic center of **14a** to position 3 of the C_5H_4 group of ferrocene. Also, the intramolecular alkylation in position 2 of the cyclopentadiene ring of ferrocene is well known for α-ferrocenylcarbocations [18] and carbenoids [19]:



20

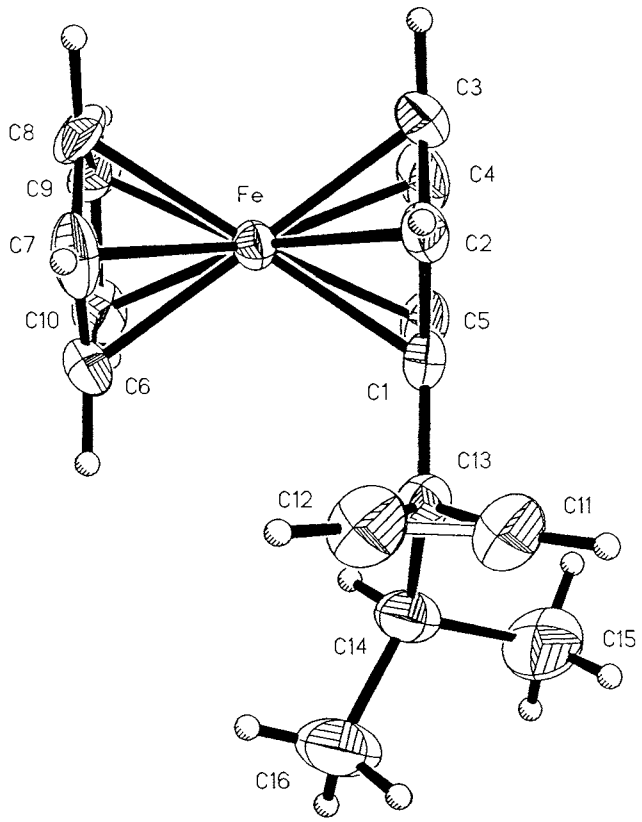


Fig. 2. One of the projections of molecule **1f**.

Comparing the ^{1}H-NMR data of compound **19** with the spectra of similar adducts (see Ref. [10]), we assigned the *endo*-1,7-diphenyl-3,4-(3-isopropylferroceno)-8,9-benzo-10-oxatricyclo[5.2.1.0^{2,4}]deca-3,8-diene structure to **19**.

In such a way, the X-ray results on monocrystals of one of the members of the 3-alkyl-3-ferrocenylcyclopropene family revealed that the ferrocenyl fragment in these compounds occupies a bisecting position relative to the three-membered ring, similar to that in 3-aryl-3-ferrocenyl-cyclopropenes. In this conformation the molecular orbitals of the ethylene fragment of the small ring cannot interact with the orbitals from the cyclopentadiene ring of ferrocene. It is the absence of this interaction that results in the predominant formation of linear products of the intramolecular transformations of 3-alkyl-3-ferrocenylcyclopropenes.

Besides, we would like to point out, that a small amount of products of intramolecular alkylation of ferrocene were obtained.

3. Experimental

The ^{1}H- and ^{13}C-NMR spectra were recorded on a Unity Inova Varian spectrometer (300 y 75 MHz) in $CDCl_3$ solutions using Me_4C as an internal standard (see Tables 1 and 2). Table 3 contains the elemental analysis results. The chromatographic separation was carried out on an Al_2O_3 (Brockmann activity III) packed column. The X-ray patterns were recorded on a Siemens P3/PC diffractometer (compound **16a**) and for compound **1f**, on a Siemens P4/PC. The crystallographic data, the experimental conditions and corrections are given in Table 4. The chemical reactions were carried out in dry argon atmosphere and absolute grade solvents.

3.1. Isopropylferrocenylketone (7)

Isopropylferrocenylketone (**7**) was prepared by Friedel–Crafts acylation of ferrocene with $(CH_3)_2CH$-COCl in the presence of $AlCl_3$ in CH_2Cl_2. The ketone **7** had a yield of 76%, orange oil [11].

3.2. 1-Ferrocenyl-1-isopropylethylene (8)

1-Ferrocenyl-1-isopropylethylene (**8**) was prepared by the Wittig reaction [12] from ketone **7** and methylenetriphenylphosphorane. The alkene **8** had 73% yield (after Al_2O_3 chromatography using hexane as eluent), orange crystals, m.p. 84–85°C.

Table 2
^{13}C-NMR spectroscopy data for compounds **1f**, **7**, **10b** and **16a** (75 MHz, $CDCl_3$, TMS) [a]

Assignment	**1f**	**7**	**10b**	**16a**
C_5H_5	68.01	69.5	68.3	68.6
C_5H_4	66.9	69.4, 72.1	66.7, 66.8, 69.1, 69.5	65.3, 67.2
C_{ipso}Fc	98.7	78.1	90.9	96.4
CH_3	20.7	19.4	19.1, 19.8	12.1, 13.1
CH	29.9	37.2	23.9, 34.2	18.3, 41.4
C	34.9	208.5	28.9	38.7, 88.7
CH=	110.6			
Ar				119.1, 125.8, 127.8, 128.1, 128.4
C_{ipso}				136.8, 151.5
CH_2			31.1	

[a] δ (ppm).

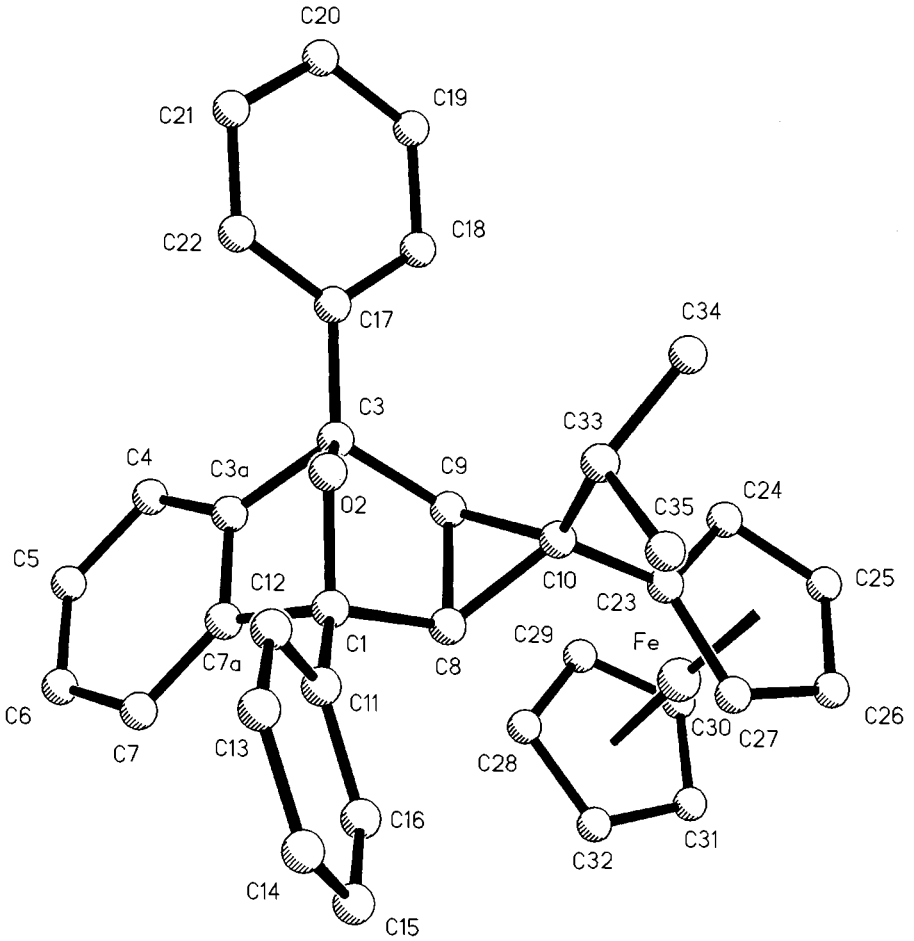


Fig. 3. Crystal structure of **16a**. Selected bond lengths (Å): C_8–C_9 = 1.510(8); C_9–C_{10} = 1.516(8); C_8–C_{10} = 1.512(7); C_{10}–C_{33} = 1.541(9); C_{10}–C_{23} = 1.506(8); C_{7a}–C_{3a} = 1.396(8). Selected bond angles (°): C_8–C_{10}–C_9 = 59.8(3); C_8–C_9–C_{10} = 60.0(4); C_9–C_8–C_{10} = 60.2(4); C_1–C_8–C_9 = 102.5(5); C_8–C_9–C_3 = 102.9(4).

3.3. 2,2-Dibromo-1-ferrocenyl-1-isopropylcyclopropane (6)

2,2-Dibromo-1-ferrocenyl-1-isopropylcyclopropane (**6**) was prepared from alkene **8** following a known procedure [13], with a yield of 74%, orange crystals, m.p. 123–124°C.

3.4. Reduction of the dibromide 6 [14]

A few drops of tetraisopropyltitanate and a solution

Table 3
Elemental analysis data for the obtained compounds

Compound	Found (%)				Molecular formula	Calculated (%)			
	C	H	Fe	Br		C	H	Fe	Br
1f	72.29	7.03	21.08		$C_{16}H_{18}Fe$	72.21	6.81	20.98	
6	44.85	4.34	13.70	37.63	$C_{16}H_{18}Br_2Fe$	45.09	4.26	13.10	37.55
7	65.52	6.43	21.74		$C_{14}H_{16}FeO$	65.65	6.30	21.80	
8	70.99	7.05	22.08		$C_{15}H_{18}Fe$	70.91	7.14	21.95	
9	71.72	7.47	20.70		$C_{16}H_{20}Fe$	71.66	7.51	20.83	
Z-, *E*-**10**	55.48	5.39	16.21	23.19	$C_{16}H_{19}$ BrFe	55.35	5.52	16.09	23.04
11	72.28	6.71	20.73		$C_{16}H_{18}Fe$	72.21	6.81	20.98	
12	72.14	6.99	21.03		$C_{16}H_{18}Fe$	72.21	6.81	20.98	
15	81.21	6.22	12.69		$C_{30}H_{28}Fe$	81.08	6.35	12.57	
16a,**b**	80.42	5.93	10.54		$C_{36}H_{32}FeO$	80.60	6.01	10.41	
17	72.87	6.03	21.19		$C_{16}H_{16}Fe$	72.75	6.11	21.14	
18a,**b**	71.52	7.65	20.98		$C_{16}H_{20}Fe$	71.66	7.51	20.83	
19	80.72	5.85	10.61		$C_{36}H_{32}FeO$	80.60	6.01	10.41	

Table 4
Crystal data, data collection and refinement parameters for **1f** and **16a**

Data	**1f**	**16a**
Molecular formula	$C_{16}H_{18}Fe$	$C_{36}H_{32}FeO \cdot 0.5C_7H_{16}$
Formula weight (g mol^{-1})	266.15	586.6
Temperature (K)	293	293
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	13.622(2)	11.199(2)
b (Å)	12.068(2)	15.521(2)
c (Å)	8.330(1)	18.646(2)
α (°)	90.0	90
β (°)	102.42(1)	102.97(2)
γ (°)	90.0	90
V (Å^3)	1337.3(3)	3158.3(7)
Z	4	4
$D_{calc.}$ (Mg m^{-3})	1.322	1.234
Absorption coefficient (mm^{-1})	1.102	0.507
$F(000)$	560	1244.08
Radiation, λ (Å)	Mo–K_α, 0.71073	Mo–K_α, 0.71073
Monochromator	Graphite	Graphite
Θ range (°)	1.50–25.00	1.50–30.0
Reflections collected	2450	9627
Reflections independent	2349	9199
R_{int}	0.0347	0.0293
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0422$, [a] $wR_2 = 0.1035$	$R_1 = 0.0725$, [b] $wR_2 = 0.0871$
R indices (all data)	$R_1 = 0.0652$, [a] $wR_2 = 0.1269$	$R_1 = 0.1627$, [b] $wR_2 = 0.1050$
Data/restraints/parameters	2349/0/155	
Reflections observed	1736($I>2\sigma(I)$)	3578($F>4.0\sigma(F)$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit	1.105	1.65
Minimum/maximum residual electron density (e Å^{-3})	−0.414/0.395	−0.38/0.56
Hydrogen atoms	Riding	Riding

[a] Weighting scheme: $w=\sigma^2(F_o^2)+(0.0735P)^2$ where $P=(F_o^2+2F_c^2)/3$.
[b] Weighting scheme: $w^{-1}=\sigma^2(F)+0.0008F^2$.

(3.3 mmol) of EtMgBr in ether were added at intensive stirring to a solution of 1.28 g (3 mmol) of dibromocyclopropane (**6**) in 50 ml of ether. The mixture was stirred at 20°C till its colour changed from dark brown to yellow and then the reaction mixture was decomposed by the addition of 50 ml of water. The organic layer was separated and the solvent was evaporated at room temperature in vacuum and then thin-layer chromatography on silica gel (*n*-hexane) was carried out. The yield of monobromides *Z*-, *E*-**10** (3:1), $R_f = 0.49$, as orange oil was 0.65 g (62%). Also, 0.1 g (12%) of cyclopropane **9**, $R_f = 0.65$, orange oil, was obtained.

3.5. 3-Ferrocenyl-3-isopropylcyclopropene (1f)

Monobromide **10** (1.05 g, 3 mmol) was added with intensive stirring to a solution of 0.35 g (3.15 mmol) of ^{t}BuOK in 30 ml of absolute DMSO. The mixture was stirred at 20°C for 6 h, then 50 ml of benzene and 50 ml of water were added. The organic layer was separated and washed with water. The solvent was removed by heating in vacuum and the remaining oil was separated by thin-layer chromatography on silica gel (*n*-hexane). Orange crystals of cyclopropene **1f**, $R_f = 0.56$, m.p. 62–63°C, were obtained with a yield of 61% (0.49 g). Also, 0.035 g (5%) of yellow powder of compound **12**, $R_f = 0.67$, m.p. 71–72°C and 0.09 g (11%) of 1,1-dimethyl-2-ferrocenyl-1,3-butadiene **11**, $R_f = 0.48$, orange oil, were obtained. The latter compound is unstable and rapidly decomposes at storage.

3.6. Intramolecular isomerization of cyclopropene (1f)

A solution of 0.27 g (1 mmol) of cyclopropene **1f** in 50 ml of solvent (*n*-hexane, benzene, chloroform) was kept at 0°C for 3 days. Then the solvent was removed in vacuum and thin-layer chromatography on silica gel (*n*-hexane) was carried out. The following compounds were separated: 0.33 g (42%) of compound **11**, $R_f =$ 0.48; 0.08 g (10%) of the initial cyclopropene **1f**, $R_f =$ 0.55, m.p. 62–63°C; 0.04 g (4%) of compound **12**, $R_f = 0.68$, m.p. 72°C.

3.7. Interaction of cyclopropene 1f with diphenylacetylene

A solution of 0.27 g (1 mmol) of cyclopropene **1f** and 0.27 g (1.5 mmol) of diphenylacetylene in 50 ml of benzene was boiled for 3 h till the disappearance of the spot of the initial cyclopropene **1f** on silica gel (*n*-hexane). After the removal of the solvent and thin-layer chromatography on silica gel (*n*-hexane–benzene, 2:1), we obtained 0.24 g (54%) of compound **15**, $R_f = 0.38$, as orange powder, m.p. 186–187°C.

3.8. Reaction of cyclopropene 1f with 1,3-diphenylisobenzofuran

A solution of 0.4 g (1.5 mmol) of cyclopropene **1f** and of 0.56 g (2 mmol) of 1,3-diphenylisobenzofuran in 60 ml of benzene was boiled for 5 h (control performed by thin-layer chromatography on silica gel, as in the previous experiment). The solvent was then removed and thin-layer chromatography on silica gel (*n*-hexane–benzene, 3:1) was carried out. The following compounds were separated: 0.06 g (13%) of 3-ferrocenyl-4-methyl-2-pentene (**18a**,**b**) (a mixture of *Z* and *E* isomers, 3:1), $R_f = 0.75$, orange oil; 0.042 g (10%) of 3-ferrocenyl-4-methyl-3-penteneine (**17**) $R_f = 0.54$,

orange oil (rapidly decomposing at storage); 0.08 g (9.8%) of the adduct **19**, $R_f = 0.42$, yellow crystals, m.p. 212–213°C; 0.40 g (49%) of the adduct **16a**,**b** (3:1), $R_f = 0.34$, yellow crystals, m.p. 198–199°C. Isomer **16a** was separated from the mixture of isomers by thin-layer chromatography on silica gel (*n*-hexane–benzene, 1:1). The following compounds were separated: 0.15 g of isomer **16a**, $R_f = 0.64$, yellow crystals, m.p. 203–204°C (formed from a solution of *n*-heptane), and 0.16 g of the mixture of adducts **16a** and **16b** (1:1), $R_f = 0.70$, m.p. 194–198°C.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 133 900 for 3-ferrocenyl-3-isopropylcyclopropene (**1f**) and no. 133 901 for *exo*-1,5-diphenyl-3-*anti*-ferrocenyl-3-*syn*-isopropyl-6,7-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**16a**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support from CONACyT (Mexico) is gratefully acknowledged. We would like to thank Oscar Salvador Yañez Muñoz for ^{1}H- and ^{13}C-NMR spectra.

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