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Retrocyclization reactions of *gem*-dibromo(ferrocenyl)cyclopropanes

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Abstract

Retrocyclization of 1-methyl-, 1-isopropyl-, 1-cyclobutyl-, 1-phenyl-, 1-*tert*-butyl-1-ferrocenyl-, 1-ferrocenyl-3-methyl- and 1,1-diferrocenyl- 2,2-dibromocyclopropanes (**2a**–**g**) under the action of ^{t}BuOK in DMSO, which occurs in parallel with reduction and dehydrobromination, is studied. Cyclic dimers of 2-ferrocenylpropene, 2-ferrocenyl-3-methylbut-1-ene, and 1-cyclobutyl-1-ferrocenylethene were obtained upon retrocyclization of compounds **2a**–**c**, respectively, while compounds **2d**,**e** gave linear dimers of 1-ferrocenyl-1-phenylethene and 2-ferrocenyl-3,3-dimethylbut-1-ene upon retrocyclization. Retrocyclization of **2f**,**g** afforded *trans*-1-ferrocenylpropene and 1,1-diferrocenylethylene, respectively. The action of ^{t}BuOK in DMSO on the dibromide **2a** in the presence of 1,3-diphenylisobenzofuran resulted in the Diels–Alder adducts derived from 2-ferrocenylpropene and 3-ferrocenyl-3-methylcyclopropene. The structures of 1,2-(1-ferrocenyl-1,3,3-trimethylpropane-1,3-diyl)ferrocene and *exo*-1,5-diphenyl-3-*anti*-ferrocenyl-3-*syn*-methyl-6,7-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene were confirmed by X-ray diffraction analysis.

Keywords: Cyclopropane; Ferrocenylalkenes; Cyclodimers; Linear dimers; Diels–Alder adducts; Retrocyclization; Alkylation; Ferrocene

1. Introduction

Previously, we have reported [1] that 1,2-(1-ferrocenyl-1,3,3-trimethylpropane-1,3-diyl)ferrocene (**1a**) is formed, together with monobromocyclopropane (**3a**) and cyclopropene (**4a**), upon treatment of 2,2-dibromo-1-ferrocenyl-1-methylcyclopropane (**2a**) with ^{t}BuOK in DMSO (Scheme 1).

It was suggested that compound **1a** resulted from retrocyclization of the dibromide **2a** into transient 2-ferrocenylpropene (**5a**), which undergoes cyclodimerization to give the final product **1a** (Scheme 2).

Homocyclization of 2-ferrocenylpropene under acidic conditions has been described earlier by Horspool et al. [2]. In a series of publications devoted to the studies of base-induced reactions of *gem*-dihalo(ferrocenyl)-cyclopropanes [3–5], it was shown that the small-ring-opening products, viz. halogen-containing ferrocenyl-1,3-dienes and ferrocenylallenes, comprised all the three carbon atoms of the small ring.

No examples of the retrocyclization-type opening of the three-carbon ring for compounds of the aromatic, aliphatic, and ferrocene series have been documented in the literature.

Retrocyclization of the dibromocyclopropane **2a** represents the first example of this unusual process. The reason for this transformation lies presumably in the specific role played by the ferrocenyl substituent, which weakens one of the C–C bonds in cyclopropanes with electron-withdrawing substituents. Investigations into the characteristic features of retrocylization reactions is of indisputable interest.

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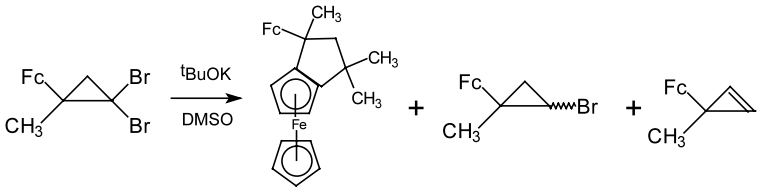


Fc = $C_5H_5FeC_5H_4$

Scheme 1.

2. Results and discussion

The present study is devoted to a more detailed investigation into retrocyclization of dibromo(ferrocenyl)cyclopropanes. Dibromides **2a**–**g** were used as the starting compounds; these were prepared by the addition of dibromocarbene to the alkenes **5a**–**g** [6–11] (Scheme 3).

We found that three competitive processes occur upon action of ^{t}BuOK in DMSO on all of the dibromides **2a**–**g**, viz. retrocyclization, reduction of the dibromocyclopropanes into monobromides, and dehydrobromination of the latter into ferrocenylcyclopropenes. The structures of the retrocyclization products depend on the nature of the substituents in the molecules of the starting dibromocyclopropanes.

*2.1. Retrocyclization reaction of 2,2-dibromo-1-ferrocenyl-1-methylcyclopropane **2a***

The homo- and heteroannular cyclodimers of 2-ferrocenylpropene **5a** (**1a** and **6a**) are formed as the retrocyclization products of the dibromide **2a** in a total yield of 31% in a 2:1 ratio (Scheme 4).

The structures of these compounds separated by TLC on silica gel followed from the ^{1}H-NMR spectral data, elemental analysis data, and coincidence of their physicochemical properties with those reported in the literature (see Section 4). The spatial structure of compound **1a** was elucidated by X-ray diffraction analysis of a single crystal grown from chloroform. The general view of the molecule **1a** is shown in Fig. 1.

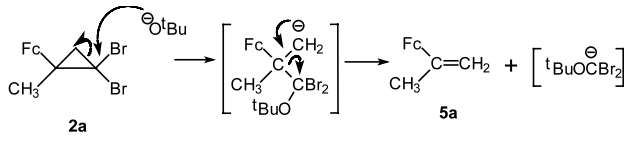
The principal fragment in the structure of **1a** is the five-membered ring fused to the cyclopentadienyl ring of ferrocene and possessing a flattened envelope conformation. The monosubstituted ferrocenyl substituent is *exo*-oriented relative to the 1,2-disubstituted ferrocene group. In the five-membered fragment, the C(21)–C(22) and C(22)–C(23) bonds ($d = 1.562$ and 1.577 Å) are somewhat longer than the C(1)–C(21) and C(2)–C(23) bonds ($d = 1.513$ and 1.516 Å). Other C–C and Fe–C bond lengths and geometrical parameters of the ferrocenyl sandwiches in the dimer **1a** have standard values.

*2.2. Retrocyclization reaction of cyclopropane **2a** in the presence of 1,3-diphenylisobenzofuran **7***

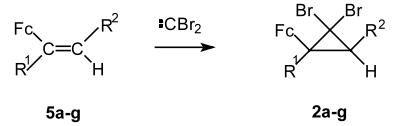
If the same reaction is carried out in the presence of 1,3-diphenylisobenzofuran (**7**), the Diels–Alder adducts of the alkene **5a** and the cyclopropene **4a** with **7**, viz. compounds **8a**,**b** and **9a**,**b**, respectively, were isolated in addition to the dimers **1a** and **6a** (Scheme 5).

The isolation of the adduct **8** is the direct proof of the intermediate formation of 2-ferrocenylpropene upon retrocyclization of the dibromocyclopropane **2a**.

The structures of compounds **8a**,**b** and **9a**,**b** were established based on the ^{1}H- and ^{13}C-NMR data (Tables 1 and 2) and data from elemental analyses (Table 4). According to the ^{1}H-NMR spectral data, the adduct **8** is formed as a ca. 1.5:1 mixture of *endo* (**8a**) and *exo* (**8b**) isomers, which could be separated by TLC on silica gel. The attribution of the isomers to *exo*- and *endo*-series was made based on the previously found criteria [12,13]. Thus the presence of signals for the

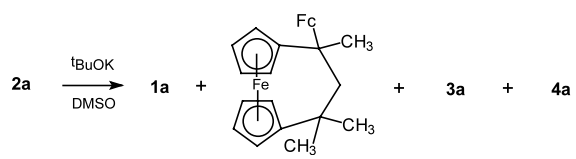


Scheme 2.



a) $R^1 = CH_3$, $R^2 = H$; b) $R^1 = {}^i$Pr, $R^2 = H$; c) $R^1 = C_4H_7$, $R^2 = H$
d) $R^1 = Ph$, $R^2 = H$; e) $R^1 = {}^t$Bu, $R^2 = H$; f) $R^1 = H$, $R^2 = CH_3$
g) $R^1 = Fc$, $R^2 = H$

Scheme 3.



Scheme 4.

Table 1
^{1}H-NMR spectral data of compounds **1a–e**; **2c,f,g**; **5f,g**; **6a**; **8a,b** and **9a,b** ($CDCl_3$, 300 MHz, TMS; δ, ppm; J/Hz)

Compound	CH_2, CH_3	C_5H_5	C_5H_4	CH, CH=	Ar
1a	0.88 s, 3H, 1.32 s, 3H, 1.87 s, 3H, 1.93 d, 1H, 2.45 d, 1H, $J = 12.6$	4.14 s, 5H, 4.27 s, 5H	3.42 m, 1H, 3.88 m, 1H, 3.91 m, 1H, 4.03 m, 1H, 4.07 m, 2H, 4.16 m, 1H	–	–
1b	1.17 d, 6H, $J = 7.0$, 1.20 d, 6H, $J = 6.9$, 1.43 s, 3H	4.08 s, 5H, 4.12 s, 5H	3.30 m, 1H, 3.75 m, 1H, 4.13 m, 1H, 4.22 m, 3H, 4.29 m, 1H	2.57 m, 1H, $J = 6.9$, 2.95 m, 1H, $J = 7.0$	–
1c	1.58 s, 3H, 1.68–2.70 m, 12H, 2.05 d, 1H, 2.44 d, 1H, $J = 9.2$	4.08 s, 5H, 4.10 s, 5H	4.03 m, 1H, 4.14 m, 2H, 4.20 m, 1H, 4.25 m, 2H, 4.37 m, 1H	2.76 m, 1H, 2.89 m, 1H	–
1d	1.51 s, 3H	4.16 s, 5H, 4.25 s, 5H	4.04 m, 4H, 4.11 m, 2H, 4.22 m, 2H	7.03 s, 1H	6.86 m, 2H, 7.07–7.24 m, 8H
1e (*Z–E*, 1:1)	1.22 s, Bu^t, 1.24 s, Bu^t, 9H, 1.26 s, Me, 1.38 s, Me, 3H	4.10 s, 4.12 s, 4.13 s, 4.15 s, 10H	4.00–4.30 m, 8H	5.61 s, 6.02 s, 1H	–
2c	1.56 s, 1H, 1.87 s, 1H, 1.70–2.55 m, 6H	4.15 s, 5H	4.03 m, 1H, 4.13 m, 1H, 4.21 m, 2H	3.46 m, 1H	–
2f	1.44 d, 3H, $J = 6.3$	4.17 s, 5H	4.05 m, 1H, 4.15 m, 1H, 4.20 m, 1H, 4.36 m, 1H	1.58 m, 1H, $J = 6.3$, 8.1, 2.10 d, 1H, $J = 8.1$	–
2g	2.36 s, 2H	4.12 s, 10H	4.05 m, 2H, 4.18 m, 4H, 4.25 m, 2H	–	–
5f (*trans*)	1.73 dd, 3H, $J = 1.5$, 6.52	4.08 s, 5H	4.13 m, 2H, 4.26 m, 2H	5.78 m, 1H, $J = 6.52$, 15.6, 6.09 dd, 1H, $J = 1.5$, 15.6	–
5g	5.41 s, 2H	4.15 s, 10H	4.26 m, 4H, 4.62 m, 4H	–	–
6a	1.27 s, 3H, 1.42 s, 3H, 1.61 s, 3H, 2.07 d, 1H, 2.78 d, 1H, $J = 13.0$	4.18 s, 5H	3.62 m, 1H, 3.81 m, 2H, 3.92 m, 4H, 4.20 m, 4H, 4.36 m, 1H	–	–
8a	1.32 s, 3H, 2.27 d, 1H, 3.12 d, 1H, $J = 11.6$	4.04 s, 5H	2.47 m, 1H, 3.65 m, 1H, 3.72 m, 1H, 3.88 m, 1H	–	6.84–7.72 m, 14H
8b	1.35 s, 3H, 2.61 d, 1H, 2.65 d, 1H, $J = 11.1$	4.06 s, 5H	3.86 m, 1H, 4.07 m, 1H, 4.11 m, 2H	–	7.02–7.56 m, 14H
9a	1.71 s, 3H	4.14 s, 5H	4.04 m, 2H, 4.06 m, 2H	1.94 s, 2H	7.0–7.18 m, 4H, 7.36–7.53 m, 6H, 7.68–7.76 m, 4H
9b	1.50 s, 3H	4.13 s, 5H	4.05 m, 4H	1.93 s, 2H	7.12–7.65 m, 14H

Table 2
^{13}C-NMR spectral data of compounds **1a**,**d**; **2f**,**g**; **5g**; **8a**,**b** and **9a** (75 MHz, $CDCl_3$, TMS; δ, ppm)

Group	**1a**	**1d**	**2f**	**2g**	**5g**	**8a**	**8b**	**9a**
C_5H_5	68.44, 68.99	68.69, 69.05	68.79	69.38, 69.41	69.52	68.30	68.08	68.50
C_5H_4	59.50, 63.66, 65.48 (2C), 67.41 (2C), 68.43	65.67, 66.13, 66.74, 67.05, 67.31, 67.32, 68.36, 68.49	67.57, 67.99, 68.64, 69.58	66.08 (2C), 66.74 (2C), 69.63, 69.96, 70.60, 71.45	67.83, 68.12	66.85, 67.61, 67.70, 68.43	66.47, 67.11, 67.71, 68.79	65.43, 67.14
$C_{ipso}Fc$	101.30, 102.90, 106.22	89.97, 102.50	83.87	94.20, 94.36	85.72	87.84	86.58	96.43
CH_3	29.80, 31.84, 31.97	27.91	17.43	–	–	24.89	25.99	15.12
CH_2	37.34	–	–	36.19	109.42	52.19	52.93	–
C	40.77, 58.21	43.59, 137.25	40.71	37.53	143.04	48.87, 92.98, 95.92	49.26, 93.19, 93.36	38.48, 90.12 (2C)
CH	–	–	31.71, 38.95	–	–	–	–	41.05 (2CH)
CH=	–	125.42	–	–	–	–	–	–
C_{ipso}	–	139.31, 149.17	–	–	–	137.43, 139.37, 146.05, 148.94	137.66, 139.48, 145.86, 149.28	136.71 (2C), 151.48 (2C)
Ar	–	126.07, 127.08 (2C), 127.23 (2C), 127.34 (2C), 129.60 (2C), 134.77	–	–	–	118.54, 121.99, 125.28, 125.56, 126.12, 126.21, 126.36, 126.54, 126.71, 127.35, 127.72, 127.76, 128.43, 128.48	118.13, 120.72, 125.27, 125.56, 125.89, 126.21, 126.36, 126.78, 126.91, 127.35, 127.76, 127.83, 128.43, 128.48	119.01 (2C), 125.87 (2C), 128.05 (4C), 128.37 (6C)

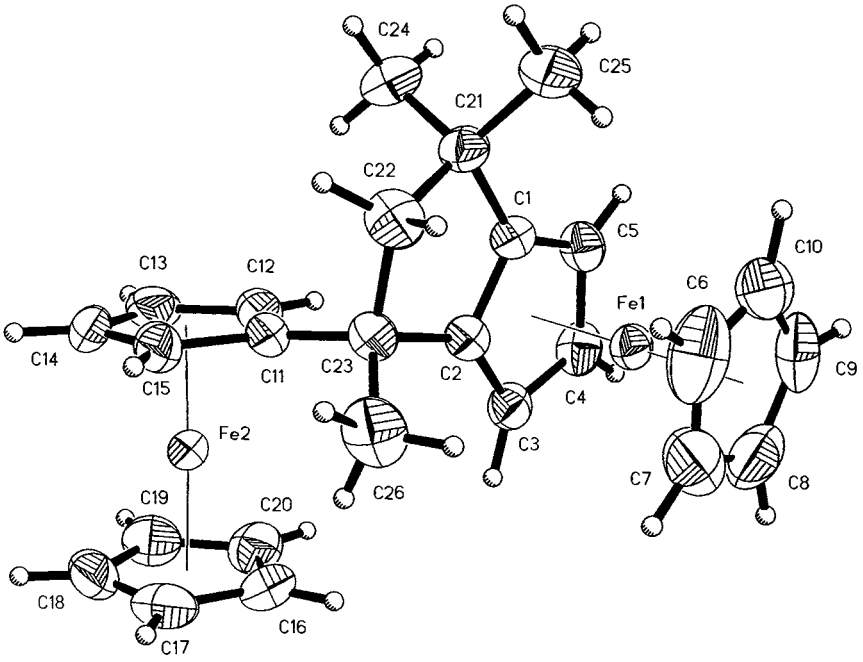
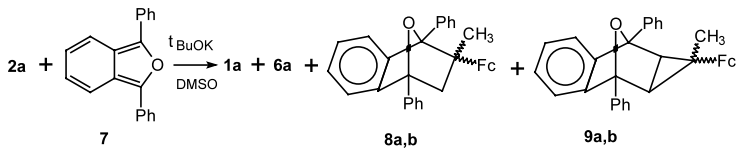


Fig. 1. Crystal structure of **1a**. Selected bond lengths (Å): C(1)–C(2) = 1.411(5); C(1)–C(21) = 1.518(5); C(2)–C(23) = 1.516(5); C(22)–C(23) = 1.577(5); C(21)–C(22) = 1.562(6); C(21)–C(25) = 1.532(6); C(21)–C(24) = 1.535(6); C(23)–C(26) = 1.536(6); C(11)–C(23) = 1.521(5). Selected bond angles (°): C(1)–C(21)–C(24) = 110.1(3); C(1)–C(21)–C(25) = 114.3(3); C(24)–C(21)–C(25) = 109.0(4); C(1)–C(21)–C(22) = 100.1(3); C(22)–C(21)–C(24) = 112.2(4); C(21)–C(22)–C(23) = 109.8(3); C(2)–C(23)–C(22) = 99.8(3); C(1)–C(2)–C(23) = 112.1(3); C(2)–C(1)–C(21) = 112.7(3).



Scheme 5.

protons of the substituted cyclopentadienyl ring of ferrocene at much higher field ($\delta = 2.47$, 3.65, 3.72 and 3.88 ppm) than the singlet of the protons of the non-substituted cyclopentadienyl ring of ferrocene is typical of the *endo*-adduct **8a**. In the *exo*-adduct **8b**, the signals for the three protons of the C_5H_4 fragment of ferrocene are located in the lower field than the singlet of the protons of the C_5H_5 group of ferrocene.

Compound **9**, which is the Diels–Alder adduct of 3-ferrocenyl-3-methylcyclopropene **4a** with 1,3-diphenylisobenzofuran **7**, was also obtained as a mixture of two isomers, viz. **9a** and **9b**, in a ca. 2:1 ratio. The isomers were separated by TLC on silica gel, their structures followed from the ^{1}H- and ^{13}C-NMR and elemental analysis data.

The spatial structure of compounds **9a** and **9b** was established based on the X-ray diffraction analysis of a single crystal of compound **9a** prepared by crystallization from dichloromethane. The general view of the molecule **9a** is shown in Fig. 2.

The X-ray results indicate that the three-membered ring is fused with the six-membered ring in a rigid boat conformation. The adduct **9a** has an *exo*-structure. The methyl group has a *syn*-position relative to the bridging oxygen atom and a 'non-bisecting' position relative to the small ring. The ferrocenyl fragment occupies *anti*-position relative to the oxygen atom. The structure of *exo*-1,5-diphenyl-3-*syn*-ferrocenyl-3-*anti*-methyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene was ascribed to the isomer **9b**.

2.3. Retrocyclization reactions of 2,2-dibromo-1-isopropyl- and 2,2-dibromo-1-cyclobutyl-1-ferrocenylcyclopropanes **2b** and **2c**

The reactions of the dibromides **2b** and **2c** with ^{t}BuOK in DMSO result exclusively in compounds **1b** and **1c**, which are the homoannular cyclodimers of 2-ferrocenyl-3-methylbut-1-ene (**5b**) and 1-cyclobutyl-1-ferrocenylethene (**5c**), respectively (Scheme 6). The ^{1}H- and ^{13}C-NMR spectral data for the dimers **1b**,**c** are given in the Section 4.

2.4. Retrocyclization reactions of 2,2-dibromo-1-phenyl- and 2,2-dibromo-1-tert-butyl-1-ferrocenylcyclopropanes **2d** and **2e**

Unlike dibromocyclopropanes **2a**–**c**, the dibromides **2d** and **2e** undergo retrocyclization to give 1-ferrocenyl-1-phenylethene and 2-ferrocenyl-3,3-dimethylbut-1-ene linear dimers (compounds **1d** and **1e**), respectively (Scheme 7).

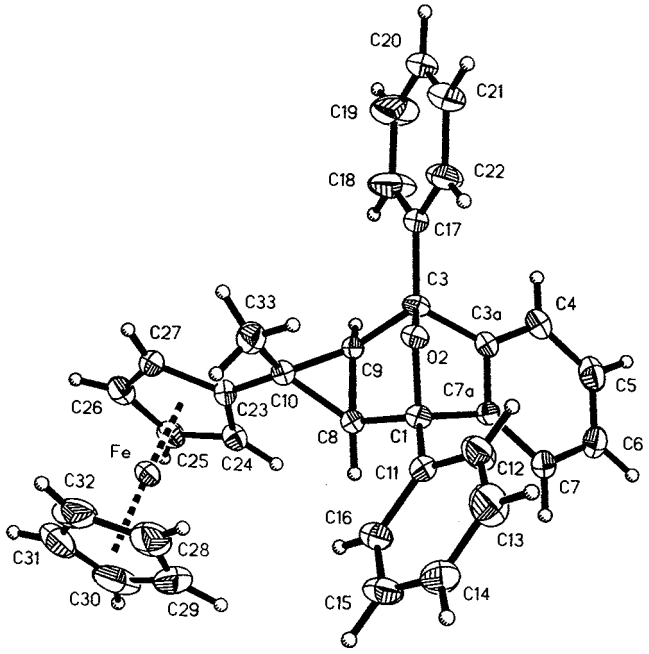
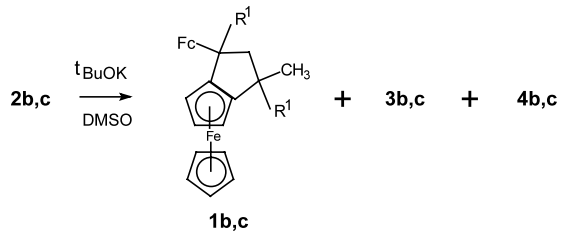
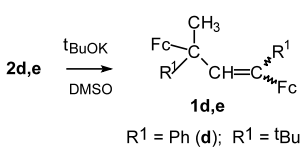


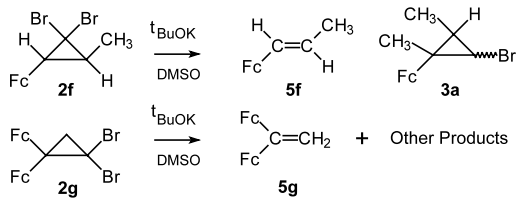
Fig. 2. Crystal structure of **9a**. Selected bond lengths (Å): C(8)–C(9) = 1.510(4); C(8)–C(10) = 1.517(4); C(9)–C(10) = 1.534(3); C(1)–C(7a) = 1.537(4); C(1)–C(8) = 1.552(4); C(3a)–C(7a) = 1.396(4); C(1)–O(2) = 1.453(3); C(3)–O(2) = 1.450(3); C(3)–C(9) = 1.546(4); C(1)–C(8) = 1.552(4). Selected bond angles (°): C(8)–C(10)–C(9) = 59.34(17); C(9)–C(8)–C(10) = 60.88(17); C(8)–C(9)–C(10) = 59.78(17); C(9)–C(8)–C(1) = 101.8(2); C(8)–C(9)–C(3) = 103.7(2); O(2)–C(3)–C(9) = 101.9(2); O(2)–C(1)–C(8) = 102.5(2); C(3)–O(2)–C(1) = 98.1(2); C(7a)–C(1)–C(8) = 104.1(2); C(3a)–C(3)–C(9) = 101.9(2).



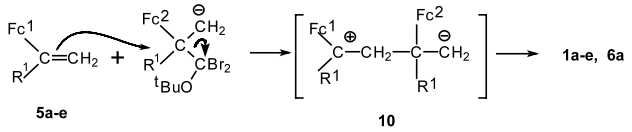
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

According to the ^{1}H-NMR data, the reaction of **2d** is stereospecific, and the dimer **1d** is formed exclusively as a single, presumably *E*-isomer. The compound **1e** is formed as a mixture of *Z*- and *E*-isomers (~ 1:1).

2.5. Retrocyclization reactions of 2,2-dibromo-1-ferrocenyl-2-methyl- and 2,2-dibromo-1,1-diferrocenylcyclopropanes **2f** and **2g**

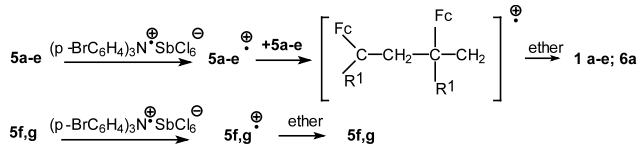
We also found that the dibromo(ferrocenyl)-cyclopropanes **2f** and **2g** undergo retrocyclization under identical conditions to yield *trans*-1-ferrocenylpropene (**5f**) and 1,1-diferocenylethene (**5g**), respectively (Scheme 8).

These results confirm additionally the formation of ferrocenylalkenes **5a**–**g** in the first step of retrocyclization of dibromo(ferrocenyl)cyclopropanes **2a**–**g**.

2.6. About the possible mechanisms of the retrocyclization reactions of gem-dibromoferrocenylcyclopropanes

To the best of our knowledge, dimerization of ferrocenyl-substituted alkenes in the presence of bases has not been documented. We have found that the ferrocenylalkenes **5a**–**g** themselves produce no dimers upon treatment with ^{t}BuOK in DMSO. Presumably, the specific conditions for the dimerization of the alkenes **5a**–**e** arise during retro cyclization as a result of the nucleophilic opening of the three-membered ring of dibromo(ferrocenyl)cyclopropanes. A possible pathway for this transformation is depicted in the Scheme 9.

The bipolar ion **10** that arose is transformed into either cyclodimers **1a**–**c**, **6a** as a result of the intramolecular alkylation of the ferrocenyl group Fc^2 or linear dimers **1d**,**e** owing to the deprotonation. These reactions are suppressed in the case of the alkenes **5f** and **5g**.



Scheme 10.

Yet another pathway is the dimerization of the alkenes **5a**–**e** following the mechanism involving single-electron transfer (SET), which can be realistic under the reaction conditions. Identification of retrocyclization products (compounds **1a**–**e**, **5f**, **5g**, and **6a**) upon reduction of the *gem*-dibromides **2a**–**g** with EtMgCl in the presence of titanium tetraisopropoxide is in favor of this mechanism.

The dimerization of arylalkenes following the SET mechanism is known to occur in the presence of aminium salts, e.g. $(p\text{-}BrC_6H_4)_3N^{+\bullet}$ $SbCl_6^-$ (**11**) [14]. Analogous reactions of the ferrocenyl-substituted alkenes **5a**–**g** with the salt **11** showed that the alkenes **5a**–**e** do produce cyclic (**1a**–**c**, **6a**) and linear (**1d**, **e**) dimers identical with those prepared as described above. The alkenes **5f** and **5g** undergo no dimerization and are recovered unchanged from the reaction mixtures (Scheme 10).

However, final conclusion concerning the reasons for, and the mechanism of, the retrocyclization of *gem*-dibromo(ferrocenyl)cyclopropanes is yet to be made, which requires further investigations into this process.

3. Conclusion

The results presented in this paper allow to conclude that, depending on the nature of the substituents R_1 and R_2, the initially formed retrocyclization products, viz. alkenes **5a**–**g**, undergo cyclodimerization, dimerization, or remain intact under the reaction conditions (Scheme 11).

4. Experimental

The ^{1}H- and ^{13}C-NMR spectra were recorded on a Unity Nova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ with Me_4Si as the internal standard (Tables 1 and 2). The separations were carried out by column chromatography on alumina (Brockmann activity III) and by preparative TLC on silica gel. The X-ray diffraction patterns were recorded on a Siemens P4/PC diffractometer. The crystallographic data, the experimental conditions, and corrections are given in Table 3. Elemental analysis data are listed in Table 4.

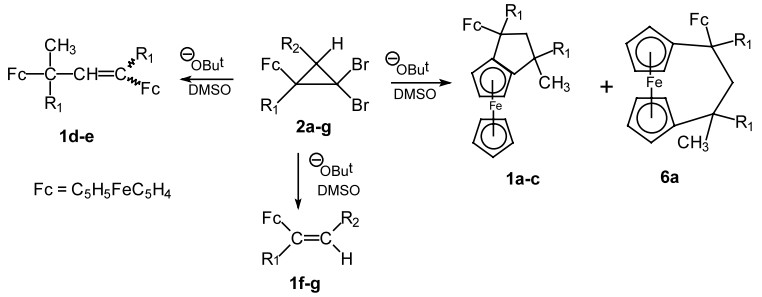
The chemical reactions were carried out in an atmosphere of dry argon and in absolute grade solvents.

4.1. Ferrocenylalkenes *5a*,*d*–*g*

These alkenes were obtained by dehydration of the corresponding alcohols by $POCl_3$ in pyridine [15,16] and isolated as orange crystals in 58–70% yields by column chromatography on alumina (hexane as the eluent): 2-ferrocenylpropene (**5a**), yield 70%, m.p. 64–65 °C (lit. [16]: m.p. 64–66 °C); 1-ferrocenyl-1-phenylethene (**5d**), yield 74%, red oil (lit. [3]: b.p. 140 °C/0.1 mm); 2-ferrocenyl-3,3-dimethylbut-1-ene (**5e**), yield 73%, red oil (lit. [3]: b.p. 116–118°/0.2 mm); *trans*–*cis*-1-ferrocenylpropene (3:1) (**5f**), yield 72%, m.p. 39–40 °C (lit. [17]: m.p. 39–40 °C); 1,1-diferrocenylethene (**5g**), yield 53%, m.p. 163–164 °C.

4.2. Ferrocenylalkenes *5b*,*c*

These alkenes were prepared by the Wittig reaction [18] from the corresponding ketones and methylenetriphenylphosphorane: 2-ferrocenyl-3-methylbut-1-ene (**5b**), yield 73%, orange crystals, m.p. 84–85 °C (lit. [6]: m.p. 84–85 °C), 1-cyclobutyl-1-ferrocenylethene (**5c**), yield 76%, m.p. 62–63 °C (lit. [7]: m.p. 62–63 °C).



$R_1 = CH_3$, $R_2 = H$ (**a**); $R_1 = {}^iPr$, $R_2 = H$ (**b**); $R_1 = C_4H_7$, $R_2 = H$ (**c**);
$R_1 = Ph$, $R_2 = H$ (**d**); $R_1 = {}^tBu$, $R_2 = H$ (**e**); $R_1 = H$, $R_2 = CH_3$ (**f**);
$R_1 = Fc$, $R_2 = H$ (**g**).

Scheme 11.

Table 3
Crystal data, data collection and refinement parameters for **1a** and **9a**

Data	**1a**	**9a**
Molecular formula	$C_{26}H_{28}Fe_2$	$C_{34}H_{28}FeO$
Molecular weight (g mol^{-1})	452.2	508.41
Temperature (K)	293	293
Crystal system	Orthorombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
a (Å)	11.366(10)	10.035(1)
b (Å)	14.737(10)	10.636(1)
c (Å)	24.667(3)	12.813(2)
α (°)	–	98.84
β (°)	–	102.79
γ (°)	–	100.80
V (Å^3)	4131.9(6)	1282.5(3)
Z	8	2
D_{calc} (g cm^{-3})	1.454	1.317
Absorption coefficient (mm^{-1})	1.413	0.613
F(000)	1888	532
Mo–K$_\alpha$ radiation, λ (Å)	0.71073	0.71073
Monochromator	Graphite	Graphite
Θ scanning range (°)	1.50–30.00	1.50–25.00
Total number of reflections	6022	4782
Independent reflections	6022	4498
R_{int}	0.00	0.0566
Number of refinable parameters	254	326
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit	1.100	1.021
Residual electron density ρ_{min}/ρ_{max} (e Å^{-3})	−0.43/0.41	−0.356/0.347
Hydrogen atoms	Riding	Riding
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$	$w^{-1} = \sigma^2(F) + 0.0024F^2$

4.3. *gem*-Dibromo(ferrocenyl)cyclopropanes **2a–g**

Dibromo(ferrocenyl)cyclopropanes **2a** [9], **2b** [6], **2c**, **2d** [1], **2e** [11], **2f** and **2g** were obtained from the alkenes **5a–g** according to the standard procedure [1,13]. The yields and physicochemical data for compounds **2c**, **2f**, **2g** are listed in Table 4.

4.4. Reaction of dibromo(ferrocenyl)cyclopropanes **2a–g** with ^{t}BuOK in Me_2SO (general procedure)

Dibromo(ferrocenyl)cyclopropane **2a–g** (2.0 mmol) was added to a solution of ^{t}BuOK (0.45 g, 4 mmol) in dry Me_2SO (30 ml). The mixture was stirred for 6 h at ambient temperature and partitioned between benzene and water (50 ml each). The organic layer was separated, washed with water, and the solvent was evaporated in vacuo. The residue was chromatographed on a column with alumina (hexane as the eluent). The following reaction products were obtained: (1) alkenes **5f** (24%), **5g** (18%) (Table 4); (2) ferrocenylcyclopropenes **4a–e** (~ 20–30%); (3) monobromcyclopropanes **3a–c**, **e–g** (~ 31–45%); (4) cyclodimers **1a–c**, **6a**; (5) linear dimers **1d**,**e** (Table 4).

4.5. The reaction of 2,2-dibromo-1-ferrocenyl-1-methylcyclopropane **2a** with ^{t}BuOK in Me_2SO in the presence of 1,3-diphenylisobenzofuran **7**

The reaction of dibromo(ferrocenyl)cyclopropane **2a** (0.4 g, 1 mmol) with ^{t}BuOK (0.23, 2 mmol) and 1,3-diphenylisobenzofuran **7** (0.3 g, 1.1 mmol) in dry Me_2SO (30 ml) was carried out as described above to give 0.044 g (19%) **1a**, 0.02 g **6a** (9%), 0.10 g (20%) **8a**,**b** (1.5:1), 0.19 g (37%) **9a**,**b** (2:1).

4.6. Reactions of ferrocenylalkenes **5a–g** with aminium salt

A catalytic amount of tris-(4-bromophenyl)aminium hexachloroantimonate (0.042 g, 0.05 mmol) is rapidly added to a methylene chloride (10 ml) solution of alkenes **5a–g** (2 mmol) at room temperature (r.t.), under stirring. The intensely green color of the solution fades within 20 min. The excess of aminium salt is destroyed by addition of ethyl ether, then the solvent is removed in vacuo. The residual, absorbed on Al_2O_3, is purified by Al_2O_3 column chromatography with the hexane as the eluent. Cyclic dimers **1a–c**, **6a**, linear dimers **1d–e** and alkenes **5f–g** were obtained in a yield 43–61%.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 159327 for 1,2-(1-ferrocenyl-1,3,4-trimethylpropan-1,3-diyl)ferrocene **1a** and no. 159328 for *exo*-1,5-diphenyl-3-*anti*-ferrocenyl-3-*syn*-methyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene **9a**. 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).

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Table 4
Yields, melting points and elemental analysis data for the compounds obtained by retrocyclization reactions **1a**–**e**; **5f**,**g**; **6a**; **8a**,**b** and compounds **2c**,**f**,**g**, and **9a**,**b**

Compound	m.p. (°C)	Yield (%)	Anal. Found (%)				Formula	Calc. (%)			
			C	H	Fe	Br		C	H	Fe	Br
1a	187–188	19	68.81	6.40	24.53	–	$C_{26}H_{28}Fe_2$	69.06	6.24	24.70	–
1b	173–174	21	70.61	7.32	25.09	–	$C_{30}H_{36}Fe_2$	70.88	7.14	21.98	–
1c	218–219	32	72.08	6.99	21.13	–	$C_{32}H_{36}Fe_2$	72.20	6.81	20.99	–
1d	147–148	31	74.83	5.82	19.19	–	$C_{36}H_{32}Fe_2$	75.02	5.60	19.38	–
1e	Orange oil	18	71.38	7.73	21.06	–	$C_{32}H_{40}Fe_2$	71.65	7.52	20.83	–
2c	127–128	73	46.71	4.28	12.58	36.63	$C_{17}H_{18}Br_2Fe$	46.60	4.14	12.74	36.52
2f	74–75	68	42.48	3.27	13.81	40.23	$C_{14}H_{14}Br_2Fe$	42.25	3.55	14.04	40.16
2g	185 (dec.)	65	48.89	3.78	19.46	28.02	$C_{23}H_{20}Br_2Fe_2$	48.64	3.55	19.67	28.14
5f (*trans*-)	39–40 [17]	24	68.93	6.38	24.87	–	$C_{13}H_{14}Fe$	69.06	6.24	24.70	–
5g	163–164	18	66.54	5.27	28.41	–	$C_{22}H_{20}Fe_2$	66.71	5.09	28.20	–
6a	106–107	9	69.31	6.06	24.92	–	$C_{26}H_{28}Fe_2$	69.06	6.24	24.70	–
8a	232–233	12	79.98	5.53	11.12	–	$C_{33}H_{28}FeO$	79.84	5.69	11.25	
8b	218–219	8	79.73	5.82	11.38	–	$C_{33}H_{28}FeO$	79.84	5.69	11.25	
9a	241–242	25	80.29	5.61	11.21	–	$C_{34}H_{28}FeO$	80.17	5.73	11.07	–
9b	216–217	12	80.33	5.84	10.98	–	$C_{34}H_{28}FeO$	80.17	5.73	11.07	

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