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3,3-Diferrocenylcyclopropene

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Abstract

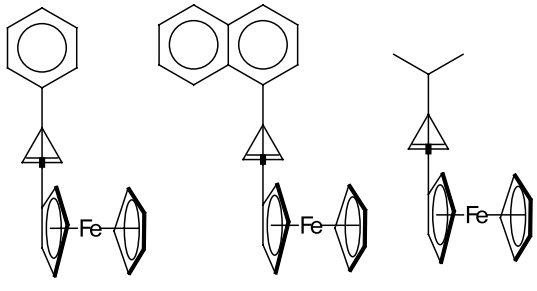
Dehydrohalogenation of isomeric 2-chloro- and 2-bromo-1,1-diferrocenylcyclopropanes (*Z*- and *E*-isomers with respect to the 'bisecting' ferrocenyl substituent) under the action of Bu^{t}OK in DMSO afforded 3,3-diferrocenylcyclopropene. In solution, this underwent facile opening of the small ring to give 3-ferrocenyl-1*H*-cyclopentaferrocene (~ 55%) and 1,1-diferrocenylpropene (15%). The spatial structure of *Z*-2-chloro-1,1-diferrocenylcyclopropane and 1,1-diferrocenylcyclopropane were elucidated by X-ray diffraction analysis of a single crystal.

Keywords: Ferrocene; Ferrocenylcyclopropane; Ferrocenylcyclopropene; Dehydrohalogenation; Ferrocenylallylic cation; Ferrocenylcarbenoid; 3-Membered ring opening

1. Introduction

Recently, we have reported [1–4] on the synthesis of crystalline 3-phenyl-, 3-(1-naphthyl)-, and 3-isopropyl-3-ferrocenylcyclopropenes (**1a**–**c**), their spatial structures, and some chemical transformations.

The conformations of these ferrocenylcyclopropenes were established by X-ray diffraction analysis. It was shown that the ferrocenyl substituents occupy the 'bisecting' positions relative to the cyclopropene rings in all three cases. The aryl and alkyl substituents are arranged in 'non-bisecting' fashion.



1a **1b** **1c**

The 'through-space' interactions of the molecular orbitals of the ethylene and aryl fragments in compounds **1a** and **1b** determine the stereoselectivities of intramolecular transformations of these compounds. For instance, they easily undergo acid-induced or thermal opening of the 3-membered ring to give ferrocenylallylic cations **2a**,**b** or carbenoid intermediates **3a**,**b**, which recyclize into compounds **4a**,**b** and **5a**,**b** involving only the aryl fragment leaving the ferrocenyl group unaffected (Scheme 1).

In compound **1c**, the molecular orbitals of the ethylene fragment of the small ring cannot interact with the orbital of the cyclopentadiene ring of ferrocene [4]. It is the absence of this interaction that is the reason for the predominant formation of the linear products **6a**–**c** upon intramolecular transformations of 3-alkyl-3-ferrocenylcyclopropenes. It is noteworthy that 3-isopropyl-1*H*-cyclopentaferrocene **7** was also obtained as a minor product (~ 4%) upon intramolecular alkylation of the ferrocenyl fragment (Scheme 2).

The formation of this minor product seems to result from the change in the spatial orientation of the ferrocenyl substituent upon rotation about the sesquialteral C(1)–C(2) bond in the intermediates **2c** and **3c** despite rather high energy barrier [5,6].

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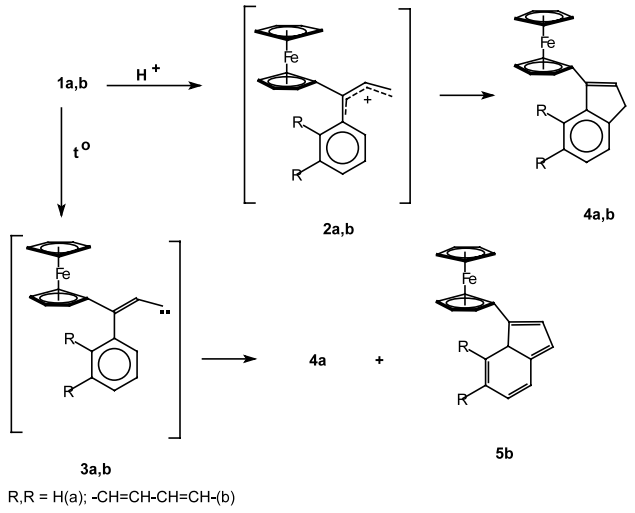


Scheme 1.

Thus, the existence of 'non-bisecting' ferrocenyl substituents in compounds of the cyclopropane and cyclopropene series remained questionable. It is quite reasonable to assume that this might be realized if two ferrocenyl groups were attached to the same carbon atom of a small ring, one of the groups being 'bisecting' (Fc^1) and the other 'non-bisecting' (Fc^2). In this case, intramolecular transformations of a three-membered ring should occur in a highly diastereoselective manner to result in predominant formation of alkylation products of the 'non-bisecting' ferrocenyl substituent.

To check this assumption, we have synthesized 3,3-differocenylcyclopropene **1d** and studied some its chemical properties.

2. Results and discussion

2,2-Dichloro- and 2,2-dibromo-1,1-diferrocenylcyclopropanes **8a** and **8b** served as the starting compounds for the synthesis of the target 3,3-differocenylcyclopropene **1d**. These were prepared according to Scheme 3 [7–14].

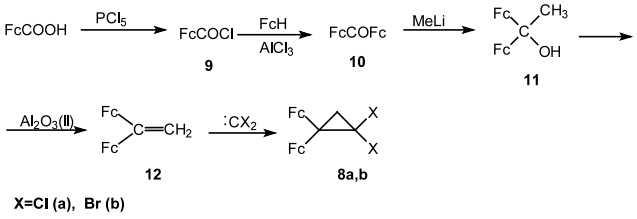
Compounds **8a**, **9**–**12** were obtained smoothly in 50–70% yields, the dibromide **8b** was isolated in 32% yield.

Dichloro- and dibromodiferrocenylcyclopropanes **8a**,**b** are crystalline pale-yellow compounds, which decompose rapidly on heating. The dichloride **8a** was much more storage-stable than the dibromide **8b** even in the crystalline state. The latter turns dark after storage for several hours, while the former remained unchanged even after prolonged storage (~ 2 months).

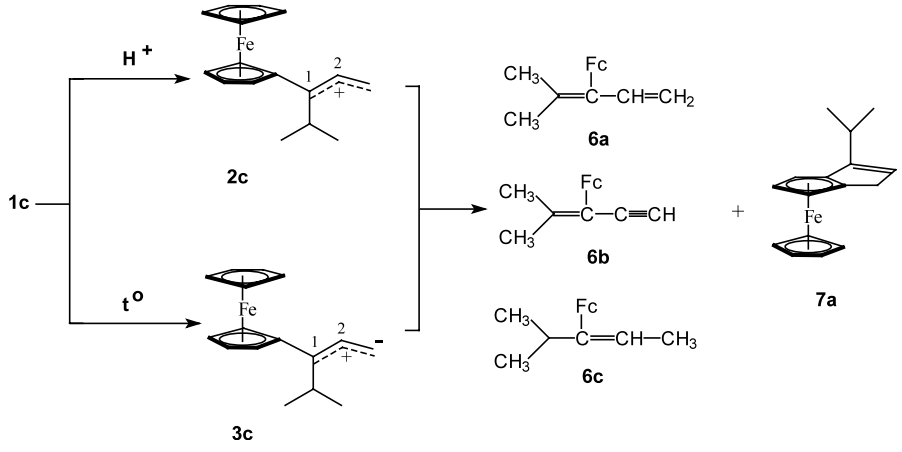
In solutions (CH_3CN, $CHCl_3$ + pyridine), the dibromide **8b**, unlike the dichloride **8a**, undergoes solvolysis, which results in the opening of the small ring and formation of 1,1-diferrocenylallene **13** (Scheme 4).

The structure of compound **13** was confirmed by the data from ^1H and ^{13}C-NMR spectroscopy (see Section 3) and elemental analysis.

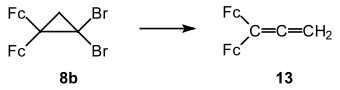
Dihalides **8a** and **8b** were reduced by a mixture of ethylmagnesium chloride and titanium tetraisopropoxide [8] to give 1,1-diferrocenyl-2-halogenocyclopropanes as ~ 1:1 mixtures of geometrical isomers (*Z*- and *E*- with respect to the 'bisecting' ferrocenyl substituents, **15a**, **16a** and **15b**, **16b**, respectively) in low overall yields (~ 15–20%). In addition, 1,1-diferrocenylcyclopropane **14**, representing the total reductive dehalogenation product, and ring-opening products, viz. 1,1,-diferrocenylpropene **17** and 3-ferrocenyl-1*H*cyclopentaferrocene **7a**, were isolated from the reaction mixtures (Scheme 5).



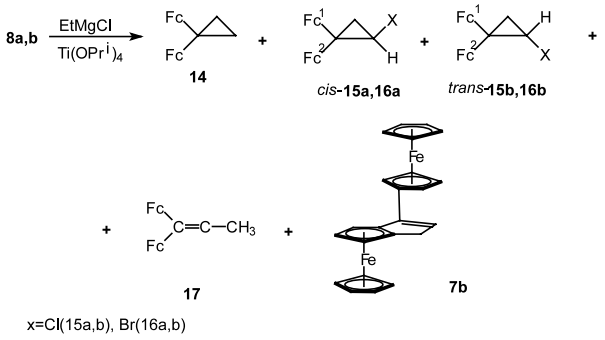
Scheme 3.



Scheme 2.



Scheme 4.



Scheme 5.

Variations of the reaction conditions did not result in any increase in the yields of the monohalides **15** and **16**. Despite the formation of mixtures of reaction products, compounds **14**, **15a**, **15b** (or **16a**, **16b**), **17**, and **7b** could be isolated by chromatography on alumina. The respective ^{1}H and ^{13}C-NMR spectra corroborate completely their structures (see Section 3).

The assignment of the monohalides **15a**, **16a** and **15b**, **16b** to the *Z*- and *E*-isomeric series has been carried out based on their ^{1}H-NMR spectroscopic data with account of the previously established NMR criteria for the assignment of *Z*- and *E*-isomers of bromo(ferrocenyl)cyclopropane with the 'bisecting' ferrocenyl substituent [1,3,10–12]. Thus the ^{1}H-NMR spectra of the *cis* isomers (**15a**, **16a**) contain two doublets of doublets at δ 1.33 and 1.90 and at δ 1.36 and 1.94, respectively, belonging to the methylene protons (AB-portion of the ABM spin system). In the ^{1}H-NMR spectra of the isomeric compounds (**15b**, **16b**), the methylene protons resonate at δ 1.50 and 1.69 (**15b**) and at δ 1.49 and 1.70 (**16b**). As can be seen, larger $\Delta\delta$ values ($\Delta\delta = \delta_A - \delta_B =$ 0.57 and 0.58 ppm) are typical of the *cis*-isomers **15a** and **16a** in contrast to the *trans* isomers **15b** and **16b** ($\Delta\delta = 0.19$ and 0.21 ppm). This difference has previously been observed in the ^{1}H-NMR spectra of the *Z*- and *E*-isomers of ferrocenyl(halogeno)cyclopropanes studied so far [1,3,9–11].

The *Z*-configuration of one of the monohalides obtained, viz. 2-chloro-1,1-diferrocenylcyclopropane **15a**, was confirmed additionally by the X-ray diffraction analysis (Table 1). The general view of the molecule **15a**

Table 1
Crystal data, data collection and refinement parameters for compounds **14** and **15a**

Data	**14**	**15a**
Molecular formula	$C_{23}H_{22}Fe_2$	$C_{46}H_{42}Cl_2Fe_4$
Formula weight (g·mol^{-1})	410.11	889.10
Temperature (K)	291	293
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)$	$P2_1/n$
a (Å)	7.383(10)	17.209(3)
b (Å)	9.967(2)	12.611(3)
c (Å)	12.967(3)	17.320(3)
α (°)	90.0	90.0
β (°)	102.77(3)	94.23(2)
γ (°)	90.0	90.0
V (Å^3)	930.6(3)	3748.6(13)
Z	2	4
D_{calc} (Mg mm^{-3})	1.464	1.575
Absorption coefficient (mm^{-1})	1.560	1.694
$F(000)$	424	1824
Radiation, λ(Å)	Mo–K$_\alpha$, 0.71073	Mo–K$_\alpha$, 0.71073
Monochromator	Graphite	Graphite
θ range (°)	1.61–25.00	1.61–25.00
Reflections collected	7585	6819
Reflections independent	3261	6585
R_{int}	0.0374	0.1779
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0274$, $wR_2 = 0.0610$	$R_1 = 0.1093$, $wR_2 = 0.2958$
R indices (all data)	$R_1 = 0.0316$, $wR_2 = 0.0623$	$R_1 = 0.1621$, $wR_2 = 0.3206$
Data/restraints/parameters	3261/1/327	6585/0/470
Refinement method	Full-matrix-least-squares on F^2	Full-matrix-least-squares on F^2
Goodness-of-fit	0.953	1.033
Mininum/maximum residual electron density (e Å^{-3})	−0.230/0.267	−0.912/1.219
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.1693P)^2 + 10.77P]$, where $P = (F_0^2 + 2Fe^2)/3$	$w = 1/[\sigma^2(F_0^2) + (0.1693P)^2 + 10.77P]$, where $P = (F_0^2 + 2Fe^2)/3$

is given in Fig. 1 and packing of the molecules on the crystals is shown in Fig. 2. An interesting feature of the crystal structure of this compound is the presence, in the unit cell, of twins molecules of chlorocyclopropanes arranged closely pairwise with oppositely directed chlorine atoms. This fact together with the low stability of compound **15a** even in the crystalline state hampered considerably the X-ray study. However, the results obtained corroborate completely the *cis*-configuration of the monohalide **15a**.

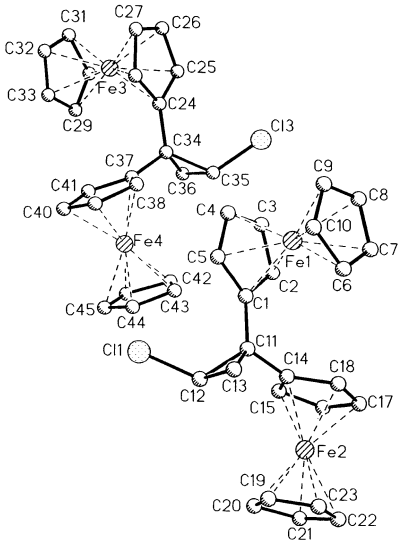


Fig. 1. Crystal structure of compound **15a**. Selected bond lengths (Å): C(11)–C(12) = 1.513(16); C(11)–C(13) = 1.540(15); C(12)–C(13) = 1.480(2); C(1)–C(11) = 1.466(17); C(11)–C(14) = 1.519(16); Cl(1)–C(12) = 1.753(15); C(34)–C(36) = 1.478(18); C(34)–C(35) = 1.520(19); C(35)–C(36) = 1.50(2). Selected bond angles (°): C(12)–C(13)–C(11) = 60.0(7); C(12)–C(11)–C(13) = 58.2(9); C(13)–C(12)–C(11) = 61.8(8); C(13)–C(12)–Cl(1) = 119.1(11); C(11)–C(12)–Cl(1) = 122.5(10); C(1)–C(11)–C(14) = 113.4(9); C(1)–C(11)–C(13) = 120.9(11); C(12)–C(11)–C(14) = 113.9(10); C(36)–C(34)–C(35) = 60.1(9); C(36)–C(35)–C(34) = 58.6(9); C(34)–C(36)–C(35) = 61.3(9).

The three-membered ring in the structure **15a** represents a scalene triangle (Fig. 1). The lengths of the C(11)–C(13) and C(34)–C(35) bonds are somewhat larger [1.540(15) and 1.520(19) Å], while those of the C(12)–C(13) and C(34)–C(36) bonds are somewhat smaller [1.480(2) and 1.478(18) Å, respectively], than the standard values (the typical C–C bond length in cyclopropanes being ~1.51 Å [15,16]). The angles of rotations of the cyclopentadiene ring planes of the Fc^1 and Fc^2 fragments correspond to the 'bisecting' and 'non-bisecting' positions relative to the three-membered ring planes, the former being in *cis*-orientation with respect to the chlorine atom. The Fe–C bond lengths and the geometry of the ferrocene sandwiches demonstrate no deviations from the ordinary ones [4].

The spatial orientation of the ferrocenyl substituents at C(1) of the cyclopropane ring was additionally confirmed by X-ray diffraction analysis of single crystals of 1,1-diferrocenylcyclopropane **14** obtained by crystallization from ether (Table 1). The general view of the molecule **14** is shown in Fig. 3 and its crystal packing is presented in Fig. 4. The geometrical parameters, the interatomic distances, and bond angles are given in the legend to Fig. 3 and do not require any additional comments. The ferrocenyl substituent Fc^1 occupies the 'bisecting' position, and Fc^2 occupies the 'non-bisecting' position relatively to the small ring plane (Fig. 4), as this is observed in the molecule **15a**.

Dehydrohalogenation of the diferrocenyl(halogeno)cyclopropanes **15a**,**b** and **16a**,**b** under the action of Bu^tOK in DMSO [1–4,12] resulted in a low yield (~20%) of 3,3-diferrocenylcyclopropene **1d**. Three by-products were also isolated, viz. 3-ferrocenyl-1*H*-cyclopentaferrocene **7b** (~30–40%), 1,1-diferrocenylpropene

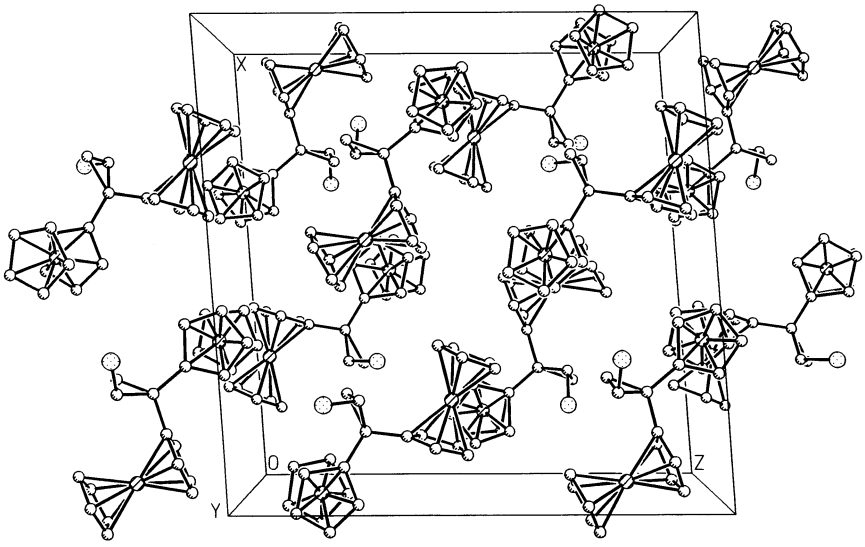


Fig. 2. Crystal packing of **15a**.

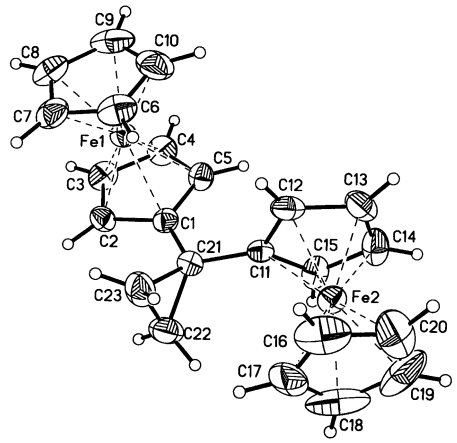
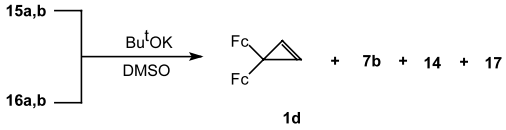
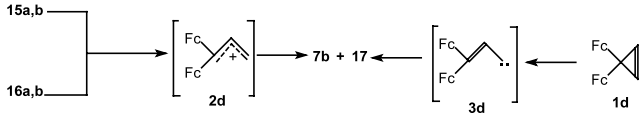


Fig. 3. Crystal structure of compound **14**. Selected bond lengths (Å): C(21)–C(22) = 1.512(4); C(21)–C(23) = 1.516(4); C(22)–C(23) = 1.494(5); C(1)–C(21) = 1.516(4); C(11)–C(21) = 1.560(4); C(11)–C(12) = 1.439(4); C(1)–C(5) = 1.420(5). Selected bond angles (°): C(23)–C(22)–C(21) = 60.55(19); C(22)–C(23)–C(21) = 60.3(2); C(22)–C(21)–C(23) = 59.1(2); C(1)–C(21)–C(11) = 115.4(2); C(12)–C(11)–C(21) = 129.1(2); C(5)–C(1)–C(21) = 124.4(3); C(2)–C(1)–C(21) = 128.2(4); C(22)–C(21)–C(11) = 119.1(2).



Scheme 6.



Scheme 7.

17 (~ 10–20%), and 1,1-diferrocenylcyclopropane **14** (~ 15–20%) (Scheme 6).

The cyclopropene **1d** is a pale-yellow crystalline compound, which decomposes rapidly on storage under ordinary conditions. In solutions, even at 0 °C, this isomerizes into compounds **7b** (up to 55%) and **17** (~ 15%). Our attempts to grow crystals of the cyclopropene **1d** and perform X-ray diffraction analysis of its spatial structure failed. However, a comparative analysis of spatial structures of the known 1-aryl-2-bromo-1-ferrocenylcyclopropanes, 1-aryl-1-ferrocenylcyclopropanes and the derived 3-aryl-3-ferrocenylcyclopropenes [1–4], taking into account the known data on the considerable steric effects at the C(3) atom of the cyclopropene ring [17–19] (even in 3,3-dimethylcyclopropene), allows us to suggest that the spatial orientation of the ferrocenyl substituents in 3,3-diferrocenylcyclopropene (**1d**) is the same as in the parental monohalides **15a**,**b** and **16a**,**b**.

Compounds **7b** and **17** seen to result from the three-membered ring-opening in the monohalides **15** and **16** under the action of Lewis acids (magnesium and titanium salts) yielding 1,1-diferrocenylallylic cation (**2d**) and from the low-temperature thermolysis of the cyclopropene **1d** to yield diferrocenylcarbenoid (**3d**) (Scheme 7).

These transient species are stabilized by two ferrocenyl substituents and one of them, viz., the 'non-bisecting' one, undergoes intramolecular alkylation. Alternatively, these intermediates undergo reduction. Analogous reduction has been observed by us previously [1–4,9–12] and seems to involve the iron atom.

Thus, the results of this study confirm the 'non-bisecting' orientation of one ferrocene substituent in *gem*-diferrocenylcyclopropene **1d** and monohalogenocyclopropanes **15** and **16**. Intramolecular transformations of this compounds occur with high regioselectivities and result predominantly in the alkylation product of the

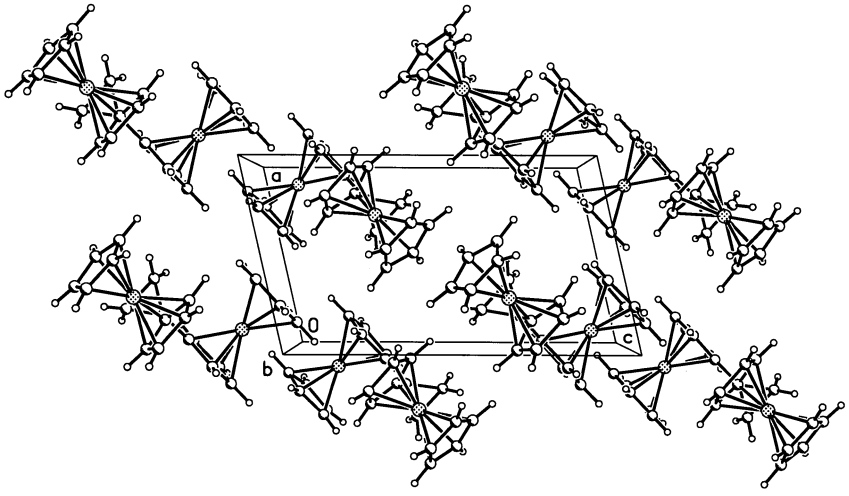


Fig. 4. Crystal packing of **14**.

'non-bisecting' ferrocenyl substituent, i.e. 3-ferrocenyl-1*H*-cyclopentaferrocene (**7b**).

3. 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. Isolation of compounds was 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 1. The chemical reactions were carried out in an atmosphere of dry argon and in absolute grade solvents.

The following reagents were purchased from Aldrich: ferrocenecarboxylic acid (97%), ferrocene (98%), methyllithium (1.4 M solution in diethyl ether), ethylmagnesium chloride (2.0 M solution in diethyl ether), titanium(IV) isopropoxide (97%), Bu^{t}OK (95%), and phosphorus pentachloride (95%).

3.1. Diferrocenylketone (*10*)

Phosphorus pentachloride (6.9 g) was added portionwise to a suspension of ferrocenecarboxylic acid (6.9 g, 0.03 mol) in dry benzene (80 ml), the mixture was stirred for 20 min at room temperature (r.t.), and the solvent was removed in vacuo. The residue (orange oil) was dissolved in dichloromethane (200 ml) containing ferrocene (6.6 g, 0.035 mol). This solution was added dropwise over ~1 h to a suspension of $AlCl_3$ (4.0 g, 0.03 mol) in dichloromethane (200 ml), the mixture was stirred for 1 h at 20 °C, and poured into ice water (500 ml). The organic layer was separated, washed with water and the solvent was evaporated in vacuo. The residue was crystallized from isopropyl alcohol to give orange crystals of differocenyl ketone, yield 5.2 g (50%), m.p. 203–204 °C (lit. m.p. 204 °C [13]). ^{1}H-NMR (δ): 4.20 (10H, s, $2C_5H_5$), 4.53 (4H, m, C_5H_4), 4.99 (4H, m, C_5H_4).

3.2. 1,1-Diferrocenylethanol (*11*)

An ethereal solution of methyllithium (0.03 mol) was added with stirring to a solution of diferrocenyl ketone (**10**) (4.0 g. 0.01 mol) in dry benzene (100 ml) and stirring was continued for an additional 1 h. The reaction mixture was then treated with 50% aqueous (aq.) NaOH, the organic layer was separated, washed with water, and dried with Na_2SO_4. The solvent was removed in vacuo and the residue was crystallized from propan-1-ol to yield 2.92 g (70%) of the alcohol **11** as yellow crystals, m.p. 221–223 °C. ^{1}H-NMR (δ): 1.88 (3H, s, CH_3), 2.59 (1H, s, OH), 4.09 (4H, m, C_5H_4), 4.11 (4H, m, C_5H_4), 4.19 (10H, s, 2 C_5H_5). Anal. Calc. for $C_{22}H_{22}Fe_2O$: C, 63.80; H, 5.36; Fe, 26.98. Found: C, 63.67; H, 5.48; Fe, 27.11%.

3.3. 1,1-Diferrocenylethylene (*12*)

Alumina (50 g, Brockmann activity II) was added to a solution of the alcohol **11** (4.14 g, 0.01 mol) in chloroform (50 ml) and the mixture was kept for a day in a hood. The red-colored alumina was applied onto a 30-cm layer of pure alumina (Brockmann activity III) and the alkene **12** was eluted with hexane, yield 2.8 g (70%), red crystals, melting point (m.p.) 163–164 °C. ^{1}H-NMR (δ): 4.15 (10H, s, $2C_5H_5$), 4.27 (4H, m, C_5H_4), 4.62 (4H, m, C_5H_4), 5.42 (2H, s, CH_2=) Anal. Calc. for $C_{22}H_{20}Fe_2$: C, 66.71; H, 5.09; Fe, 28.20. Found: C, 66.54; H, 5.27; Fe, 28.41%.

3.4. 2,2-Dichloro-1,1-diferrocenylcyclopropan (*8a*) [14]

A solution of 1,1-diferrocenylethylene (**12**) (3.96 g, 0.01 mol) in chloroform (40 ml) was mixed with 50% aq. NaOH (40 ml), dichloromethane (100 ml), and benzyltriethylammonium chloride (1 g). The mixture was stirred whereupon spontaneous boiling up occurred. Stirring was continued for 1 h and the mixture was poured into ice water (200 ml). The organic layer was washed with water, dried with $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on alumina in hexane to give compound **8a** in a yield of 3.21 g (67%), yellow powder, decomposes at ~178 °C. ^{1}H-NMR (δ): 2.24 (2H, s, CH_2), 4.00 (2H, m, C_5H_4), 4.13 (5H, s, C_5H_5), 4.14 (5H, s, C_5H_5), 4.16 (2H, m, C_5H_4), 4.175 (2H, m, C_5H_4), 4.195 (2H, m, C_5H_4). Anal. Calc. for $C_{23}H_{20}Cl_2Fe_2$: C, 57.66; H, 4.20; Cl, 14.82; Fe, 23.32. Found: C, 57.87; H, 4.08; Cl, 14.73; Fe, 23.49%.

3.5. 2,2-Dibromo-1,1-diferrocenylcyclopropane (*8b*) [12,20,21]

Bromoform (15 ml) was added dropwise to a vigorously stirred mixture of 50% aq. NaOH, benzyltriethylammonium chloride (0.5 g), and 1,1-diferrocenylethylene (**12**) (4.0 g, 0.01 mol) at 25–35 °C. Then the mixture was stirred for 4 h at r.t. and poured into ice water (300 ml). The reaction products were extracted with chloroform (3 × 100 ml), the extract was dried with Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on alumina in hexane to yield 1.83 g (32%) of the dibromide **8b** as yellow crystals, which darkened in air rapidly, decomposes at ~130 °C. ^{1}H-NMR (δ): 2.37 (2H, s, CH_2), 4.05 (2H, m, C_5H_4), 4.116 (5H, s, C_5H_5), 4.123 (5H, s, C_5H_5), 4.18 (4H, m, C_5H_4), 4.25 (2H, m, C_5H_4). ^{13}C-NMR (δ): 32.46 (C), 36.19 (CH_2), 37.53 (C), 66.08 (2C), 66.74 (2C),

69.63, 69.96, 70.60, 71.45 ($2C_5H_4$), 69.38, 69.41 ($2C_5H_5$), 94.20, 94.36 ($2C_{ipso}$ Fc). Anal. Calc. for $C_{23}H_{20}Br_2Fe_2$: C, 48.64; H, 3.55; Br, 28.14; Fe, 19.67. Found: C, 48.49; H, 3.71; 28.23; Fe, 19.51%.

3.6. Solvolysis of 2,2-dibromo-1,1-diferrocenylcyclopropane (*8b*)

A solution of the dibromide **8b** (0.57 g, 0.001 mol) in a mixture of chloroform (10 ml) and pyridine (0.5 ml) was kept at r.t. for 7 days. The solvent was evaporated in vacuo and the residue was subjected to TLC on alumina in hexane to give 0.17 g (41%) of 1,1-diferrocenylallene (**13**), R_f 0.78, yellow crystals, m.p. 128–129 °C. ^{1}H-NMR (δ): 3.96 (5H, s, C_5H_5), 4.03 (5H, s, C_5H_5), 4.10 (2H, s, CH_2=), 4.28 (2H, m, C_5H_4), 4.286 (2H, m, C_5H_4), 4.293 (2H, m, C_5H_4), 4.97 (2H, m, C_5H_4). ^{13}C-NMR (δ): 66.87, 67.31, 70.67, 70.97 ($2C_5H_4$), 69.52, 69.68 ($2C_5H_5$), 87.85, 88.74 ($2C_{ipso}$ Fc), 112.56 (CH_2=), 116.55, 124.69 (2C). Anal. Calc. for $C_{23}H_{20}Fe_2$: C, 67.70; H, 4.93; Fe, 27.37. Found: C, 67.56; H, 5.08; Fe, 27.54%.

3.7. Reduction of the dihalides *8a* and *8b*

A solution of EtMgCl (6 mmol) in ether and several drops of $Ti(OPr^i)_4$ were added with stirring to a solution of the dichloride **8a** (2.4 g, 5.0 mmol) or the dibromide **8b** (2.84 g, 5.0 mmol) in dry tetrahydrofuran (100 ml). The mixture was stirred for 3 h at r.t. and quenched with water (50 ml). The organic layer was separated, washed with water, dried with Na_2SO_4, and concentrated in vacuo and the residue was subjected to TLC on silica-gel (hexane–ether, 10:1).

The following products were obtained from the dichloride **8a**: 1,1-diferrocenylcyclopropane (**14**), 0,26 g (13%), R_f 0.75, yellow crystals, m.p. 147–149 °C. ^{1}H-NMR (δ): 1.20 (4H, s, $2CH_2$), 3.94 (4H, m, C_5H_4), 4.05 (4H, m, C_5H_4), 4.10 (5H, s, C_5H_5), 4.11 (5H, s, C_5H_5). ^{13}C-NMR (δ): 17.82 (C), 19.24 ($2CH_2$), 66.69, 67.52 ($2C_5H_4$), 68.40 ($2C_5H_5$), 96.78 ($2C_{ipso}$ Fc). Anal. Calc. for $C_{23}H_{22}Fe_2$: C, 67.36; H, 5.40; Fe, 27.24. Found: C, 67.49; H, 5.27; Fe, 27.37%.

1,1-Diferrocenylpropene (**17**), 0.2 g (10%), R_f 0.68, yellow crystals, m.p. 136–138 °C. ^{1}H-NMR (δ): 1.98 (3H, d, $J = 7.5$ Hz, CH_3), 4.09 (5H, s, C_5H_5), 4.13 (5H, s, C_5H_5), 4.18 (1H, m, C_5H_4), 4.23 (1H, m, C_5H_4), 4.49 (3H, m, C_5H_4), 4.51 (3H, m, C_5H_4), 6.23 (1H, q, $J = 7.5$ Hz, CH=). ^{13}C-NMR (δ): 19.22 (CH_3), 67.19, 67.39, 68.17, 69.71 (2 C_5H_4), 69.21, 69.32 (2 C_5H_5), 84.38, 90.41 (2 C_{ipso} Fc), 123.27 (CH=), 133.46 (C=). Anal. Calc. for $C_{23}H_{22}Fe_2$: C, 67.36; H, 5.40; Fe, 27.24. Found: C, 67.54; H, 5.18; Fe, 27.43%.

Z-2-chloro-1,1-diferrocenylcyclopropane (**15a**), 0.25 g (11%), R_f 0.60, yellow crystals, decomposes at ~162 °C. ^{1}H-NMR (δ): 1.33 (1H, dd, $J = 4.8$, 5.7 Hz, CH_2), 1.90 (1H, dd, $J = 5.7$, 7.5 Hz, CH_2), 3.94 (1H, dd, $J = 4.8$, 7.5 Hz, CH), 3.83 (1H, m, C_5H_4), 4.01 (1H, m, C_5H_4), 4.04 (1H, m, C_5H_4), 4.05 (5H, s, C_5H_5), 4.07 (1H, m, C_5H_4), 4.16 (5H, s, C_5H_5), 4.18 (1H, m, C_5H_4), 4.21 (3H, m, C_5H_4). ^{13}C-NMR (δ): 24.46 (CH_2), 25.25 (C), 43.68 (CH), 66.50, 67.00, 67.20, 67.42, 67.83, 68.01, 68.87, 69.03 (2 C_5H_4), 68.53, 68.69 ($2C_5H_5$), 90.26, 94.96 ($2C_{ipso}$ Fc). Anal. Calc. for $C_{23}H_{21}ClFe_2$: C, 62.13; H, 4.76; Cl, 7.99; Fe, 25.12. Found: C, 62.24; H, 4.58; Cl, 8.12; Fe, 25.21%.

E-2-chloro-1,1-diferrocenylcyclopropane (**15b**), 0.2 g (9%), R_f 0.54, yellow crystals, decomposes at ~170 °C. ^{1}H-NMR (δ): 1.40 (1H, dd, $J = 2.7$, 7.3 Hz, CH_2), 1.69 (1H, dd, $J = 4.2$, 7.3 Hz, CH_2), 3.92 (1H, dd, $J = 2.7$, 4.2 Hz, CH), 4.03 (2H, m, C_5H_4), 4.06 (2H, m, C_5H_4), 4.08 (5H, s, C_5H_5), 4.12 (5H, s, C_5H_5), 4.16 (2H, m, C_5H_4), 4.21 (2H, m, C_5H_4). Anal. Calc. for $C_{23}H_{21}ClFe_2$: C, 62.13; H, 4.76; Cl, 7.99; Fe, 25.12. Found: C, 61.97; H, 4.99; Cl, 7.84; Fe, 25.27%.

3-Ferrocenyl-1*H*-cyclopentaferrocene (**7b**), 0.7 g (33%), R_f 0.36, orange crystals, m.p. 153–154 °C. ^{1}H-NMR (δ): 2.80 (2H, d, $J = 7.3$ Hz, CH_2), 4.11 (5H, s, C_5H_5), 4.15 (5H, s, C_5H_5), 4.20 (2H, m), 4.24 (2H, m), 4.26 (1H, m), 4.55 (2H, m) (C_5H_3, C_5H_4), 6.20 (1H, t, $J =$ 7.3 Hz, CH=). ^{13}C-NMR (δ): 30.59 (CH_2), 67.32, 67.55, 68.33, 68.55, 69.24, 69.53, 69.77 (C_5H_4, C_5H_3), 69.29, 69.44 ($2C_5H_5$), 84.45, 90.27, 98.73 ($3C_{ipso}$ Fc), 128.95 (CH=), 133.38 (C). Anal. Calc. for $C_{23}H_{20}Fe_2$: 67.69; H, 4.94; Fe, 27.37. Found: C, 67.82; H, 4.79; Fe, 27.49%.

The following products were obtained from the dibromide **8b**: 1,1-diferrocenylcyclopropane (**14**), 0,37 g (18%), m.p. 148 °C; 1,1-diferrocenylpropene (**17**) 0.24 g (12%), m.p. 137–138 °C; *Z*-2-bromo-1,1-diferrocenylcyclopropane (**16a**), 0.4 g (16%), R_f 0.56, yellow powder, decomposes at ~163 °C. ^{1}H-NMR (δ): 1.34 (1H, dd, $J = 4.8$, 5.9 Hz, CH_2), 1.89 (1H, dd, $J = 5.9$, 7.6 Hz, CH_2), 3.92 (1H, dd, $J = 4.8$, 7.6 Hz, CH), 3.82 (1H, m, C_5H_4), 4.00 (1H, m, C_5H_4), 4.02 (1H, m, C_5H_4), 4.03 (5H, s, C_5H_5), 4.06 (1H, m, C_5H_4), 4.17 (5H, s, C_5H_5), 4.19 (1H, m, C_5H_4), 4.21 (3H, m, C_5H_4). Anal. Calc. for $C_{23}H_{21}BrFe_2$: Br, 16.34; C, 56.50; H, 4.33; Fe, 22.83. Found: Br, 16.18; C, 56.34; H, 4.58; Fe, 22.99%; *E*-2-bromo-1,1-diferrocenylcyclopropane (**16b**), 0.34 g (14%), R_f 0.45, yellow powder, decomposes at ~168 °C. ^{1}H-NMR (δ): 1.42 (1H, dd, $J = 3,5$, 6.0 Hz, CH_2), 1.69 (1H, dd, $J = 6.0$, 7.5 Hz, CH_2), 3.92 (1H, dd, $J = 3.5$, 7.5 Hz, CH), 4.00 (2H, m, C_5H_4), 4.04 (2H, m, C_5H_4), 4.10 (5H, s, C_5H_5), 4.14 (5H, s, C_5H_5), 4.18 (2H, m, C_5H_4), 4.22 (2H, m, C_5H_4). Anal. Calc. for $C_{23}H_{21}BrFe_2$: Br, 16.34; C, 56.50; H, 4.33; Fe, 22.83. Found: Br, 16.12; C, 56.73; H, 4.52; Fe, 22.68%; 3-ferrocenyl-1*H*-cyclopentaferrocene (**7b**), 0.61 g (30%), m.p. 154 °C.

3.8. Dehydrohalogenation of diferrocenyl(halogeno)-cyclopropanes (*15a,b*) and (*16a,b*)

A mixture of a diferrocenyl(halogeno)cyclopropane **15a**, **15b**, **16a**, or **16b** (3 mmol) and Bu^tOK (4 mmol) in

Me_2SO (30 ml) was stirred for 7 h at ~35–45 °C. Benzene (100 ml) and water (50 ml) were then added, the organic layer was washed with water and concentrated in vacuo. The residue was subjected to TLC on alumina in hexane to give:

1,1-diferrocenylcyclopropane (**14**), yield 0.18–0.25 g (15–20%), R_f 0.70, m.p. 147–149 °C.
3,3-Diferrocenylcyclopropene (**1d**), yield 0.20–0.25 g (18–21%), R_f 0.64, yellow powder, m.p. 131–132 °C. ^{1}H-NMR (δ): 3.80 (4H, m, C_5H_4), 3.94 (4H, m, C_5H_4), 4.06 (5H, s, C_5H_5), 4.08 (5H, s, C_5H_5), 6.96 (2H, s, CH=). Anal. Calc. for $C_{23}H_{20}Fe_2$: C, 67.69; H, 4.94; Fe, 27.37. Found: C, 67.86; H, 5.04; Fe, 27.13%.
1,1-Diferrocenylpropene (**17**), yield 0.12–0.24 g (10–20%), R_f 0.57, m.p. 137 °C.
3-Ferrocenyl-1*H*-cyclopentaferrocene **7**, yield 0.36–0.48 g (30–40%), R_f 0.30, m.p. 154 °C.

3.9. Thermolysis of 3,3-diferrocenylcyclopropene (*1d*)

A solution of the cyclopropene **1d** (0.4 g, 1 mmol) in benzene (50 ml) was stirred for 1 h at ~20 °C. The solvent was evaporated in vacuo, and the residue was subjected to TLC on silica-gel (hexane–ether, 10:1) to give 0.06 g (15%) of the alkene **17**, R_f 0.70, m.p. 136–138 °C, and compound **7b**, yield 0.25 g (61%), R_f 0.40, m.p. 154 °C.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 186890 and 178187 for compounds **14** and **15a**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambrige CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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