Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Organometallic Chemistry 691 (2006) 507–513
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

3-Ferrocenyl-1-methyl- and 1-ferrocenyl-3-methylcyclopropenes

Elena I. Klimova [a], Tatiana Klimova [a,*], Leon V. Bakinovsky [b], Marcos Martínez García [c]

[a] Universidad Nacional Autónoma de México, Facultad de Química, Cd. Universitaria, Coyoacán, C.P. 04510 México, D.F., México
[b] N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation
[c] Universidad Nacional Autónoma de México, Instituto de Química, Cd. Universitaria, Coyoacán, C.P. 04510 México, D.F., México

Received 9 September 2005; accepted 12 September 2005
Available online 17 October 2005

Abstract

Dehydrobromination of isomeric 3-bromo-1-ferrocenyl-2-methylcyclopropanes afforded 3-ferrocenyl-1-methyl- and 1-ferrocenyl-3-methylcyclopropenes. These undergo smooth opening of the three-membered ring to give 1- and 2-ferrocenylbuta-1,3-dienes and 1- and 2-methyl-1*H*-cyclopentaferrocenes; with 1,3-diphenylisobenzofuran they give the classical Diels–Alder adducts.

Keywords: Cyclopropene; Cyclopropane; Intramolecular transformations; Opening of the three-membered ring; Ferrocene

1. Introduction

3-Aryl- and 3-alkyl-3-ferrocenylcyclopropenes have been the subject of studies in recent years [1–8]. Characteristic features of intramolecular transformations of 3, 3-disubstituted cyclopropenes have been established experimentally, they were shown to depend on mutual influence of the ferrocenyl and cyclopropene fragments. The geometry of the small ring, viz., the C=C and C–C bond lengths and the values of the bond angles at C(1), C(2), and C(3), as well as spatial orientation of the substituents at position 3 were established by X-ray diffraction analysis. The ferrocenyl substituent always occupied the 'bisector' position relative to the plane of the three-membered ring, other substituents being in 'non-bisector' positions.

In 3-aryl-3-ferrocenylcyclopropenes [1,2,4,5] with these conformations **1a**,**b**, the MO of the ethylene and arene fragments interact through space as in the case of 3-alkyl-3-phenylcyclopropenes [9], which seems to determine stereoselectivities of the intramolecular transformations of 3-arylcyclopropenes (Scheme 1).

Thus, the small ring in the cyclopropenes **1a**,**b** undergoes smooth opening on heating with the formation of carbenoid intermediates **2a**,**b** [1–3], which then recyclize with involvement of only the aryl fragment, the ferrocenyl substituent remaining unaffected (see Scheme 1).

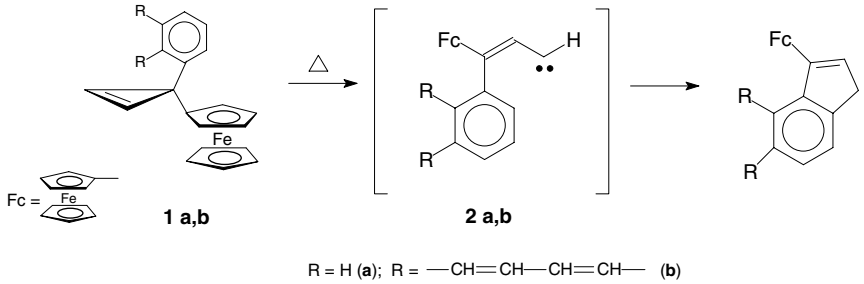
Unlike 3-arylcyclopropenes **1a**,**b**, ring-opening of the small ring in 3-alkyl analogs **3a**,**b** [3,6–8] results in predominant formation of ferrocenyl-substituted 1,3-dienes (**4a**–**c**) and 3-alkyl-1*H*-cyclopentaferrocenes (**5a**–**c**) as the minor products (Scheme 2).

Little information concerning the chemistry of ferrocenylcyclopropenes with ferrocenyl group as the only substituent in positions 1 or 3 of the small ring is available. To date, only the preparation of 1-ferrocenylcyclopropene (**6**) in an attempt at synthesizing 3-ferrocenylcyclopropene is described [10] together with some of its chemical properties (cycloaddition and protonation reactions) (Scheme 3).

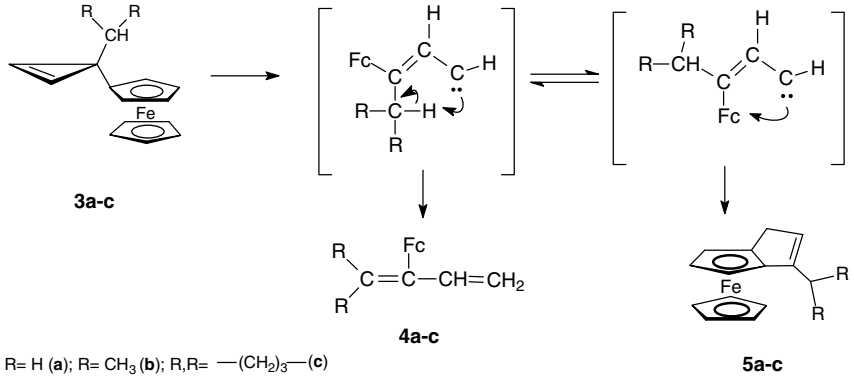
The effect of the ferrocenyl substituents in small rings is rather well pronounced and their influence is often highly selective, therefore, it was of interest to reveal features of the electronic interaction of the ferrocenyl group with the small ring, which is attractive from both the theoretical point of view and in connection with a search for selective reactions of cyclopropenes and cyclopropanes.

* Corresponding author. Tel./fax: +52 55 56225371.
E-mail address: klimova@servidor.unam.mx (T. Klimova).

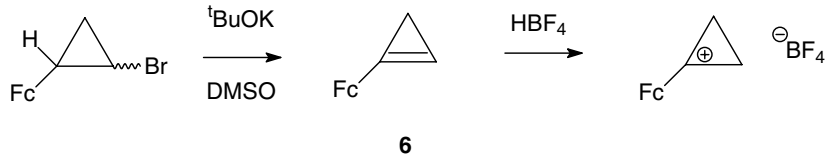
0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.09.016



Scheme 1.



Scheme 2.

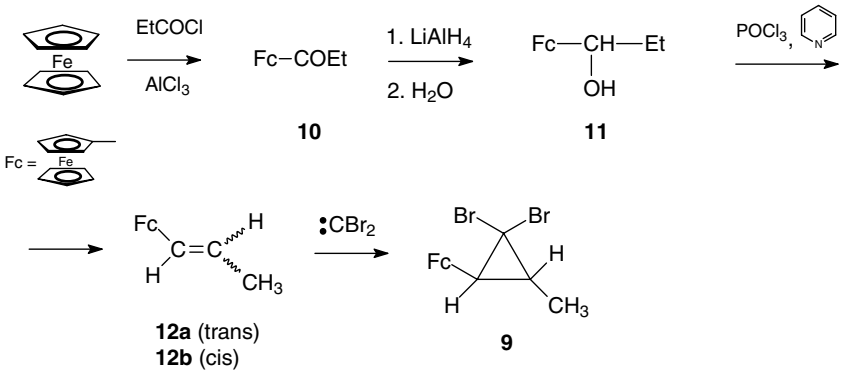


Scheme 3.

2. Results and discussion

In continuation of our studies in the area of ferrocenylcyclopropanes, we synthesized 3-ferrocenyl-1-methyl- and 1-ferrocenyl-3-methylcyclopropenes (**7** and **8**, respectively) and studied some of their chemical properties. *trans*-1,1-Dibromo-2-ferrocenyl-3-methylcyclopropane (**9**) served as the starting material for the preparation of compounds **7** and **8**. This was synthesized in Scheme 4.

Acylation of ferrocene (→**10**), reduction to (1-hydroxypropyl)ferrocene (**11**), and dehydration (→ **12**) occurred smoothly in 65–75% yields. According to ^{1}H NMR spectroscopic data, 1-ferrocenylpropene (**12**) was obtained as a ca. 3:1 mixture of *trans*- and *cis*-isomers.



Scheme 4.

Dibromocyclopropanation of the alkene **12** occurred stereoselectively: dibromocyclopropane (**9**) was isolated as a single *trans* isomer ($J_{H(2),H(3)} = 8.1$ Hz [11,12]), in 75% yield. This compound represents orange powder; it decomposes on heating but can be stored unchanged in a sealed tube at 20 °C.

The dibromide **9** was reduced with a mixture of EtMgCl and $Ti(O^iPr)_4$ as described [13] to give 1-bromo-2-ferrocenyl-3-methylcyclopropane (**13**) as a ca. 1:1 mixture of two isomers (**13a** and **13b**) in rather low total yield (34%) (Scheme 5). In addition, *trans*-1-ferrocenyl-2-methylcyclopropane (**14**) and three-membered ring-opening products, viz., 1-ferrocenylbuta-1,3-diene (**15**) and 1-methyl-1*H*-cyclopentaferrocene (**16**) were also isolated from the reaction mixture (Scheme 5).

Variation of the reduction conditions did not result in increase in the yields of the monobromides (**13a**,**b**). Despite the formation of a mixture of the reaction products, all of them were isolated in individual form by TLC on Al_2O_3. Their structures were unequivocally established based on ^1H and ^{13}C NMR spectroscopic data. The assignment of (Fc, Br-*Z*)- and (Fc, Br-*E*)-configurations to the isomeric monobromides, **13a** and **13b**, has been made based on the ^1H NMR spectroscopic data with account of the previously established NMR criteria for the determination of *Z* and *E* configurations of bromo- (ferrocenyl)cyclopropanes [1–7]. The ^1H NMR spectra of these compounds contain each two multiplets (δ 1.09 and 1.16) for the methine protons of the CH–CH_3 fragments and two doublets of doublets (δ 1.62 and 1.48) for the methine protons of the CH–Fc fragments as AB-parts of ABM spin systems with $|\Delta\delta| = \delta_A - \delta_B = 0.53$ and 0.32 ppm. The value $|\Delta\delta| =$ 0.53 ppm is characteristic of (*Z*)-position of the ferrocenyl and bromo sub- stituents, while $|\Delta\delta| = 0.32$ ppm is characteristic of (*E*)-position.

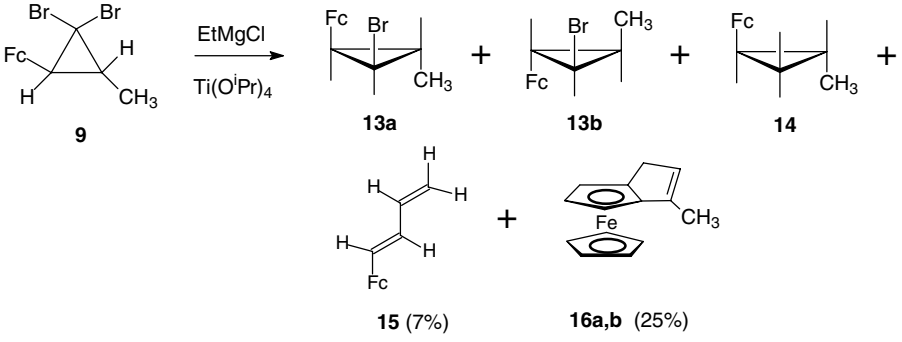
1-Methyl-1*H*-cyclopentaferrocene (**16**) was isolated as two diastereomers (**16a** and **16b**, ca. 2:1), which could not be separated by chromatography. However, their identification based on spectroscopic data did not present any problems (see Section 4). The formation of compounds **15**, **16a**, and **16b** resulted apparently upon opening of the three-membered rings in monobromides **13a** and **13b** into allylic cation (**18**) (Scheme 6).

Deprotonation of the cation **18** affords 1-ferrocenylbuta-1,3-diene (**15**) and intramolecular alkylation of the ferrocene unit results in compounds **16a**,**b**.

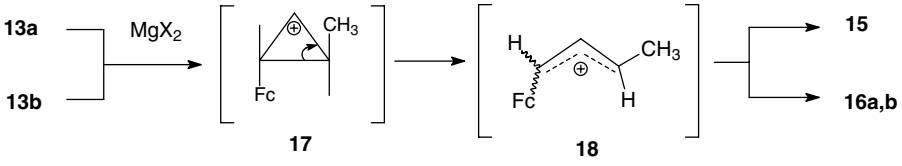
Dehydrobromination of the monobromides **13a** and **13b** with Bu^tOK in DMSO [1–7] gave rise to 3-ferrocenyl-1-methyl- and 1-ferrocenyl-3-methylcyclopropenes (**7** and **8**) in yields of 15–20%. In addition, 1-ferrocenylbuta-1,3-diene (**15**), 2-ferrocenylbuta-1,3-diene (**19**), 1-methyl-1*H*-cyclopentaferrocene (**16a**,**b**), and 2-methyl-1*H*-cyclopentaferrocene (**20**) were obtained (Scheme 7).

All reaction products were separated by TLC on Al_2O_3 and characterized by ^1H and ^{13}C NMR spectroscopic data, which confirm their structures, and data from elemental analyses.

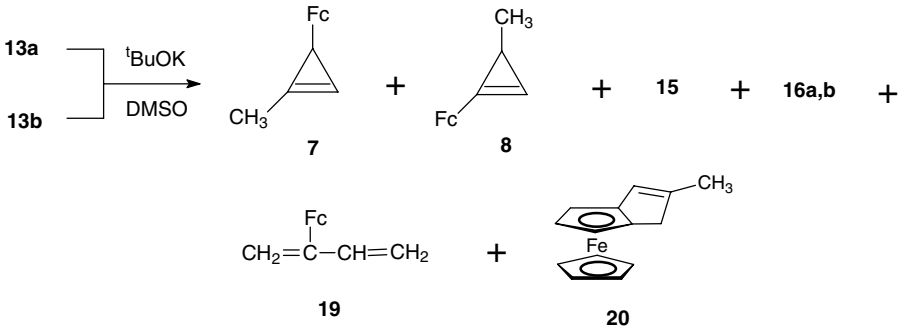
Ferrocenyl(methyl)cyclopropenes (**7**) and (**8**) represent orange oils that are unstable in solutions and on storage. In $CHCl_3$, Me_2CO, and CH_2Cl_2, they undergo rapid intramolecular transformations to give compounds **15**, **16a**,**b**, **19**, and **20**. Tentative mechanisms of the transformations of ferrocenyl(methyl)cyclopropenes (**7**) and (**8**) are depicted in Scheme 8.



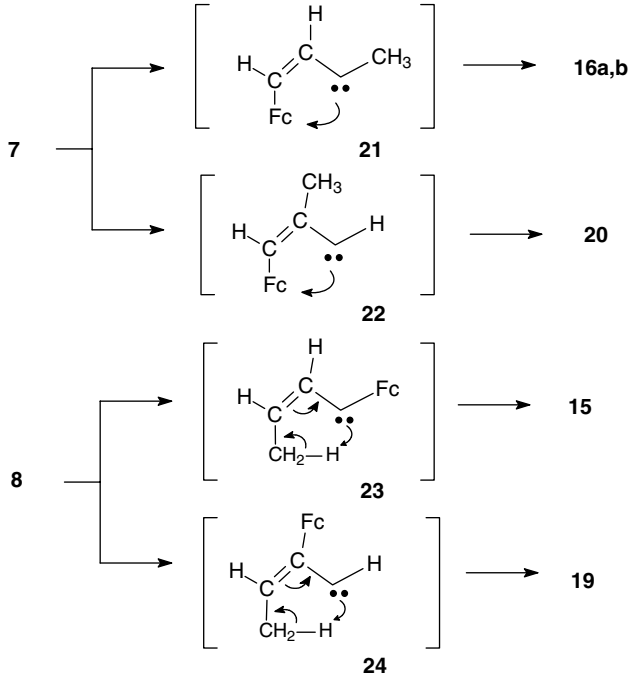
Scheme 5.



Scheme 6.



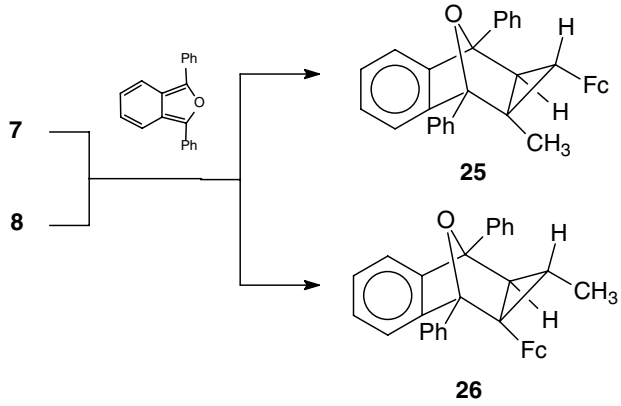
Scheme 7.



Scheme 8.

Opening of the small ring in ferrocenyl(methyl)cyclopropene (**7**) gives rise in carbenoid intermediates **21** and **22**, which produce isomeric methyl-1*H*-cyclopentaferrocenes **16a**,**b** and **20** as a result of intramolecular alkylation of ferrocene. The carbenoids **23** and **24** formed from ferrocenyl(methyl)cyclopropene (**8**) are transformed into ferrocenylbuta-1,3-dienes (**15**) and (**19**).

Ferrocenyl(methyl)cyclopropenes (**7**) and (**8**) react stereospecifically with 1,3-diphenylisobenzofuran to give classical [4 + 2]-cycloadducts **25** and **26**, respectively, isolated as single diastereomeric forms. By analogy with previously described adducts of ferrocenylcyclopropenes [1–7,10], compounds **25** and **26** have structures of *exo*-3-ferrocenyl-2-methyl- and *exo*-2-ferrocenyl-3-methyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-enes, respectively, with *anti*-arranged ferrocenyl and methyl fragments (Scheme 9).

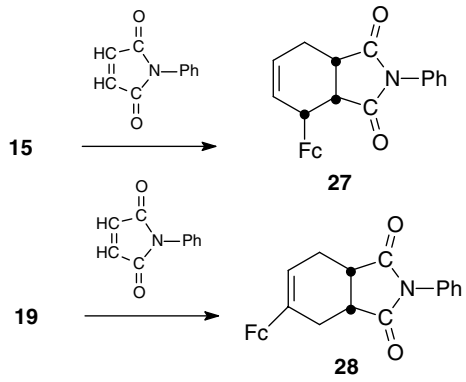


Scheme 9.

Data from ^{1}H and ^{13}C NMR spectra and elemental analyses corroborate structures of these compounds.

Ferrocenylbuta-1,3-dienes (**15**) and (**19**) were characterized as the Diels–Alder adducts with *N*-phenylmaleimide, viz., compounds **27** and **28** (Scheme 10).

The cycloaddition occurs stereospecifically, the adducts are formed as single *endo* isomers. The assignment to the *endo*-series was made on the basis of the known [14,15] NMR criterion, viz., the high-field positions of the signals for two protons of the substituted cyclopentadienyl rings and one proton of the phenyl substituent relative to the singlets of the protons of the C_5H_5 groups and multiplets



Scheme 10.

of four protons of the phenyl substituents, which is typical of *endo* isomers.

3. Conclusion

The results obtained in the present study make it possible to conclude that 3- and 1-ferrocenylcyclopropenes are much less stable than 3-alkyl- and 3-aryl-3-ferrocenylcyclopropenes. They undergo smooth and rapid opening of the three-membered rings at 20 °C to give intramolecular transformation products. They also give easily the [4 + 2]-cycloadducts with 1,3-diphenylisobenzofuran. The observed ease of intramolecular transformations is not typical of alkyl- and aryl-substituted analogs, which seems to be related to peculiarities of reciprocal influence of the ferrocene and cyclopropene fragments.

4. Experimental

All the solvents were dried according to the standard procedures and were freshly distilled before use. Column chromatography was carried out on alumina (Brockmann activity III). The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ with Me_4Si as the internal standard. The mass spectra were obtained on JEOL SX-102 A instrument (EI MS, 70 eV). An Elemental Analysis System GmbH was used for elemental analyses.

The following reagents were purchased from Aldrich: ferrocene, 98%; propionyl chloride, 98%; ethylmagnesium chloride (2.0 M solution in diethyl ether); titanium(IV) isopropoxide 99.999%; phosphorus oxychloride, 99%; *N*-phenylmaleimide, 97%; 1,3-diphenylisobenzofuran, 97%; bromoform, 96%; potassium *tert*-butoxide, 95%.

Propionylferrocene (**10**) was prepared by Friedel–Crafts acylation of ferrocene with propionyl chloride in the presence of $AlCl_3$ as described in [16], the yield was 86%, orange oil. 1-(Hydroxypropyl)ferrocene (**11**) was obtained by reduction of the ketone **10** with lithium aluminum hydride in dry ether in an atmosphere of argon [17], the yield was 80%, orange oil.

4.1. trans/cis-1-Ferrocenylpropene (*12a,b*)

Dehydration of the alcohol **11** with $POCl_3$ in pyridine [18] afforded the alkene **12** (**12a**:**12b** ~ 3:1) isolated by column chromatography on alumina (hexane as the eluent) in 70% yield, orange crystals, m.p. 39–40 °C (lit. [19]: m.p. 39–40 °C).

4.2. trans-1,1-Dibromo-2-ferrocenyl-3-methylcyclopropane (*9*)

gem-Dibromocyclopropane (**9**) was obtained from the alkenes **12a**,**b** according to a standard procedure [3,4]. It was isolated by column chromatography on alumina (hexane as the eluent) in 68%, orange powder, m.p. 74–75 °C. MS *m*/*z*(%): 398 (100). ^{1}H NMR: δ 1.44 (3H, d, CH_3, $J = 6.3$ Hz), 1.58 (1H, m, CH_3, $J = 6.3$, 8.1 Hz), 2.18 (1H, d, CH, $J = 8.1$ Hz), 4.17 (5H, s, C_5H_5), 4.05 (1H, m, C_5H_4), 4.15 (1H, m, C_5H_4), 4.20 (1H, m, C_5H_4), 4.36 (1H, m, C_5H_4). ^{13}C NMR: δ 17.43 (CH_3); 31.71, 38.95 (2CH), 40.71 (C), 67.57, 67.99, 68.64, 69.58 (C_5H_4); 68.79 (C_5H_5); 83.87 (C_{ipso}Fc). Anal. Calc. for $C_{14}H_{14}Br_2Fe$: C, 42.25; H, 3.55; Br, 40.16; Fe, 14.04. Found: C, 42.48; H, 3.27; Br, 40.23; Fe, 13.81%.

4.3. Reduction of the dibromide *9* with ethylmagnesium chloride in the presence of titanium isopropoxide

Dibromo(ferrocenyl)methylcyclopropane (**9**) (1 mmol) was added to a solution of EtMgCl (1.2 mmol) in dry ether followed by several drops of titanium isopropoxide. The mixture was stirred in an inert atmosphere for 3 h at room temperature and quenched by addition of water (100 ml) and benzene (100 ml). The organic layer was separated, washed with water (2 × 20 ml) and benzene was evaporated in vacuo. The residue was chromatographed on alumina (hexane as the eluent) to give compounds **13a**,**b**, **14**, **15**, and **16a**,**b**.

trans-1-Ferrocenyl-2-methylcyclopropane (**14**), yield 0.025 g (10%), yellow oil. MS *m*/*z* (%): 240 (100). ^{1}H NMR: δ 0.57 (1H, m, CH_2, $J = 1.2$, 5.4, 7.8 Hz), 0.64 (1H, m, CH_2, $J = 1.1$, 5.4, 8.0 Hz), 0.85 (1H, m, CH, $J = 5.4$, 7.2, 8.0 Hz), 1.11 (3H, d, CH_3, $J = 6.0$ Hz), 1.21 (1H, m, CH), 4.12 (5H, s, C_5H_5), 3.98 (3H, m, C_5H_4), 4.10 (1H, m, C_5H_4). Anal. Calc. for $C_{14}H_{16}Fe$: C, 70.02; H, 6.72; Fe, 23.26. Found: C, 69.89; H, 6.85; Fe, 23.31%.

(Fc, Br-*Z*)-1-Bromo-2-ferrocenyl-3-methylcyclopropane (**13a**), yield 0.055 g (17%), yellow oil. MS *m*/*z* (%): 319 (100). ^{1}H NMR: δ 1.09 (1H, m, MeCH, $J = 6.3$, 7.5 Hz), 1.31 (3H, d, CH_3, $J = 6.3$ Hz), 1.62 (1H, m, CH, $J = 3.9$, 6.3 Hz), 3.25 (1H, dd, CH, $J = 3.9$, 7.5 Hz), 4.17 (5H, s, C_5H_5), 3.97 (1H, m, C_5H_4), 4.01 (1H, m, C_5H_4), 4.05 (2H, m, C_5H_4). ^{13}C NMR: δ 15.35 (CH_3); 22.41, 28.69, 31.27 (3CH), 40.71 (C), 65.58, 66.34, 66.82, 68.96 (C_5H_4); 68.09 (C_5H_5); 88.07 (C_{ipso}Fc). Anal. Calc. for $C_{14}H_{15}BrFe$: C, 52.71; H, 4.78; Br, 25.00; Fe, 17.51. Found: C, 52.84; H, 4.93; Br, 24.82; Fe, 17.71%.

(Fc, Br-*E*)-1-Bromo-2-ferrocenyl-3-methylcyclopropane (**13b**), yield 0.052 g (16%), yellow oil. MS *m*/*z* (%): 320 (100). ^{1}H NMR: δ 1.16 (1H, m, CH), 1.25 (3H, d, CH_3, $J = 6.9$ Hz), 1.48 (1H, m, CH), 3.05 (1H, dd, CH, $J = 4.2$, 8.1 Hz), 4.11 (5H, s, C_5H_5), 4.00 (2H, m, C_5H_4), 4.24 (2H, m, C_5H_4). ^{13}C NMR: δ 16.23 (CH_3); 24.05, 27.64, 33.12 (3CH), 42.16 (C), 67.04, 67.32, 67.45, 68.56 (C_5H_4); 68.23 (C_5H_5); 87.19 (C_{ipso}Fc). Anal. Calc. for $C_{14}H_{15}BrFe$: C, 52.71; H, 4.78; Br, 25.00; Fe, 17.51. Found: C, 52.56; H, 4.59; Br, 25.11; Fe, 17.32%.

1-Ferrocenyl-1,3-butadiene (**15**), Yield 0.017 g (7%), yellow oil. MS *m*/*z* (%): 238 (100). ^{1}H NMR: δ 4.10 (5H, s, C_5H_5), 4.18 (2H, m, C_5H_4), 4.27 (2H, m, C_5H_4), 5.03 (1H, dd, CH_2=, $J = 1.5$, 10.5 Hz), 5.15 (1H, dt, CH_2=, $J = 1.5$, 10.5 Hz), 6.15 (1H, d, CH=, $J = 17.4$ Hz), 6.40

(1H, dd, CH=, $J = 7.8$, 17.4 Hz), 7.00 (1H, m, CH=). Anal. Calc. for $C_{14}H_{14}Fe$: C, 70.62; H, 5.92; Fe, 23.46. Found: C, 70.47; H, 6.07; Fe, 23.29%.

1-Methyl-1H-cyclopentaferrocene (**16a**,**b**) (~2:1), yield 0.10 g (40%), orange crystals, m.p. 89–91 °C. MS *m*/*z* (%): 238 (100). Anal. Calc. for $C_{14}H_{14}Fe$: C, 70.62; H, 5.92; Fe, 23.46. Found: C, 70.81; H, 5.87; Fe, 23.58%.

Compound **16a**, ^{1}H NMR: δ 1.32 (3H, d, CH_3, $J = 6.3$ Hz), 4.09 (5H, s, C_5H_5), 4.20 (2H, m, C_5H_3), 4.32 (1H, m, C_5H_3), 4.37 (1H, q, CH, $J = 6.3$ Hz), 5.86 (1H, dd, CH=, $J = 6.3$, 15.9 Hz), 6.29 (1H, d, CH=, $J = 15.9$ Hz). ^{13}C NMR: δ 23.50 (CH_3); 66.72 (CH), 67.00, 68.62, 68.68 (C_5H_3); 69.14 (C_5H_5); 82.47, 82.54 ($2C_{ipso}$Fc).

Compound **16b**, ^{1}H NMR: δ 1.56 (3H, d, CH_3, $J = 4.8$ Hz), 4.11 (5H, s, C_5H_5), 4.24 (2H, m, C_5H_3), 4.36 (1H, m, C_5H_3), 4.41 (1H, qd, CH, $J = 4.8$, 6.1 Hz), 5.80 (1H, dd, CH=, $J = 6.1$, 15.0 Hz), 6.31 (1H, d, CH=, $J = 15.0$ Hz). ^{13}C NMR: δ 23.62 (CH_3); 66.57 (CH), 67.15, 68.35, 68.74 (C_5H_3); 69.18 (C_5H_5); 82.44, 82.58 ($2C_{ipso}$Fc).

*4.4. Dehydrobromination of bromo(ferrocenyl)-methylcyclopropanes (**13a**) and (**13b**)*

A mixture of monobromide **13a** (or **13b**) (1 mmol) and Bu^{t}OK (1.5 mmol) in DMSO (20 ml) was stirred for 4 h at 20 °C. The reaction mixture was then partitioned between benzene (50 ml) and water (50 ml), the organic layer was washed with water and concentrated in vacuo. Chromatography of the residue on alumina (hexane as the eluent) afforded compounds **7**, **8**, **15**, **16a**,**b**, **19**, and **20**.

3-Ferrocenyl-1-methylcyclopropene (**7**), yield 0.05 g (20%), yellow oil. MS *m*/*z* (%): 238 (100). ^{1}H NMR: δ 1.81 (1H, d, CH, $J = 1.8$ Hz), 1.91 (3H, s, CH_3), 4.12 (5H, s, C_5H_5), 4.05 (2H, m, C_5H_4), 4.02 (2H, m, C_5H_4), 6.83 (1H, d, CH=, $J = 1.8$ Hz). Anal. Calc. for $C_{14}H_{14}Fe$: C, 70.62; H, 5.92; Fe, 23.46. Found: C, 70.74; H, 5.87; Fe, 23.63%.

1-Ferrocenyl-3-methylcyclopropene (**8**), yield 0.06 g (25%), yellow oil. MS *m*/*z* (%): 238(100). ^{1}H NMR: δ 1.20 (3H, d, CH_3, $J = 6.3$ Hz), 1.86 (1H, qd, CH, $J = 1.5$, 6.3 Hz), 4.08 (5H, s, C_5H_5), 4.10 (2H, m, C_5H_4), 4.12 (2H, m, C_5H_4), 7.02 (1H, d, CH=, $J = 1.5$ Hz). Anal. Calc. for $C_{14}H_{14}Fe$: C, 70.62; H, 5.92; Fe, 23.46. Found: C, 70.51; H, 5.97; Fe, 23.31%.

Compounds **16a**,**b** (~1:1), yield 0.03 g (12.5%), orange crystals, m.p. 90–91 °C. MS *m*/*z* (%): 238 (100).

2-Ferrocenyl-1,3-butadiene (**19**), yield 0.024 g (10%), yellow oil. MS *m*/*z* (%): 238 (100). ^{1}H NMR: δ 4.14 (5H, s, C_5H_5), 4.22 (2H, m, C_5H_4), 4.37 (2H, m, C_5H_4), 5.09 (1H, s, CH_2=), 5.17 (1H, s, CH_2=), 5.57 (1H, dd, CH_2=, $J = 2.1$, 10.2 Hz), 5.46 (1H, dd, CH_2=, $J = 4.8$, 10.2 Hz), 6.37 (1H, dd, CH=, $J = 2.1$, 4.8 Hz). Anal. Calc. for $C_{14}H_{14}Fe$: C, 70.62; H, 5.92; Fe, 23.46. Found: C, 70.79; H, 5.78; Fe, 23.58%.

2-Methyl-1H-cyclopentaferrocene (**20**), yield 0.025 g (10%), orange crystals, m.p. 95–96 °C. MS *m*/*z* (%): 238 (100). 1.82 (3H, d, CH_3, $J = 0.9$ Hz), 2.36 (2H, s, CH_2), 4.12 (5H, s, C_5H_5), 4.19 (2H, m, C_5H_3), 4.32 (1H, m, C_5H_3), 7.11 (1H, d, CH=, $J = 0.9$ Hz). Anal. Calc. for $C_{14}H_{14}Fe$: C, 70.62; H, 5.92; Fe, 23.46. Found: C, 70.73; H, 6.11; Fe, 23.60%.

4.5. Reaction of cyclopropenes 7 and 8 with 1,3-diphenylisobenzofuran

A mixture of compound **7** (or **8**) (1 mmol) and 1,3-diphenylisobenzofuran (1.5 mmol) was stirred for 10 h at 20 °C in an inert atmosphere. The solvent was distilled off *in vacuo*. Chromatography of the residue on alumina (hexane – ether, 3:1, as the eluent) afforded compound **25** (or **26**).

Adduct **25**, yield of 0.37 g (72%), yellow crystals, m.p. 192–193 °C. MS *m*/*z* (%): 508 (100). ^{1}H NMR: δ 2.04 (3H, s, CH_3), 2.28 (1H, d, CH, $J = 5.7$ Hz), 2.45 (1H, d, CH, $J = 5.7$ Hz), 4.09 (5H, s, C_5H_5), 3.96 (1H, m, C_5H_4), 4.02 (1H, m, C_5H_4), 4.06 (1H, m, C_5H_4), 4.16 (1H, m, C_5H_4), 7.32–7.67 (14H, m, Ar). ^{13}C NMR: δ 21.18 (CH_3); 27.34, 43.90 (2CH), 35.06 (C), 65.85, 66.43, 68.52, 70.24 (C_5H_4); 68.56 (C_5H_5); 88.12 (2C–O), 91.09 (C_{ipso}Fc); 119.19, 120.12, 124.98, 126.03 (C_6H_4); 127.97, 128.14, 128.42, 128.55, 128.64, 129.19 ($2C_6H_5$); 135.81, 136.62, 148.99, 151.17 ($4C_{ipso}$). Anal. Calc. for $C_{34}H_{28}FeO$: C, 80.32; H, 5.55; Fe, 10.98. Found: C, 80.46; H, 5.63; Fe, 10.82%.

Adduct **26**, yield of 0.4 g (78%), yellow powder, m.p. 200–201 °C. MS *m*/*z* (%): 508 (100). ^{1}H NMR: δ 1.60 (1H, m, CH), 1.71 (3H, d, CH_3, $J = 6.6$ Hz), 2.51 (1H, d, CH, $J = 4.2$ Hz), 4.01 (5H, s, C_5H_5), 3.46 (1H, m, C_5H_4), 3.79 (1H, m, C_5H_4), 3.96 (1H, m, C_5H_4), 4.00 (1H, m, C_5H_4), 7.00–7.60 (14H, m, Ar). ^{13}C NMR: δ 13.44 (CH_3); 26.92, 42.94 (2CH), 37.41 (C), 66.25, 66.33, 68.69, 70.95 (C_5H_4); 68.96 (C_5H_5); 88.29 (2C–O), 91.90 (C_{ipso}Fc); 119.30, 122.79, 125.11, 125.97 (C_6H_4); 127.90, 127.99, 128.12, 128.14, 128.32, 128.39 ($2C_6H_5$); 135.72, 136.68, 148.92, 150.93 ($4C_{ipso}$). Anal. Calc. for $C_{34}H_{28}FeO$: C, 80.32; H, 5.55; Fe, 10.98. Found: C, 80.19; H, 5.70; Fe, 11.04%.

4.6. Reaction of ferroceny-1,3-butadienes 15 and 19 with N-phenylmaleimide

A mixture of 1-ferrocenylbuta-1,3-diene **15** (or **19**) (1 mmol) and *N*-phenylmaleimide (1.2 mmol) in dry benzene (20 ml) was stirred for 10 h at 30 °C in an inert atmosphere. The solvent was distilled off in vacuo and the residue was chromatographed on alumina (hexane – ether, 3:1, as the eluent) to give *N*-phenyl-c-3-ferrocenyl-r-1, c-2-cyclohex-4-enedicarboximide (**27**) (or *N*-phenyl-4-ferrocenylcyclohex-4-ene-*cis*-1,2-dicarboximide (**28**)).

Adduct **27**, yield of 0.26 g (65%), yellow powder, m.p. 173–174 °C. MS *m*/*z* (%): 411 (100). ^{1}H NMR: δ 2.50 (1H, m, CH_2), 2.58 (1H, m, CH_2), 3.04 (1H, dd, CH,

$J = 9.0$, 18.0 Hz), 3.25 (1H, dd, CH, $J = 6.0$, 9.0 Hz), 3.84 (1H, dd, CH, $J = 6.0$, 7.2 Hz), 4.11 (5H, s, C_5H_5), 3.92 (1H, m, C_5H_4), 4.08 (1H, m, C_5H_4), 4.12 (1H, m, C_5H_4), 4.18 (1H, m, C_5H_4), 5.96 (1H, m, CH=), 6.42 (1H, dd, CH=, $J = 7.2$, 8.9 Hz), 6.90–7.40 (5H, m, Ph). ^{13}C NMR: δ 24.72 (CH_2); 38.25, 41.15, 47.64 (3CH), 67.25, 67.72, 68.70, 68.95 (C_5H_4); 68.80 (C_5H_5); 84.02 (C_{ipso}Fc); 120.98, 122.15 (2CH=); 126.75, 128.30, 128.93 (C_6H_5); 138.59 (C_{ipso}), 177.64, 179.18 (2C=O). Anal. Calc. for $C_{24}H_{21}FeNO_2$: C, 70.09; H, 5.15; Fe, 13.58; N, 3.40. Found: C, 69.92; H, 5.23; Fe, 13.74; N, 3.29%.

Adduct **28**, yield 0.28 g (70%), yellow plates, m.p. 164–165 °C. MS *m/z* (%): 411 (100). ^{1}H NMR: δ 2.32 (1H, m, CH_2), 2.54 (1H, m, CH_2), 2.63 (1H, dd, CH_2, $J = 4.5$, 9.3 Hz), 2.74 (1H, dd, CH_2, $J = 5.7$, 9.3 Hz), 3.21 (1H, m, CH), 3.62 (1H, m, CH), 4.17 (5H, s, C_5H_5), 3.98 (1H, m, C_5H_4), 4.05 (1H, m, C_5H_4), 4.19 (1H, m, C_5H_4), 4.28 (1H, m, C_5H_4), 6.09 (1H, dd, CH=, $J = 8.1$, 17.3 Hz),7.06–7.53 (5H, m, Ph). ^{13}C NMR: δ 24.72,26.45 ($2CH_2$); 41.06, 46.89 (2CH), 67.12, 67.67, 68.56, 69.08 (C_5H_4); 68.89 (C_5H_5); 84.31 (C_{ipso}Fc); 121.34 (CH=); 126.98, 127.37, 128.78 (C_6H_5); 131.12 (C); 139.24 (C_{ipso}), 178.03, 179.27 (2C=O). Anal. Calc. for $C_{24}H_{21}FeNO_2$: C, 70.09; H, 5.15; Fe, 13.58; N, 3.40. Found: C, 70.21; H, 5.09; Fe, 13.39; N, 3.32%.

Acknowledgements

This work was supported by the grant DGAPA-UNAM (Mexico, grant IN 207102-3). Thanks are due to J.M. Martínez Mendoza and R.I. Del Villar Morales for their technical assistance.

References

[1] E.I. Klimova, M. Martínez García, T. Klimova, C. Alvarez Toledano, R.A. Toscano, R. Moreno Esparza, L. Ruíz Ramírez, J. Organomet. Chem. 566 (1998) 175.
[2] E.I. Klimova, T. Klimova Berestneva, L. Ruíz Ramírez, M. Martínez García, C. Alvarez Toledano, P.G. Espinoza, R.A. Toscano, J. Organomet. Chem. 545–546 (1997) 191.
[3] E.I. Klimova, L. Ruíz Ramírez, R. Moreno Esparza, T. Klimova Berestneva, M. Martínez García, N.N. Meleshonkova, A.V. Churakov, J. Organomet. Chem. 559 (1998) 1.
[4] E.I. Klimova, C. Alvarez Toledano, M. Martínez García, J. Gomez Lara, N.N. Meleshonkova, I.G. Bolesov, Russ. Chem. Bull. 45 (1996) 550.
[5] E.I. Klimova, C. Alvarez Toledano, M. Martínez García, J. Gomez Lara, N.N. Meleshonkova, I.G. Bolesov, Russ. Chem. Bull. 45 (1996) 613.
[6] E.I. Klimova, M. Martinez Garcia, T. Klimova, C. Alvarez Toledano, R.A. Toscano, L. Ruíz Ramírez, J. Organomet. Chem. 598 (2000) 254.
[7] E.I. Klimova, M. Martinez Garcia, T. Klimova, C. Alvarez Toledano, R.A. Toscano, L. Ruíz Ramírez, J. Organomet. Chem. 605 (2000) 89.
[8] E.I. Klimova, M. Martinez Garcia, T. Klimova, L. Ruíz Ramírez, N.N. Meleshonkova, Russ. Chem. Bull. 48 (1999) 2153.
[9] V.V. Plemenkov, J.S. Giniyatov, Ya.Ya. Willem, N.B. Willem, L.S. Surmina, I.G. Bolesov, Dokl. Akad. Nauk SSSR. 254 (1980) 895.
[10] T. Klimova, E.I. Klimova, M. Martinez Garcia, C. Alvarez Toledano, P.G. Espinosa, R.A. Toscano, J. Organomet. Chem. 665 (2003) 23.
[11] J.A. Connor, J.P. Lloyd, J. Chem. Soc. Perkin I (1973) 17.
[12] I.D. Méndez, E.I. Klimova, M. Martinez Garcia, T. Klimova, J.M. Méndez Stivalet, C. Alvarez Toledano, A.R. Toscano, L. Ruíz Ramírez, J. Organomet. Chem. 645 (2002) 183.
[13] J.R. Al Dulayymi, S.M. Baird, I.G. Bolesov, V. Tveresovsky, M. Rubin, Tetrahedron Lett. 37 (1996) 8933.
[14] A.N. Pushin, E.I. Klimova, V.A. Sazonova, J. Gen. Chem. USSR 57 (1987) 1102.
[15] A.N. Chekhlov, V.N. Solov'ev, A.N. Pushin, V.A. Sazonova, E.I. Klimova, I.V. Martinov, Bull. Akad. Sci. USSR, Div. Chem. Sci. 35 (1986) 642.
[16] M. Raush, H. Vogel, H. Rosenberg, J. Organomet. Chem. 22 (1957) 903.
[17] G. Schröder, U. Prange, B. Putze, T. Thio, J.F.M. Oth, Chem. Ber. 104 (1971) 3406.
[18] G.W. Gokl, J.P. Shepherd, W.P. Weber, J. Org. Chem. 38 (1973) 1913.
[19] K.R. Berger, E.R. Biehl, P.C. Reeves, J. Org. Chem. 39 (1974) 477.