ELSEVIER

Journal of Organometallic Chemistry 559 (1998) 1–10

Journal of Organometallic Chemistry

Formation of acetylenic compounds and ring transformations of 3-alkyl-3-ferrocenylcyclopropenes in the reaction with 1,3-diphenylisobenzofuran

Elena I. Klimova [a,c,*], Lena Ruíz Ramírez [a], Rafael Moreno Esparza [a], Tatiana Klimova Berestneva [a], Marcos Martinez García [b], Natalya N. Meleshonkova [c], Andrei V. Churakov [c]

[a] *Universidad Nacional Autónoma de México, Facultad de Química, Circuito Interior, Cd. Universitaria, Coyoacán, CP 04510, México D.F., Mexico*

[b] *Universidad Nacional Autónoma de México, Instituto de Química, Circuito Exterior, Cd. Universitaria, Coyoacan, CP 04510, México D.F., Mexico*

[c] *Moscow State University M.V. Lomonosov, Chemistry Department, Vorobjovy Gory, 119899, Moscow, Russia*

Received 20 June 1997

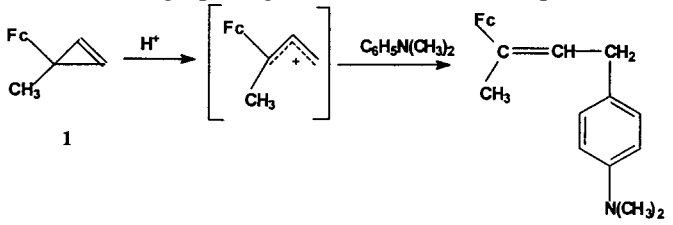
Abstract

The reaction of 3-ferrocenyl-3-methylcyclopropene with 1,3-diphenylisobenzofuran leads to the formation of *exo*- and *endo*-1,4-epoxy-2-ethynyl-2-ferrocenyl-1,4-diphenyltetralines as the main products in addition to the isomeric Diels–Alder *exo*-adducts. At the same time, 3-*tert*-butyl- and 3-(1-adamantyl)-3-ferrocenylcyclopropenes form the *endo*- and *exo*-adducts of 3-alkyl-1,2-(1-propene-1,3-diyl)ferrocene. The structures of the acetylenic compounds and of the adduct containing a ^{t}Bu-substituent are established by X-ray structural analysis. A possible reaction pathway via intermediate zwitter-ion is discussed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Ferrocene; Cyclopropene; Three-membered ring opening; Zwitter-ion; X-ray analysis

1. Introduction

In previous papers [1,2], we reported the synthesis of 3-ferrocenyl-3-methylcyclopropene **1** and the three-membered ring opening under the action of superacids:



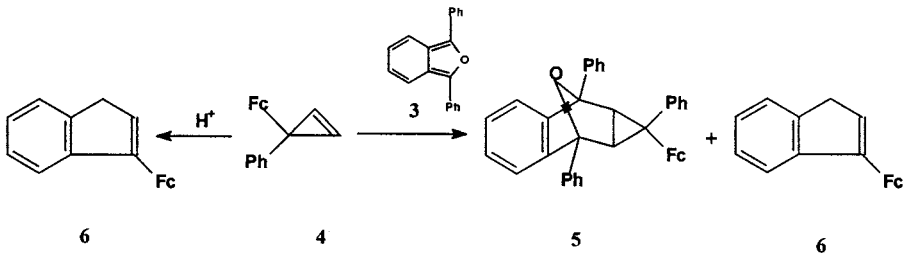
1

Fc=ferrocenyl

We have also noted that all our attempts to isolate the expected product of a regular [4 + 2]-cycloaddition of cyclopropene **1** to 1,3-diphenylisobenzofuran **3** failed. Contrary to cyclopropene **1**, 3-ferrocenyl-3-phenylcyclopropene **4** reacts with diphenylisobenzofuran **3** to give the expected product of stereospecific [4 + 2]-cycloaddition **5** together with 3-ferrocenylindene **6** as a product of an intramolecular transformation of **4** [3,4]. 3-Ferrocenylindene **6** was also obtained by protonation of cyclopropene **4** with superacids, followed by treatment of the reaction mixture with *N*,*N*-dimethylaniline:

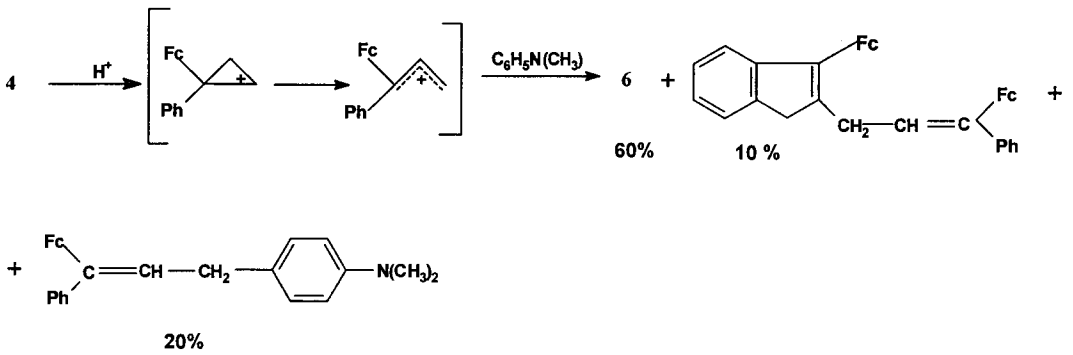
* Corresponding author. Fax: + 52 5 6225366; e-mail: klimova@servidor.unam.mx

PII S0022-328X(97)00670-0



6 4 5 6

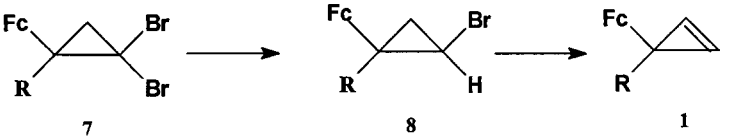
The mechanism of the three-membered ring opening in **4**, caused by protonation, seems to be similar to that observed for ferrocenylmethylcyclopropene **1**, i.e. it possesses a distinct ionic character:



60% 10 %

20%

The formation of the same product **6** in both thermal and ionic processes is a sign of an easy cleavage of the σ C–C bonds in the 3-ferrocenyl substituted cyclopropenes and of the possibility to influence this cleavage with the second substituent at position 3 [3,4].



7 8 1

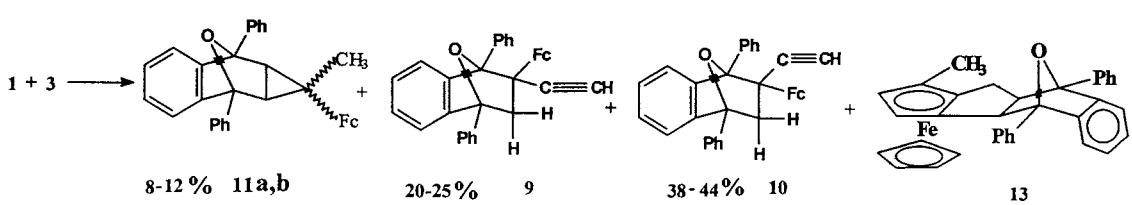
R = CH_3- (a), ^{t}Bu- (b), ^{1}Ad- (c)

2. Results and discussion

In a continuation of our investigations, we studied the reaction of 3-alkyl-3-ferrocenylcyclopropenes **1a–c** with 1,3-diphenylisobenzofuran **3** in detail. We found that the initial cyclopropenes **1a–c** can be prepared easily by reduction of the 2,2-dibromo-1-alkyl-1-ferrocenylcyclopropanes **7a–c** into the *Z*-2-bromo-1-alkyl-1-ferrocenylcyclopropanes **8a–c** with ^{t}BuOK in DMSO, followed by dehydrobromination of **8a–c** into the desired cyclopropenes **1a–c** using the same reagents. Both **8a–c** and **1a–c** are obtained in good yields. It should be also noted that while the previously employed reduction of **1a** with zinc powder gives significant amounts of by-products (the yield of 1-ferrocenyl-1-methylcyclopropane being as high as 20% [1]), the reduction with ^{t}BuOK/DMSO is highly selective [5]:

One should note that such a reduction of *gem*-dibromocyclopropanes bearing either aliphatic or aromatic substituents has never been reported. We believe that the most plausible explanation of the above reaction is a one-electron reduction of **7a–c** by the mixture of ^{t}BuOK/DMSO followed by an H atom transfer from the solvent. The high yield of monobromo derivatized **8a–c** demonstrates a sufficient stability of the suggested intermediate.

Prolonged reflux of a mixture of 3-ferrocenyl-3-methylcyclopropene **1a** and 1,3-diphenylisobenzofuran **3** in benzene or toluene leads to four products: classical Diels–Alder adducts (**11a,b**) and adducts **9**, **10** and **13**:



8-12 % 11a,b 20-25% 9 38-44% 10 13

CH_3 - syn, Fc - anti (a); CH_3 - anti, Fc - syn (b)

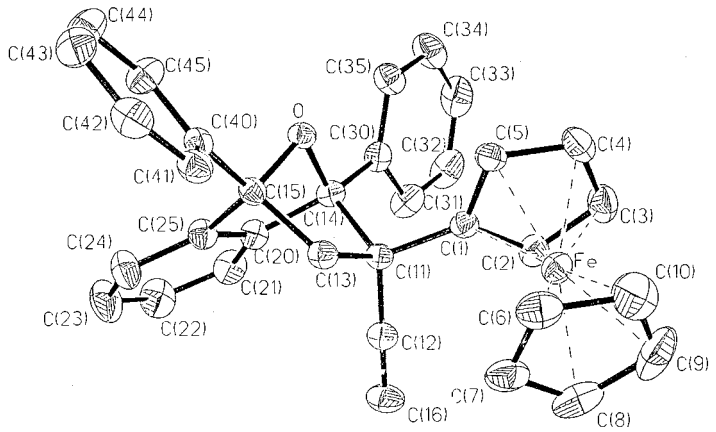
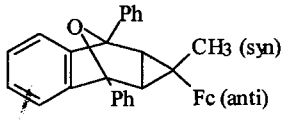


Fig. 1. Crystal structure of **9**. Selected bond lengths (Å) and bond angles (°): C(1)–C(11) 1.503 (3); C(11)–C(12) 1.469 (3); C(12)–C(16) 1.174 (4); C(11)–C(13) 1.564 (3); C(11)–C(12)–C(16) 179.1 (2); C(14)–O–C(15) 98.0 (2); C(13)–C(11)–C(14) 99.6 (2).

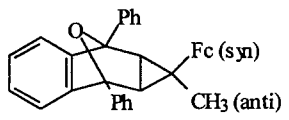
The above scheme shows the structure of compound **13**, which is obtained in minor quantities. This structure is assigned to **13** on the basis of ^{1}H-NMR spectral data (see Experimental part). The formation of adducts with similar structure will be discussed below.

The ^{1}H-NMR spectra of compounds **11a**,**b** contain two signals of the protons of the methyl group with intensity ratio 2:1. These signals prove the formation of two isomeric compounds **11a** and **11b** (see Section 3, Experimental).

The analysis of the ^{1}H-NMR spectral parameters of the methyl and ferrocenyl groups allows one to suggest the existence of a three-membered ring with an *exo*-configuration. The absence of a screening effect of the *o*-phenylene ring on the methyl and ferrocenyl groups (typical of *endo*-adducts [6,7]) also confirms the suggested structure. The comparison of the chemical shifts of the protons of the CH_3 groups of the adducts **11a** and **11b** with those in analogous compounds [4,6,7] allows us to suggest that the adduct **11a** formed in a higher yield is 3-*anti*-ferrocenyl-3-*syn*-methyl-1,5-diphenyl-6,7-benzo-8-oxa-*exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene, and **11b** is 3-*syn*-ferrocenyl-3-*anti*-methyl-1,5-diphenyl-6,7-benzo-8-oxa-*ex o*-tricyclo[3.2.1.0^{2,4}]oct-6-ene:



11 a

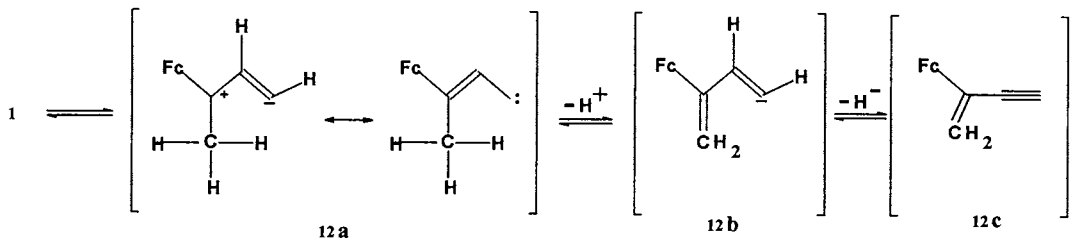


11 b

The ^{1}H-NMR spectra of compounds **9** and **10** unexpectedly indicated the presence of both ethynyl and aliphatic methylene groups (see Section 3, Experimental).

In order to establish the structure of **9** and **10** by an independent method, we carried out an X-ray investigation of single crystals of these compounds obtained from hexane solution. The structures of *exo*-1,4-epoxy-2-ethynyl-2-ferrocenyl-1,4-diphenyltetraline **9** and its *endo*-isomer **10** are shown in Figs. 1 and 2, respectively.

In our viewpoint, the formation of adducts **9** and **10** in the reaction of **1a** with **3** is the result of a thermal heterolysis of a σ C–C bond in the initial cyclopropene **1**. One of the possible mechanisms is shown below:



12 a **12 b** **12 c**

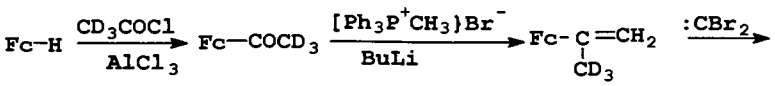
Examples of similar cleavage of the single C–C bonds in carbocycles have been described previously for compounds of the 1,2,3-triferrocenylcyclopropene [9–11] and 3-ferrocenyl-3-phenylcyclopropene [3,4] series. In solution and under various reaction conditions, these compounds undergo ring opening followed by recyclization to give new condensed carbocyclic systems with alkylated ferrocenyl and/or aryl fragments.

In our opinion, this ring opening is due to the thermal heterolysis of 3-ferrocenyl-3-methylcyclopropene **1a**, which results in the formation of an intermediate **12a**. This intermediate is easily deprotonated into the structure **12b**, as it is well known for α-ferrocenyl-α-methyl-carbocations [12–17], with subsequent elimination of a hydride ion.

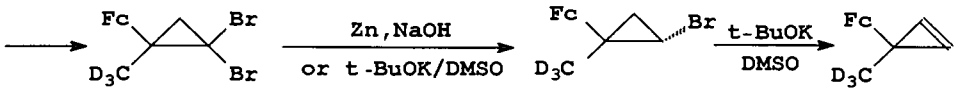
1,3-Diphenylisobenzofuran is a proton and hydride ion acceptor. We observed in the reaction products the

presence of 1,3-dihydro-1,3-diphenylisobenzofurane **15** as a mixture of *cis* and *trans* isomers, ~1:1. The final product of the thermal heterolysis should be 2-ferrocenylbut-1-en-3-yne **12c**, which forms the Diels–Alder adducts **9** and **10** with diphenylisobenzofuran **3**. As follows from the reaction mechanism presented above, the methylene group in **12c** is formed from the methyl group of the initial cyclopropene **1a**.

In order to verify our conclusions, we synthesized the deuterium analogues of ferrocenylmethylcyclopropanes **7-D**, **8-D** and of cyclopropene **1-D**:

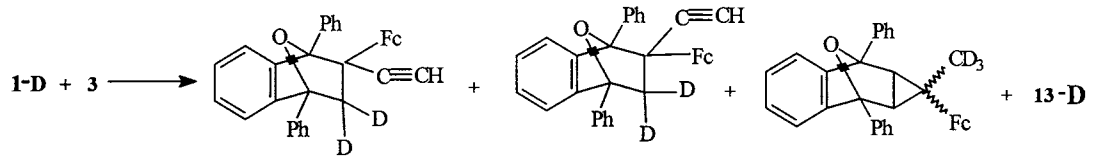


14-D



7-D **8-D** **1-D**

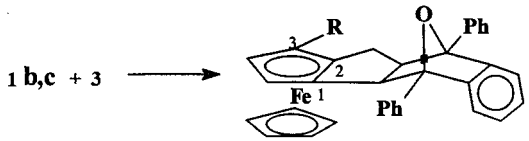
The percentage of the isotopomer in **1-D** is 92% according to the ^{1}H-NMR spectral data (see Table 1). The adducts **9-D**, **10-D** and **11-D a**,**b** were prepared from the cyclopropene **1-D**:



9-D **10-D** **11-Da,b**

No doublets for the protons of the methylene groups in the ^{1}H-NMR spectra of compounds **9-D** and **10-D** were observed (see Table 1). However, we observed singlets for the protons of the acetylenic fragments. These results support our previous conclusion that the methylene group originates from the methyl group of the initial cyclopropene **1a**.

Further we studied the interaction of 3-*tert*-butyl- and 3-(1-adamantyl)-3-ferrocenylcyclopropenes **1b** and **1c** with 1,3-diphenylisobenzofuran **3**. Unlike to the methyl group, the bulky, tertiary ^{t}Bu and ^{1}Ad substituents cannot be deprotonated under the applied reaction conditions. That is why we did not observe the classical Diels–Alder adducts **11**-^{t}Bu and **11**-^{1}Ad in the reaction products. According to ^{1}H- and ^{13}C-NMR spectroscopic data, compounds **16a**,**b** and **17a**,**b** (see Section 3, Experimental) contain 1,2,3-trisubstituted cyclopentadiene cycles in ferrocenes. The spectroscopic data also indicate the presence of four aliphatic protons, of alkyl and phenyl fragments. The ratios **16a**:**16b** and **17a**:**17b** between the isomers is approximately 3:1:



16a,b (R = ^{t}Bu-) and **17a,b** (R = ^{1}Ad-)

The isomer adducts were separated by thin layer chromatography on SiO_2. The structure of the **16a** adduct was established by X-ray analysis. The general view of the molecule of 1,7-diphenyl-3,4-(3-*tert*-butyl-ferroceno)-8,9-benzo-10-oxatricyclo[5.2.1.0^{2,4}]deca-3,8-diene **16a** is shown in Fig. 3. The data of X-ray diffraction analysis of compound **16a** indicate that the obtained adduct has an *endo*-structure. The ^{1}H- and ^{13}C-NMR data allow to assign to compound **17a** an *endo*-structure and to compounds **13**, **16b** and **17b** an *exo*-structure.

It is obvious that this is possible only if the small tricycle in the initial cyclopropenes **1b** and **1c** is opened according to the possible reaction mechanism given above. The intermediates **18a**,**b** cannot be deprotonated. During the reaction they undergo intramolecular transformations, which include:

1. Rearrangement of the α-ferrocenylcarbocation centre with migration of the bulky substituent *R* to position 3 of the C_5H_4-group of the ferrocenyl;
2. Alkylation of the C_5H_4-group in position 2:

Table 1
^{1}H-NMR spectral data of compounds **1-D**, **7-D**, **8-D**, **9-D**, **10-D**, **11-D**, **13-D** and **14-D** ($CDCl_3$, 200 MHz, d, J Hz)

Compound	CH_2, CH_3	C_5H_5	C_5H_4	CH, CH=, CH=	Ar
1-D	1.50[a] br	4.15 s (5H)	4.01 m (4H)	7.15 s (2H)	—
7-D	1.75 dd (2H), $J = 6.0$, 1.82[a] s	4.13 s (5H)	3.95 m (4H)	—	—
8-D (**E-**, **Z-**)	1.0–1.8 m (2H), 1.56[a] s, 1.52[a]s	4.13 s, 4.07 s (5H)	4.15–3.8 m	2.99–3.2 m (1H)	—
9-D	—	4.095 s (5H)	4.12 m (1H), 3.98 m (1H), 3.88 m (1H), 3.77 m (1H)	2.25 s (1H)	7.0–7.08 m, 7.1–7.20 m, 7.24–7.28 m, 7.24–7.28 m, 7.40–7.85 m (14H)
10-D	—	4.128 s (5H)	4.47 m (1H), 4.12 m (1H), 3.87 m (1H), 2.50 m (2H)	2.122 s (1H)	6.88–7.04 m, 7.18 m, 7.35 m, 7.6 m, 7.69–7.8 m (14H)
11-D a,b	1.72[a]br.s, 1.52[a] br.s ~2:1	4.14 s (5H)	4.07 m (2H), 4.05 m (2H)	1.94 s (2H)	7.75 m, 7.70 m, 7.45 m, 7.13 m, 7.05 m (14H)
13-D	1.61[a]br.s, 1.75 dd (1H), $J = 11.2$, 4.3, 2.88 dd (1H), $J = 11.4$, 10.6	4.14 s (5H)	4.13 d (1H), $J = 1.8$, 4.17 d (1H), $J = 1.8$	3.72 td (1H), $J = 11.2$, 4.3, 4.96 d (1H), $J = 10.6$	6.95–7.20 m, 7.40–7.85 m (14H)
14-D	5.11 d (1H), $J = 1.66$, 4.82 d (1H), $J = 1.66$, 2.04[a], s	4.08 s (5H)	4.37 m (2H), 4.19 m (2H)	—	—

[a] Signals for protons remaining in the methyl groups.

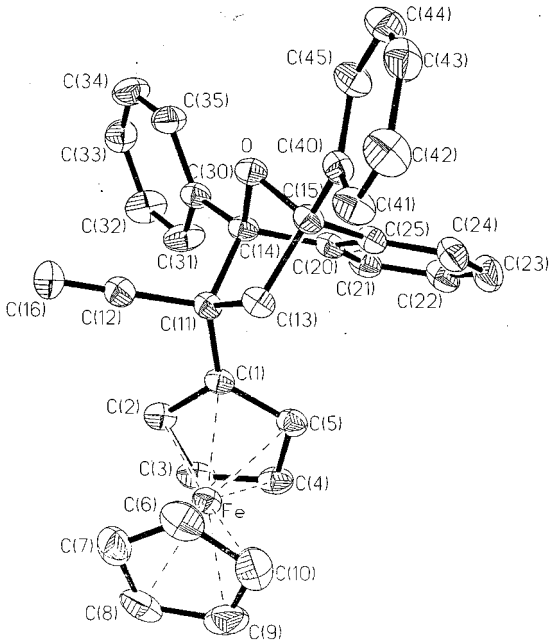


Fig. 2. Crystal structure of **10**. Selected bond lengths (Å) and bond angles (°): C(1)–C(11) 1.521 (3); C(11)–C(12) 1.471 (3); C(12)–C(16) 1.178 (3); C(11)–C(13) 1.565 (3); C(11)–C(12)–C(16) 178.4 (2); C(14)–O–C(15) 98.3 (1); C(13)–C(11)–C(14) 99.6 (2).

The yield of compounds **21a** and **21b** was up to 30%. Their structure was established by elemental analysis and from ^{1}H-NMR spectroscopic data (see Section 3, Experimental).

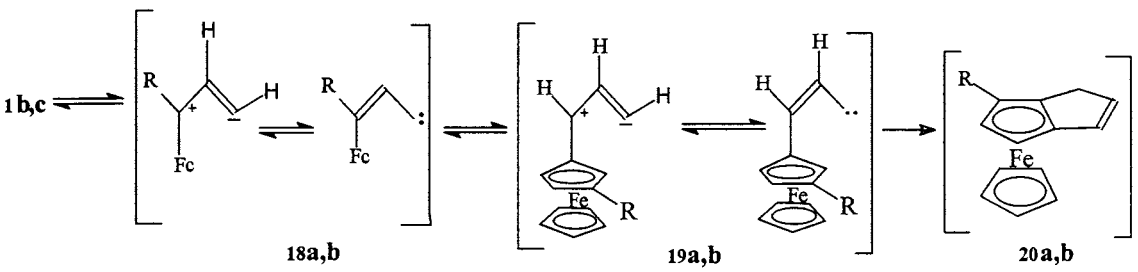
In such a way we could confirm experimentally the opening of the small cycle in 3-alkyl-3-ferrocenylcyclopropenes **1a–c** and the formation of a carbene intermediate. The further chemical transformations of the intermediate carbene depend both on the nature of the alkyl substituent and on the type of compound interacting with the ferrocenylcyclopropanes.

3. Experimental section

The ^{1}H- and ^{13}C-NMR spectra were recorded on a 'Gemini 200 Varian' spectrometer in $CDCl_3$, with Me_4Si as the internal standard. All reactions were performed in an atmosphere of dry argon.

*3.1. 2,2-dibromo-1-alkyl-1-ferrocenylcyclopropanes **7a–c***

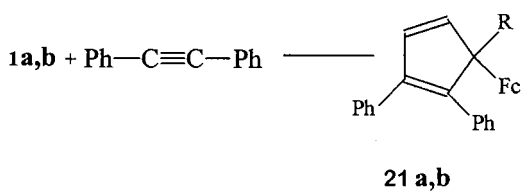
Dibromides **7a–c** were prepared as reported earlier [18] from alkenylferrocenes: **7a**—orange crystals, yield 78%, m.p. 91°C [19]; **7b**—orange crystals, yield 72%, m.p. 127°C [19]; **7c**—orange crystals, yield 74%, m.p. 75–76°C; ^{1}H-NMR, δ: 1.45, 1.74, 1.85, 2.40 (15H, m, Ad), 4.08 (5H, s, C_5H_5), 4.09 (2H, m, C_5H_4), 4.12 (1H, m, C_5H_4), 4.32 (1H, m, C_5H_4), 1.58 (1H, d, $J = 7.2$ Hz), 2.81 (1H, d, $J = 7.2$ Hz); Anal. Calcd. for $C_{23}H_{26}Br_2Fe$, %: C, 53.29; H, 5.06; Br, 30.87; Fe, 10.78; Found: C, 53.42; H, 5.21; Br, 21.03; Fe, 10.82.



R = ^{t}Bu- (a), ^{1}Ad- (b)

These two processes are well known in the chemistry of ferrocenylcarbocations and ferrocenylallylcations [21–24]. We observe for the first time the simultaneous proceeding of the two transformations. As a result, the intermediate 3-alkyl-1,2-(1-propene-1,3-diyl)ferrocenes **20a,b** are formed, which then convert to the adducts **16a,b** and **17a,b**.

We could not observe in the reaction products the compounds **20a,b**. However, we registered compounds **12a** and **18a** using as a trap diphenylacetylene:



21 a,b

R = CH_3- (a), ^{t}Bu- (b)

*3.2. Z-2-bromo-1-alkyl-1-ferrocenylcyclopropanes **8a–c***

Dibromides **7a–c** (1 mmol) were added to a solution of ^{t}BuOK (1.3 mmol) in 25 ml of absolute DMSO and the mixture was stirred for 3–4 h. Then, 50 ml of benzene and 30 ml of water were added to the resulting mixture. The organic layer was separated, washed with water, and concentrated. Monobromides **8a–c** were

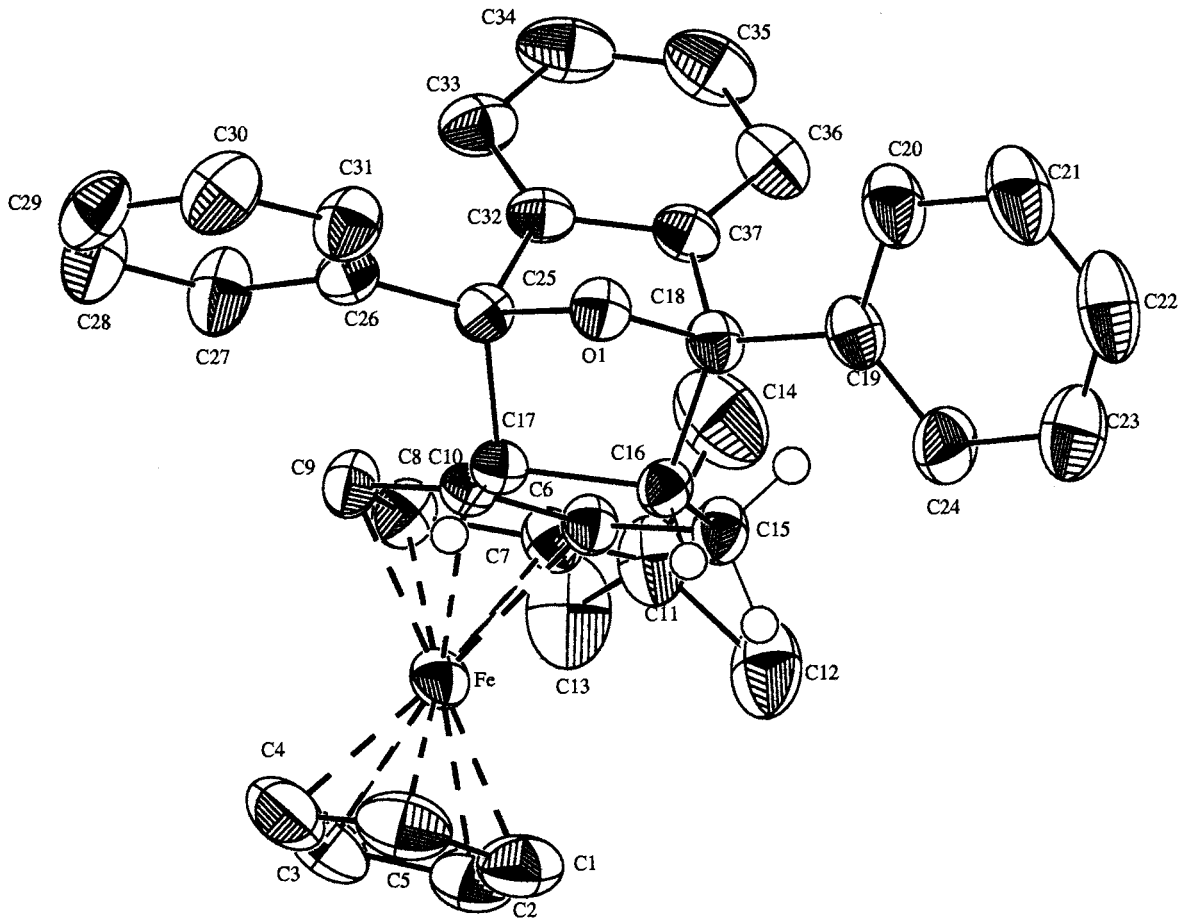


Fig. 3. Crystal structure of **16a**. Selected bond lengths (Å) and bond angles (°): C(10)–C(16) 1.502 (4); C(15)–C(17) 1.557 (4); C(6)–C(10) 1.422 (4); C(6)–C(15) 1.511 (4); C(16)–C(17) 1.584 (4); C(10)–C(16)–C(15) 111.5 (3); C(6)–C(10)–C(16) 112.8 (2); C(6)–C(15)–C(17) 103.8 (2); C(10)–C(16)–C(17) 102.8 (2); C(15)–C(17)–C(16) 109.0 (2).

isolated by chromatography on Al_2O_3 (III grade) using hexane as eluent.

8a [5]—orange oil (yield 72%, Rf = 0.74); ^{1}H-NMR, δ: 1.36 (1H, dd, J = 8.1, 5.6 Hz), 1.53 (3H, s), 1.74 (1H, t, J = 5.6 Hz), 3.12 (1H, dd, J = 8.1, 5.6 Hz), 4.06 (5H, s, C_5H_5), 4.25–3.85 (4H, m, C_5H_4); Anal. Calcd. for $C_{14}H_{15}BrFe$, %: C, 52.71; H, 4.74; Br, 25.06; Fe, 17.50. Found: C, 52.94; H, 4.61; Br, 24.95; Fe, 17.72.

8b—yellow cristals, yield 74%, m.p. 54–55°C, ^{1}H-NMR, δ: 0.76 (9H, s), 1.39 (1H, dd, J = 8.5, 5.68 Hz), 1.71 (1H, t, J = 5.68 Hz), 3.35 (1H, dd, J = 8.5, 5.68 Hz), 4.13 (5H, s, C_5H_5), 4.10 (2H, m, C_5H_4); 4.15 (1H, m, C_5H_4); 4.19 (1H, m, C_5H_4); ^{13}C-NMR, δ: 20.36 (CH_2), 26.15 (CH), 27.88 (CH_3), 31.31, 33.68 (C), 65.30, 66.14, 71.19 (C_5H_4), 69.57 (C_5H_5), 93.22 (C_{quat} F_c); Anal. Calcd. for $C_{17}H_{21}BrFe$, %: C, 56.54; H, 5.86; Br, 22.13; Fe, 15.47. Found: C, 56.29; H, 6.03; Br, 21.96; Fe, 15.71.

8c—yellow cristals, yield 76%, m.p. 106–107°C, ^{1}H-NMR, δ: 1.44 (1H, dd, J = 8.5, 5.6 Hz), 1.69 (1H, t, J = 5.6 Hz), 1.22 (6H, m), 1.55 (6H, m), 1.89 (3H, m, Ad), 3.40 (1H, dd, J = 8.5, 5.6 Hz), 4.12 (5H, s, C_5H_5), 4.10 (1H, m, C_5H_4); 4.11 (1H, m, C_5H_4); 4.22 (2H, m, C_5H_4); Anal. Calcd. for $C_{23}H_{27}BrFe$, %: C, 62.89; H, 6.20; Br, 18.19; Fe, 12.72. Found: C, 63.10; H, 6.04; Br, 18.27; Fe, 12.93.

3.3. 3-alkyl-3-ferrocenylcyclopropenes **1a–c**

A mixture of ^{t}BuOK (1.3 mmol) and monobromides **8a–c** (1 mmol) in 25 ml of DMSO was stirred at room temperature for 10 h. The reaction mixture was treated as described above to give the cyclopropenes **1a–c**:

1a—orange oil (yield 68%) [5]. Compound **1-D** was synthesized from **7-D** following a method reported earlier [5].

1b—yellow crystals, yield 74%, m.p. 39–40°C, ^{1}H-NMR, δ: 0.70 (9H, s), 4.12 (5H, s, C_5H_5), 4.08 (2H, m, C_5H_4); 4.10 (2H, m, C_5H_4); 7.35 (2H, s, CH=CH); ^{13}C-NMR, δ: 29.73 (CH_3), 31.92, 34.53 (C), 68.60, 66.05 (C_5H_4), 68.12 (C_5H_5), 99.53 (C_{quat} F_c), 116.19 (CH=CH); Anal. Calcd. for $C_{17}H_{20}Fe$, %: C, 72.87; H, 7.19; Fe, 19.94. Found: C, 72.62; H, 6.94; Fe, 20.23.

1c—yellow crystals, yield 71%, m.p. 109–110°C, ^{1}H-NMR, δ: 1.20–1.96 (15H, m, Ad), 4.02 (5H, s, C_5H_5), 3.97–4.01 (4H, m, C_5H_4); 7.42 (2H, s, CH=CH); ^{13}C-

NMR, δ: 27.80, 29.98 (CH_2), 33.80, 35.60(CH), 32.40, 30.01(C), 68.63, 65.79 (C_5H_4), 68.06 (C_5H_5), 98.12 (C_{quat} F_c), 118.20 (CH=CH); Anal. Calcd. for $C_{23}H_{26}Fe$, %: C, 77.10; H, 7.31; Fe, 15.59. Found: C, 77.21; H, 7.37; Fe, 15.28.

3.4. Interaction of 3-alkyl-3-ferrocenylcyclopropenes **1a–c** with 1,3-diphenylisobenzofuran **3**

3.4.1. A

A mixture of cyclopropene **1a** (0.12 g, 0.5 mmol) and isobenzofuran **3** (0.27 g, 1 mmol) in 50 ml of dry benzene was refluxed for 60 h until the disappearance of the initial cyclopropene **1a** (TLC). Following removal of the solvent, the residue was subjected to preparative TLC on silica gel in a 2:1 light petroleum–benzene mixture. This resulted in:

0.02 g as a mixture of **3** and 1,3-dihydro-1,3-diphenylisobenzofuran **15a**,**b** (*cis*-/*trans*-, ~1:1, R_f = 0.75), ^{1}H-NMR, δ: 6.25 (CH, s), 6.51 (CH, s), 6.88–7.80 (m, C_6H_5, C_6H_4) [8], 0.03 g (12%) of a mixture of Diels–Alder adducts **11a**,**b** (~2:1, $R_f = 0.6$, m.p. 209–211°C); ^{1}H-NMR, δ: 1.50 s, 1.71 s (3H, ~2:1), 1.93 (2H, s), 4.14 (5H, s, C_5H_5), 4.05 (4H, m, C_5H_4), 7.06, 7.12, 7.57, 7.70, 7.76 (14H, m); Anal. Calcd. for $C_{34}H_{28}FeO$, %: C, 80.32; H, 5.55; Fe, 10.98; Found: C, 80.17; H, 5.73; Fe, 11.07.

0.05 g (20%) of *exo*-1,4-epoxy-2-ethynyl-2-ferrocenyl-1,4-diphenyltetraline **9** ($R_f = 0.31$, m.p. 195–196°C); ^{1}H-NMR, δ: 2.26 (1H, s), 2.87 (1H, d, $J = 11.7$ Hz), 3.27 (1H, d, $J = 11.7$ Hz), 4.09 (5H, s, C_5H_5), 4.12 (1H, m, C_5H_4), 3.99 (1H, m, C_5H_4), 3.87 (1H, m, C_5H_4), 3.78 (1H, m, C_5H_4), 6.99–7.04, 7.16–7.21, 7.24–7.28, 7.36–7.59, 7.63–7.83 (14H, m); Anal. Calcd. for $C_{34}H_{26}FeO$, %: C, 80.64; H, 5.18; Fe, 11.03; Found: C, 80.78; H, 5.08; Fe, 10.83.

0.095 g (38%) of its *endo*-isomer **10** ($R_f = 0.28$, m.p. 204–205°C); ^{1}H-NMR, δ: 2.12 (1H, s), 2.85 (1H, d, $J = 11.7$ Hz), 3.35 (1H, d, $J = 11.7$ Hz), 4.13 (5H, s, C_5H_5), 4.48 (1H, m, C_5H_4), 4.13 (1H, m, C_5H_4), 3.86 (1H, m, C_5H_4), 2.46 (1H, m, C_5H_4), 6.87, 6.92, 7.02, 7.18, 7.36–7.59, 7.69–7.74 (14H, m); Anal. Calcd. for $C_{34}H_{26}FeO$, %: C, 80.64; H, 5.18; Fe, 11.03; Found: C, 80.54; H, 5.27; Fe, 11.21.

And 0.007 g (~3%) of adduct **13** ($R_f = 0.44$, m.p. 181–182°C); ^{1}H-NMR, d: 1.60 (3H, s), 1.75 (1H, dd, $J = 11.4$, 4.2 Hz), 2.88 (1H, dd, $J = 11.4$, 10.6 Hz), 4.14 (5H, s, C_5H_5), 4.13 (1H, d, $J = 1.8$ Hz, C_5H_2), 4.17 (1H, d, $J = 1.8$ Hz, C_5H_2), 3.72 (1H, td, $J = 11.4$, 4.2 Hz), 4.96 (1H, d, $J = 10.6$ Hz), 6.95–7.20, 7.40–7.85 (14H, m); Anal. Calcd. for $C_{34}H_{28}FeO$, %: C, 80.32; H, 5.55; Fe, 10.98; Found: C, 80.47; H, 5.38; Fe, 10.73.

3.4.2. B

The reaction was carried in 50 ml of toluene instead of benzene and the reaction time decreased to approximately 20 h. The following products were isolated: 0.025 g as a mixture of **3** and **15a**,**b** (**15a**:**15b**, ~1:1, $R_f = 0.76$) [8]; 0.02 g (8%) **11a**,**b** (~2:1, $R_f = 0.60$, m.p. 209–211°C); 0.062 g (25%) **9** ($R_f = 0.32$, m.p. 195–196°C), and 0.11 g (44%) **10** ($R_f = 0.28$, m.p. 204–205°C) and 0.008 g (~3.1%) **13** ($R_f = 0.45$, m.p. 180–182°C).

3.5. Reaction of cyclopropene **1b** with 1,3-diphenylisobenzofuran **3**

A similar procedure (see method B) applied to 1.14 g (0.5 mmol) of **1b** and 0.27 g (1 mmol) of **3** in 50 ml of toluene (10 h) gave:

0.16 g (57%) of *endo*-1,7-diphenyl-3,4-(3-*tert*-butylferroceno)-8,9-benzo-10-oxatricyclo [5.2.1.$0^{2,4}$]deca-3,8-diene **16a** ($R_f = 0.29$, m.p. 206–207°C); ^{1}H-NMR, δ: 0.96 (9H, s), 2.08 (1H, dd, $J = 15.1$, 3.4 Hz), 2.96 (1H, dd, $J = 15.1$, 9.0 Hz), 3.67 (1H, d, $J = 2.15$ Hz, C_5H_2), 3.98 (1H, d, $J = 2.15$ Hz, C_5H_2), 4.01 (5H, s, C_5H_5), 4.19 (1H, td, $J = 9.0$, 3.4 Hz), 4.37 (1H, d, $J = 9.0$ Hz), 6.75–6.98, 7.35–7.70 (14H, m); ^{13}C-NMR, δ: 138.73, 138.90, 144.74, 146.45 (C_{ipso}), 120.53, 120.72, 125.98, 126.27, 126.92, 126.98, 127.98, 128.08, 128.39, 128.41 (Ph), 69.97 (C_5H_5), 59.12, 66.79 (C_5H_2), 91.46, 91.55, 94.93 (C_{quat} F_c), 54.31, 56.48 (CH), 30.54 (CH_2), 30.65 (CH_3), 30.80, 91.40, 91.79 (C); Anal. Calcd. for $C_{37}H_{34}FeO$, %: C, 80.72; H, 6.22; Fe, 10.15; Found: C, 80.98; H, 6.15; Fe, 9.91.

And 0.051 g (18%) of its *exo*-isomer **16b** ($R_f = 0.37$, m.p. 228–229°C); ^{1}H-NMR, δ: 1.07 (9H, s), 2.25 (1H, dd, $J = 15.5$, 3.6 Hz), 2.76 (1H, dd, $J = 15.5$, 8.6 Hz), 3.43 (1H, d, $J = 1.8$ Hz, C_5H_2), 3.61 (1H, d, $J = 1.8$ Hz, C_5H_2), 3.94 (5H, s, C_5H_5), 3.85 (1H, td, $J = 8.6$, 3.6 Hz), 4.12 (1H, d, $J = 8.6$ Hz), 7.0–7.15, 7.20–7.70 (14H, m); Anal. Calcd. for $C_{37}H_{34}FeO$, %: C, 80.72; H, 6.22; Fe, 10.15; Found: C, 80.63; H, 6.41; Fe, 10.24.

3.5.1. Reaction of cyclopropene **1c** with 1,3-diphenylisobenzofuran **3**

Analogously, a similar procedure applied to 0.18 g (0.5 mmol) of **1c** and 0.27 g (1 mmol) of **3** in 50 ml of toluene (8 h) gave:

0.17 g (54%) of *endo*-**17a** ($R_f = 0.31$, m.p. 213–214°C); ^{1}H-NMR, δ: 1.48–1.70 (12H, m, Ad), 1.92 (3H, m, Ad), 2.08 (1H, dd, $J = 15.1$, 3.2 Hz), 2.95 (1H, dd, $J = 15.1$, 9.2 Hz), 3.67 (1H, d, $J = 2.4$ Hz, C_5H_2), 3.97 (1H, d, $J = 2.4$ Hz, C_5H_2), 4.03 (5H, s, C_5H_5), 4.22 (1H, td, $J = 9.2$, 3.3 Hz), 4.37 (1H, d, $J = 9.2$ Hz), 6.60–7.00, 7.40–7.80 (14H, m); ^{13}C-NMR, δ: 138.81, 139.11, 144.80, 147.12 (C_{ipso}), 120.65, 120.78, 125.93, 126.30, 126.98, 127.64, 128.10, 128.23, 128.54, 128.67 (Ph), 69.43 (C_5H_5), 66.75, 67.51 (C_5H_2), 92.13, 92.28, 95.08 (C_{quat} F_c), 54.72, 56.70, 28.55, 28.63 (CH), 30.63, 35.73, 36.05 (CH_2), 41.71, 91.58, 91.73 (C); Anal. Calcd. for $C_{43}H_{40}FeO$, %: C, 82.16; H, 6.41; Fe, 8.88; Found: C, 81.94; H, 6.68; Fe, 8.55;

Table 2
Crystal data, data collection and refinement parameters for **9**, **10** and **16a**

Data	**9**	**10**	**16a**
Empirical molecular formula	$FeC_{34}H_{26}O$	$FeC_{34}H_{26}O$	$FeC_{37}H_{34}O$
Formula weight	506.40	506. 40	550.49
Colour; habit	Yellow, prism	Yellow, prism	Orange, prism
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.609(6)	9.639(11)	10.300(2)
b (Å)	11.440(13)	11.140(7)	11.623 (2)
c (Å)	11.539(9)	12.054(6)	13.465 (3)
α (°)	73.60 (8)	80.23(5)	102.3 8(1)
β (°)	82.0 8(6)	87.27(8)	112. 36(1)
γ (°)	71. 80(7)	82.23(8)	98. 30(1)
V (Å^3)	1274. 3(2.0)	1263.5(2.0)	1409.8(6)
Z	2	2	2
D_{calc} (g cm^{-3})	1.320	1.33 1	1.297
$F(000)$	528	528	580
Absorption coefficient (mm^{-1})	0.614	0.618	0.563
Radiation, λ (Å)	Mo K_α, 0.71069	Mo K_α, 0.71069	Mo K_α, 0.71073
Monochromator	Graphite	Graphite	Highly oriented graphite crystal
Temperature, K	293	293	298
2Θ range (°)	$2<2\Theta<60$	$2<2\Theta<54$	$3<2\Theta<56$
Scan type	ω	ω	Θ/2Θ
Total reflections	6834	5446	7841
Unique reflections	6521	5193	6733
Reflections with $I>2\sigma(I)$	4627	4458	4530
R_{int}	0.012	0.016	0.035
Solution	SHELX-86	SHELX-86	SHELX-97
Refinement method	Full-matrix least-squares on F^2		
Number of parameters refined	430	431	389
Hydrogen atoms	Riding	Riding	Riding
R (obs. data)	0.045	0.039	0.0582
Weighting scheme	$w^{-1}=\sigma^2(F)+0.001832F^2$	$w^{-1}=\sigma^2(F)+0.003679F^2$	$w^{-1}=\sigma^2(F)+0.0008F^2$
Goodness-of-fit	1.19	0.93	1.077
Min/max residual electron density, eÅ^{-3}	−0.473/0.760	−0.403 /0.307	−0.667/0.415

And 0.057 g (18%) of its *exo*-isomer **17b** ($R_f=0.40$, m.p. 245–247°C); ^{1}H-NMR, δ: 1.38–1.73 (12H, m, Ad), 2.01 (3H, m, Ad), 2.18 (1H, dd, $J=15.2$, 3.3 Hz), 2.68 (1H, dd, $J=15.2$, 9.0 Hz), 3.38 (1H, d, $J=2.1$ Hz, C_5H_2), 3.65 (1H, d, $J=2.1$ Hz, C_5H_2), 3.96 (5H, s, C_5H_5), 3.87 (1H, td, $J=9.0$, 3.3 Hz), 4.25 (1H, d, $J=9.0$ Hz), 6.98–7.80 (14H, m); Anal. Calcd. for $C_{43}H_{40}FeO$, %: C, 82.16; H, 6.41; Fe, 8.88; Found: C, 82.35; H, 6.37; Fe, 8.92.

3.5.2. Reaction of cyclopropene **1a** and **1b** with diphenylacetylene

Analogously, a similar procedure applied to 0.12 g (0.5 mmol) of **1a** and to 0.18 g (1 mmol) of diphenylacetylene gave 0.064 g (30%) of 1,2-diphenyl-5-ferrocenyl-5-methylcyclopentadiene **21a** ($R_f=0.42$, m.p. 164–165.5°C); ^{1}H-NMR, δ: 1.97 (3H, s), 3.61 (1H, m, C_5H_4), 4.01 (1H, m, C_5H_4), 4.12 (1H, m, C_5H_4), 4.14 (1H, m, C_5H_4), 4.10 (5H, s, C_5H_5), 6.70 (1H, d, $J=5.6$ Hz), 6.77 (1H, d, $J=5.6$ Hz), 6.90 (2H, m, Ph), 7.16 (8H, m, Ph); Anal. Calcd. for $C_{28}H_{24}Fe$, %: C, 80.78; H, 5.81; Fe, 13.41; Found: C, 80.53; H, 5.97; Fe, 13.23.

0.14 g (0.5 mmol) of **1b** and 0.18 g (1 mmol) of diphenylacetylene gave 0.07 g (30%) of 5-*tert*-butyl-1,2-diphenyl-5-ferrocenylcyclopentadiene **21b** ($R_f=0.44$, m.p. 186–187°C); ^{1}H-NMR, δ: 0.86 (9H, s), 3.60 (1H, m, C_5H_4), 4.02 (1H, m, C_5H_4), 4.05 (1H, m, C_5H_4), 4.15 (1H, m, C_5H_4), 4.11 (5H, s, C_5H_5), 6.69 (1H, d, $J=5.4$ Hz), 6.79 (1H, d, $J=5.4$ Hz), 6.84 (2H, m, Ph), 7.10–7.20 (8H, m, Ph); Anal. Calcd. for $C_{31}H_{30}Fe$, %: C, 81.22; H, 6.60; Fe, 12.18; Found: C, 81.38; H, 6.46; Fe, 12.40.

3.5.3. Crystal structure investigation

The data were collected on an Enraf–Nonius CAD4 diffractometer (compounds **9** and **10**) and on a Siemens P4/PC diffractometer (compound **16a**). Crystal data, data collection and refinement parameters are listed in Table 2.

3.5.4. Synthesis of deuterated compounds

The deuterated compounds were synthesized following known methods [1,5,15,20]. Their ^{1}H-NMR spectral

Table 3
FAB^+ mass spectral data for compounds **1-D**, **7-D**, **8-D**(**E-**, **Z-**), **9-D**, **10-D**, **11-Da**,**b**, **13-D** and **14-D**

Compound	Formula	FW	*m*/*z*
1-D	$C_{14}H_{11}D_3Fe$	240.87	241
7-D	$C_{14}H_{11}Br_2D_3Fe$	400.88	399
8-D (**E-**, **Z-**)	$C_{14}H_{12}BrD_3Fe$	321.99	321
9-D	$C_{34}H_{24}D_2FeO$	508.28	508
10-D	$C_{34}H_{24}D_3FeO$	508.28	508
11-D a,**b**	$C_{34}H_{25}D_3FeO$	511.40	511
13-D	$C_{34}H_{25}D_3FeO$	511.40	511
14-D	$C_{13}H_{11}D_3Fe$	229.07	229

data are listed in Table 1. FAB^+-mass spectral data (positive mode) are listed in Table 3.

Acknowledgements

Financial support from CONACyT (Mexico) is gratefully acknowledged.

References

[1] V.N. Postnov, E.I. Klimova, N.N. Meleshonkova, I.G. Bolesov, Dokl. Akad. Nauk 339 (1994) 362.
[2] V.N. Postnov, E.I. Klimova, N.N. Meleshonkova, I.G. Bolesov, Dokl. Akad. Nauk 339 (1994) 496.
[3] E.I. Klimova, N.N. Meleshonkova, V.N. Postnov, T.C. Alvarez, L.J. Gomez, G.M. Martinez, Dokl. Akad. Nauk 344 (1995) 639.
[4] E.I. Klimova, T.C. Alvarez, G.M. Martinez, L.J. Gomez, N.N. Meleshonkova, I.G. Bolesov, Izv. Akad. Nauk Ser. Khim. (1996) 652 (Russ. Chem. Bull. 45 (1996) 613 (English Translation).
[5] E.I. Klimova, N.N. Meleshonkova, V.N. Postnov, T.C. Alvarez, L.J. Gomez, G.M. Martinez, Dokl. Akad. Nauk 344 (1995) 498.
[6] V.V. Plemenkov, Kh.Z. Giniyatov, Ya.Ya. Villem, N.V. Villem, L.S Surmina, I.G. Bolesov, Dokl. Akad. Nauk SSSR. 254 (1980) 895.
[7] W. Welter, A. Hartmann, M. Regitz, Chem. Ber. 111 (1978) 3068.
[8] J.G. Smith, R.B. McCall, J. Org. Chem. 45 (1980) 3982.
[9] A.J. Fry, P.S. Jain, R.L. Krieger, I. Agranat, E. Aharon-Shalom, J. Organomet. Chem. 214 (1981) 381.
[10] A.J. Fry, R.L. Krieger, I. Agranat, E. Aharon-Shalom, Tetrahedron Lett. 32 (1976) 4803.
[11] I. Agranat, E. Aharon-Shalom, R.L. Krieger, W.O. Krug, Tetrahedron 35 (1979) 733.
[12] J.A. Connor, J.P. Leloyd, J. Chem. Soc. Perkin I (1973) 17.
[13] A.N. Nesmeyanov, B.A. Surkov, V.A. Sazonova, V.M. Kramarov, Dokl. Akad. Nauk SSSR 215 (1974) 1128.
[14] E.I. Klimova, A.N. Pushin, V.A. Sazonova, J. Organomet. Chem. 270 (1984) 319.
[15] E.G. Perevalova, E.I. Klimova, V.V. Kruchkova, A.N. Pushin, Zh. Obsch. Khim. 59 (1989) 873.
[16] A.N. Pushin, E.I. Klimova, V.A. Sazonova, Zh. Obsch. Khim. 57 (1987) 1102.
[17] E.G. Perevalova, Yu.T. Struchkov, E.I. Klimova, A.N. Pushin, Yu.L. Slovokhotov, Metalloorg. Khim. 2 (1989) 1405.
[18] N.V. Bovin, L.S. Surmina, N.I. Yakushkina, I.G. Bolesov, Zh. Org. Khim. 3 (1977) 1188.
[19] W.M. Horspool, R.G. Sutherland, B.J. Thomson, J. Chem. Soc. C. (1971) 1550.
[20] G. Wittig, U. Schoellkopf, Org. Syn. 40 (1960) 66.
[21] T.S. Abram, W. Watts, J. Chem. Soc. Perkin Trans. I (1975) 116.
[22] T.D. Turbitt, W.E. Watts, Chem. Communs. (1972) 951.
[23] T.D. Turbitt, W.E. Watts, J. Chem. Soc. Perkin Trans. II (1974) 189.
[24] E.I. Klimova, A.N. Pushin, V.A. Sazonova, J. Organomet. Chem. 270 (1984) 319.