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Synthesis of stable 1-ethoxy-2,3-diferrocenylcyclopropenylium tetrafluoroborate and its reactions with lithium reagents

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Abstract

1-Ethoxy-2,3-diferrocenylcyclopropenylium tetrafluoroborate selectively reacts with MeLi, *n*-BuLi, *sec*-BuLi with formation of the 3,3-dialkyl-1,2-diferrocenylcyclopropenes, while with *tert*-BuLi both 2-*tert*-butyl-1,3-diferrocenylcyclopropene and 1,3-di-*tert*-butyl-2,3-diferrocenylcyclopropene are obtained. The structures of 3,3-dimethyl-, 3,3-dibutyl-1,2-diferrocenyl and 2-*tert*-butyl-1,3-diferrocenylcyclopropenes were confirmed by X-ray crystallographic analysis.

Keywords: Cyclopropenylium cation; Cyclopropenes; Ferrocene

1. Introduction

Since the first syntheses of cyclopropenone by Breslow and Vol'pin [1,2] in 1959, several publications have appeared describing properties and reactions of this interesting small ring [3]. Later, the reaction of trichlorocyclopropenylium tetrachloroaluminate **1** with benzene reported by West [4] has led to 2,3-diphenylcyclopropenone **2** (Scheme 1). This facile method has been used to afford a great variety of cyclopropenones and cyclopropenylium derivatives [5–7].

It was found that the cyclopropenone **1** yielded 1-ethoxy-2,3-diphenylcyclopropenylium tetrafluoroborate **3** upon alkylation with triethyloxonium fluoroborate, which is able to react with secondary amines, thiols, bases, transition metal and diazo compounds [8].

It is known that the introduction of ferrocenyl substituents into the three-membered cyclopropene ring markedly changes its properties, as was observed in the case of 3-ferrocenylcyclopropenes [9–12].

Recently, the synthesis of diferrocenyl cyclopropenone (**4**) has been performed in our group. It was found that its reaction with ethyl- and benzylmagnesium chlorides afford not only 3,3-diethyl- and 3,3-dibenzyl-1,2-diferrocenylcyclopropenes (**4a** and **4b**), respectively, but also products of nucleophilic opening of the three-membered ring resulting from the addition of RMgCl to the carbonyl group (**5** and **6**) (Scheme 2). Similar behavior of diferrocenylcyclopropenone was also observed in its reactions with methyl and phenyllithium [13,14].

In continuation of our investigations into the chemistry of diferrocenyl cyclopropenes, we report the synthesis of stable 1-ethoxy-2,3-diferrocenyl cyclopropenylium tetrafluoroborate, and its behavior in the reactions with organolithium reagents.

2. Results and discussion

Diferrocenylcyclopropenone (**4**) was synthesized following the previously described methodology [13]. Treatment

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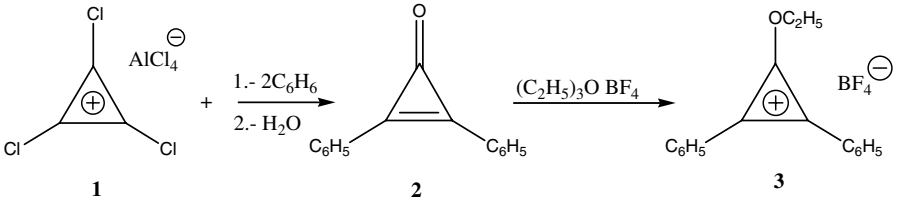
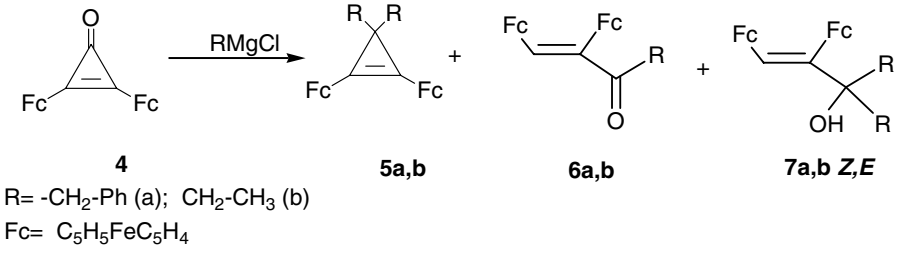


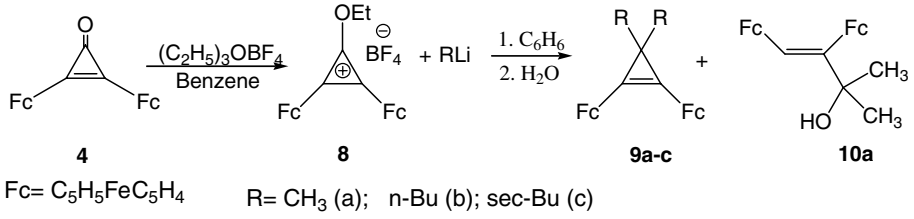
Scheme 1.



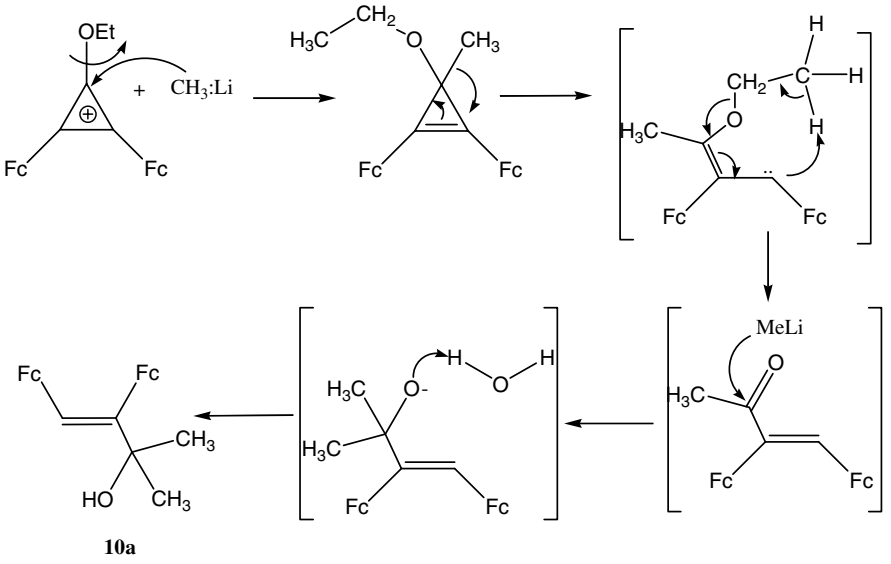
Scheme 2.

of diferrocenylcyclopropenone with triethyloxonium tetrafluoroborate in benzene and precipitation of the resulting product with diethyl ether affords crystalline 1-ethoxy-2,3-diferrocenylcyclopropenylium terafluoroborate (**8**) (Scheme 3).

The cyclopropenylium tetrafluoroborate (**8**) was characterized by ^{1}H NMR spectroscopy (for a solution of CD_2Cl_2), it manifest high stability in the crystalline state as it was stored at room temperature for a long period of time.



Scheme 3.



Scheme 4.

In the spectrum of the compound (**8**) the following signals were observed: a triplet at δ 2.96 ($J = 7.0$ Hz) assigned to the CH_3 group and a quadruplet at δ 6.48 ($J = 3.0$ Hz) ascribed to the CH_2 group. The characteristic signals for the ferrocenyl units were significantly shifted to lower fields. Thus, the signals for the C_5H_5 and C_5H_4 moieties observed in the ^{1}H NMR spectrum of the starting diferrocenylcyclopropenone (**4**) at δ 4.25 (C_5H_4) and δ 4.58 and 4.84 (C_5H_4) were shifted to δ 6.12 (C_5H_4) and at δ 6.62, 6.83 (C_5H_4) in the spectrum of the cation **8**.

The action of alkyllithium reagents on diferrocenylcyclopropenylium tetrafluoroborate **8**, affords the corresponding 1,2,3-substituted cyclopropenes **9a**–**c** and in the case of methyllithium, the product of opening of the three-membered ring **10a** (Scheme 3).

It is quite obvious that the carbinol **10a** resulted from small cycle opening. It seems probably obtained by the formation of the vinylcarbene intermediate (Scheme 4), and the addition of the other molecule of MeLi to this intermediate and when it is treated with water wives the carbinol **10a**.

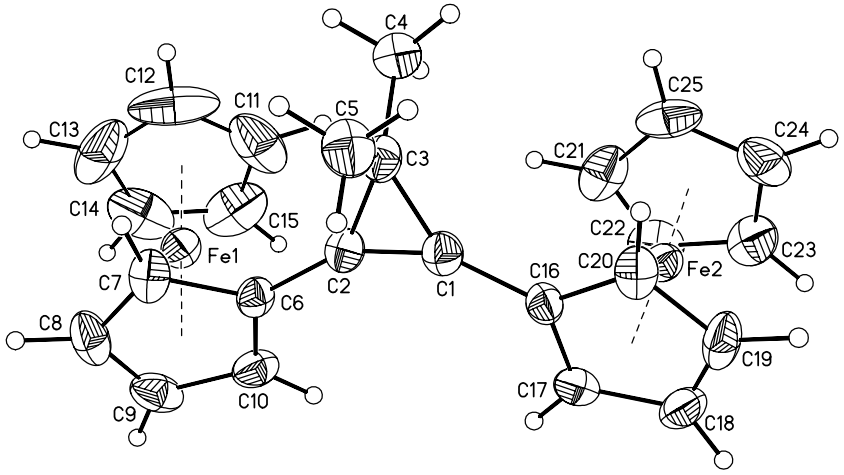


Fig. 1. Crystal structure of compound **9a**. The probability level of the thermal ellipsoid was 40%. Selected bond lengths (Å): C(1)–C(2) 1.291 (3); C(1)–C(3) 1.504 (3); C(2)–C(3) 1.499 (3); C(2)–C(6) 1.438(3); C(3)–C(4) 1.502 (4); C(3)–C(5) 1.511 (3).

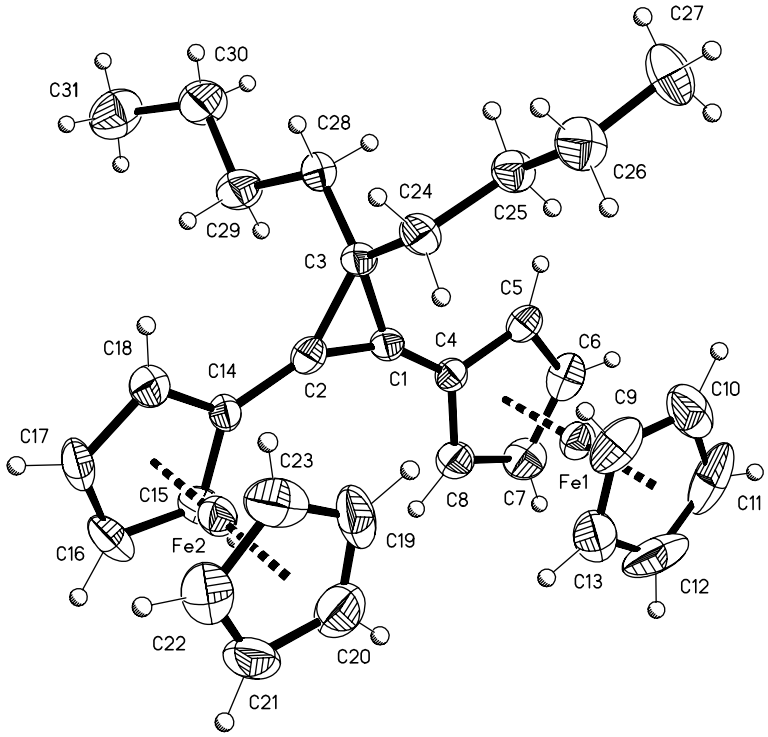


Fig. 2. Crystal structure of compound **9b**. The probability level of the thermal ellipsoid was 30%. Selected bond lengths (Å): C(1)–C(2) 1.313 (4); C(1)–C(3) 1.503 (5); C(2)–C(3) 1.500 (4); C(1)–C(4) 1.420(4); C(3)–C(24) 1.530 (4); C(3)–C(28) 1.513 (4); C(2)–C(14) 1.444 (4).

The structure of the 1,2-diferrocenyl-3,3-dimethylcyclopropene **9a**, was established based on the ^{1}H NMR spectroscopy and X-ray diffraction analysis, and is shown in Fig. 1.

Crystals of 3,3-dibutyl-1,2-diferrocenylcyclopropene (**9b**) were obtained by crystallization from hexane and also were suitable for X-ray crystallographic studies. Fig. 2 shows the crystal structure of the compound (**9b**).

A comparison of the structures in Figs. 1 and 2 shows that in both cases the ferrocenyl substituents occupy the non-bisecting position relative to the small ring plane. However in the case of the 1,2-diferrocenyl-3,3-dimethylcyclopropene (**9a**) the ferrocenyl groups are oriented towards the C3 atom of the small cycle, whereas in the case of the 3,3-dibutyl-1,2-diferrocenylcyclopropene **9b** these are arranged perpendicular to the small ring plane.

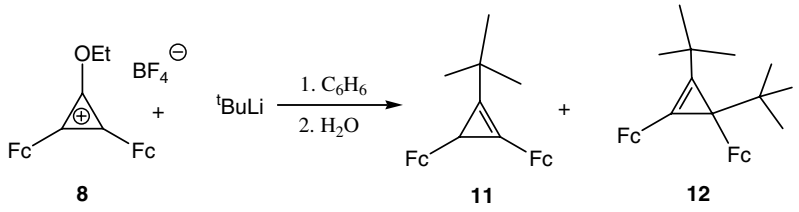
The reaction of diferrocenylcyclopropenylium tetrafluoroborate (**8**) with *tert*-butyllithium results in 2- *tert*-butyl-1,3-diferrocenylcyclopropene (**11**), and the bisaddition product of the *tert*-butyl group, viz., compound **(12),** where the second *tert*-butyl group is located in the position 3 (Scheme 5).

2-*tert*-Butyl-1,3-diferrocenylcyclopropene (**11**) was obtained as red crystals and its structure was confirmed by X-ray diffraction analysis. The crystal structure of compound (**11**) are shown in Fig. 3. The crystallographic data, parameters of the X-ray experiment, and refinements for **9a**, **9b** and **11** are listed in Table 1.

In the ^{1}H NMR spectrum of the compound (**12**) the following signals were observed: two singlets at δ 0.93 and 1.29 for the *tert*-butyl groups, two signals at δ 4.02 and at 4.18 assigned to the C_5H_5 moiety, and four signals at δ 4.07, 4.23 and at 4.32–4.58 ascribed to the C_5H_4 group. The multiplicity in the signals confirmed the loss of the symmetry in cyclopropene (**12**).

The formation of the compound (**11**) could be rationalized as being due to the attack by the hydride anion of the *tert*-butyl on the carbon atom in position 2 (Scheme 6).

The formation of the compound (**12**) is due to the addition of the *tert*-butyl anion at the position 2 of the cyclopropenylium cation **13** (Scheme 7). The absence of the addition product of the second *tert*-butyl group at position 3 of the cyclopropene ring could be due to high steric hindrance.



Scheme 5.

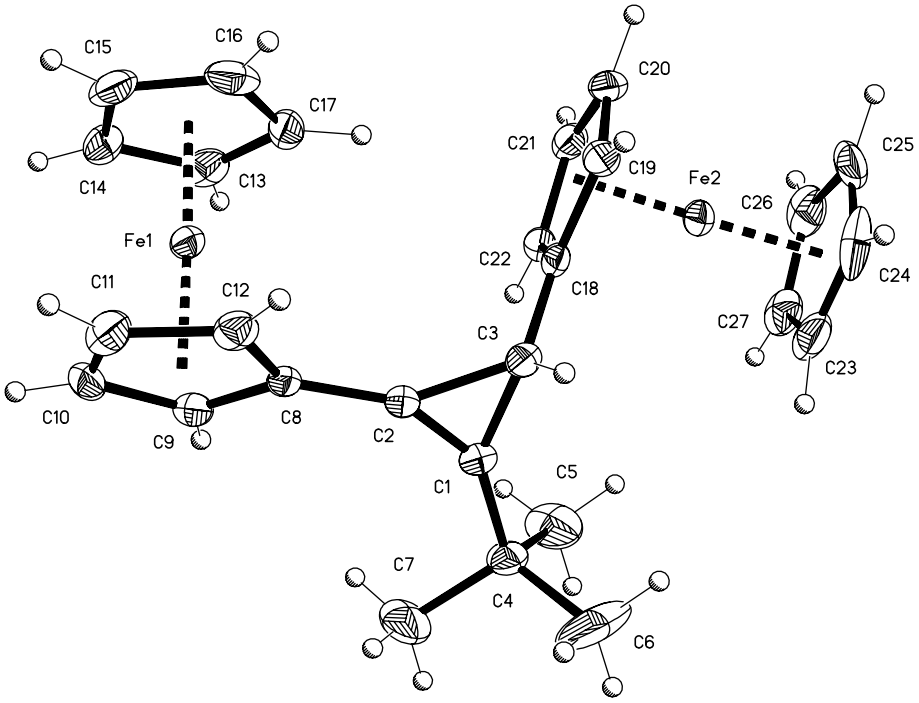
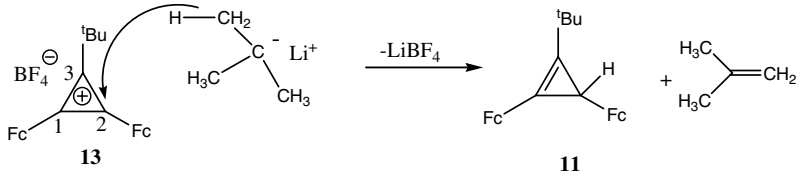


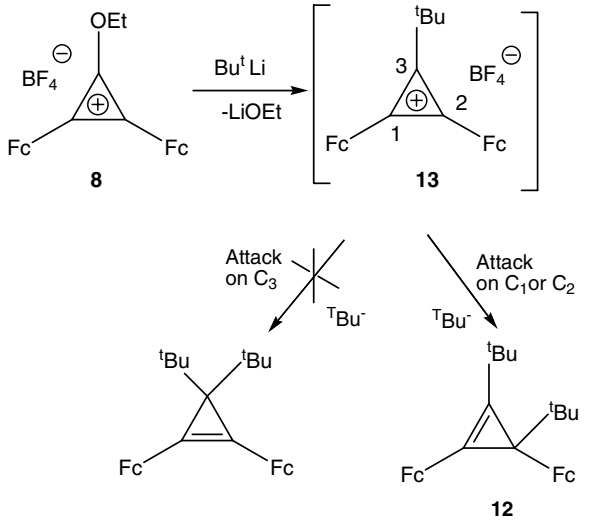
Fig. 3. Crystal structure of compound **11**. The probability level of the thermal ellipsoid was 30%. Selected bond lengths (Å): C(1)–C(2) 1.279 (5); C(1)–C(3) 1.489 (6); C(2)–C(3) 1.511 (6); C(2)–C(8) 1.433(6); C(1)–C(4) 1.496 (6); C(3)–C(18) 1.485 (6).

Table 1
Crystal data, data collection and refinement parameters for **9a**, **9b** and **11**

Data	**9a**	**9b**	**11**
Molecular formula	$C_{25}H_{24}Fe_2$	$C_{31}H_{36}Fe_2$	$C_{27}H_{28}Fe_2$
Formula weight (g mol^{-1})	436.14	520.30	464.19
Temperature (K)	291(2)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
a (Å)	14.6262(8)	10.5726(6)	5.834(1)
b (Å)	7.9589(4)	13.0146(7)	30.014(4)
c (Å)	17.0144(9)	18.709(1)	12.410(2)
α (°)	90.0	90.0	90.0
β (°)	94.965(1)	90.0	100.886(3)
γ (°)	90.0	90.0	90.0
V (Å^3)	1973.2(2)	2574.3(2)	2133.9(6)
Z	4	4	4
D_{calc} (Mg m^3)	1.468	1.342	1.445
Absorption coefficient (mm^{-1})	1.476	1.143	1.370
F(000)	904	1096	968
Radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Monochromator	Graphite	Graphite	Graphite
θ Range (°)	1.76–25.00	1.91–32.63	1.36–32.57
Reflections collected	15624	35779	29388
Reflections independent	3482	9354	7740
R_{int}	0.0402	0.0831	0.0991
Final R indices [$I > 2$ (I)]	$R_1 = 0.0355$, $wR_2 = 0.0733$	$R_1 = 0.0588$, $wR_2 = 0.0551$	$R_1 = 0.0472$, $wR_2 = 0.1375$
R indices (all data)	$R_1 = 0.0470$, $wR_2 = 0.0770$	$R_1 = 0.1870$, $wR_2 = 0.0677$	$R_1 = 0.1663$, $wR_2 = 0.1691$
Data/restraints/parameters	3482/0/246	9354/0/300	7740/0/ 265
Refinement method	Full-matrix-least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of fit	1.000	0.979	0.993
Minimum/maximum residual electron density (e Å^{-3})	0.346/−0.174	0.373/−0.624	0.648/−0.362



Scheme 6.



Scheme 7.

3. Conclusions

Treatment of 1,2-diferrocenylcyclopropenone with triethyloxonium tetrafluoroborate gives highly stable 1-ethoxy-2,3-diferrocenylcyclopropenylium tetrafluoroborate storage-stable at room temperature in the crystalline state. Its reactions with alkyllithium reagents afford alkylation products of different structures depending on RLi reagents used and products of small ring opening.

4. Experimental

Infrared (IR) spectra were recorded on a Nicolet FT-IR Magna 700 Spectrometer. ^{1}H and ^{13}C NMR spectra for solutions in $CDCl_3$ were collected on a Varian Unity operating at 300 and 75 MHz, respectively. For both ^{1}H and ^{13}C, chemical shifts are expressed in ppm relative to tetramethylsilane (Me_4Si δ 0.00) as the internal standard.

Column chromatography was carried out on alumina (Brockmann activity III). Elemental analyses were performed at Galbraith Laboratories, INC. Knoxville. USA. FAB^+ mass spectra were taken with a JEOL JMS AX505 HA mass spectrometer.

4.1. 2,3-Diferrocenylcyclopropenone (*4*)

$AlCl_3$ (0.67 g, 0.005 mol) was added by portions with stirring to a solution of ferrocene (5.6 g, 0.03 mol) and tetrachlorocyclopropene (3.6 g, 0.02 mol) in anhydrous CH_2Cl_2 (200 ml). Stirring was continued for 1 h at 20 °C, and then the mixture was poured in cold water (200 ml). The organic layer was separated, washed with water (2×50 ml), and dried with $MgSO_4$. After the solvent was distilled off in vacuo, the residue was chromatographed on Al_2O_3 using a hexane–CH_2Cl_2 (3:1) mixture as eluent. Compound **1** was obtained as orange crystals in 92% yield (5.8 g), m.p. 182–183 °C (cf. [11]: m.p. 181 °C (with decomp.)). FTIR (KBr), ν/cm^{-1}: 729, 821, 850, 887, 1003, 1100, 1109, 1480, 1602, 1825, 1850, 2917, 3100. UV–Vis (CH_2Cl_2) $\lambda_{max} = 469$, 344, 238 nm: ^{1}I NMR, (300 MHz, $CDCI_3$) δ: 4.25 (s, 10H, $2C_5H_5$); 4.58, (m, 4H, C_5H_4), 4.84 (m, 4H, C_5H_4). ^{13}C NMR, δ: 65.16 (2 C_{ipso}Fc); 70.0 (2 C_5H_5); 70.9, 71.93 (2 C_5H_4); 144.9 (2C); 152.3 (C=O). Calc. for $C_{23}H_{18}Fe_2O$ (422): C, 65.58; H, 4.28; Fe, 26.36 (%). Found: C, 65.71; H, 4.09; Fe, 26.54%.

4.2. Reaction of 2,3-diferrocenylcyclopropenone (*4*) with triethyloxonium tetrafluoroborate (*8*)

A solution of the triethyloxonium tetrafluoroborate (2.2 g, 4.0 mmol) and diferrocenylcyclopropenone (**4**) (1 g, 2.0 mmol) in benzene (50 ml) were kept at ambient temperature for 3 h. Then dry diethyl ether (100 ml) was added, the precipitate formed was filtered off, washed on a filter with several portions of dry ether, and dried in a vacuum desiccators to give 1-ethoxy-2,3-diferrocenylcyclopropenylium fluoroborate (**8**) as a dark brown powder, yield 1.17 g (92%), FTIR (KBr), ν/cm^{-1}: 2927, 2855, 1896, 1523, 1503, 1390, 1149, 870: UV–Vis (CH_2Cl_2) $\lambda_{max} = 497$, 358, 297, 236 nm: ^{1}I NMR (300 MHz, CD_2CI_2) δ: 2.96 (3H, t, $J = 7.0$, CH_3), 6.12 (10H, s, C_5H_5), 6.48 (2H, q, $J = 3.0$, CH_2), 6.62 (4H, s, C_5H_4), 6.83 (4H, s, C_5H_4). Calc. for $C_{25}H_{23}OBF_4Fe_2$ (538): C, 55.81; H, 4.31. Found: C, 55.823; H, 4.30%.

4.3. Reaction of 1-ethoxy-2,3-diferrocenylcyclopropenylium tetrafluoroborate (*8*) with methyllithium

A 1.6 M solution of methyllithium in diethyl ether (8.0 ml) was added with stirring in an inert atmosphere to a solution of **8** (1.00 g, 1.85 mmol) in dry benzene (200 ml). The mixture was stirred for 3 h at ambient temperature and then water (100 ml) was added. The organic layer was separated, washed with water (250 ml), the solvent was removed in vacuum, and the residue was chromatographed on alumina (hexane–diethyl ether, 3:1) to give dimethylcyclopropene **9a** and the alcohol **10a.**

4.4. 1,2-Diferrocenyl-3,3-dimethylcyclopropene (*9a*)

Orange crystals yield, 0.520 g (64%), m.p. 132–133 °C (lit. [6]: m.p. 132–133 °C); FTIR (KBr), ν/cm^{-1}: 3093, 2922, 2852, 1711, 1640, 1449, 1411, 1373,1218, 1105, 1001, 817, 756: UV–Vis (CH_2Cl_2) $\lambda_{max} = 456$, 236 nm: (300 MHz, CD_2CI_2) δ: 1.33 (6H, s, CH_3), 4.17 (10H, s, C_5H_5), 4.41 (4H, s, C_5H_4) 4.50 (4H, s, C_5H_4). ^{13}C NMR, (75 MHz, $CDCl_3$) δ: 28.24 (C), 29.65 (CH_3), 67.99 (C_5H_4), 69.70 (C_5H_4), 69.81 (2 C_5H_5), 76.06 (2 C_{ipso}Fc); 110.9 (C=); 119.65 (C=). Calc. for $C_{25}H_{24}Fe_2$ (436): C, 68.80; H, 5.50; Fe, 25.68. Found: C, 68.87; H, 5.53; Fe, 25.68%.

4.5. 3,4-Diferrocenyl-2-methylbut-3-en-2-ol (*10a*)

Orange crystals, yield 0.125 g (15%), m.p. 132–133 °C. FTIR (KBr), ν/cm^{-1}: 3095, 2920, 2850, 1646, 1440, 1401, 1363, 1218, 1001, 756: UV–Vis (CH_2Cl_2) $\lambda_{max} = 452$, 231 nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.63 (s, 6H, $2CH_3$), 3.66 (m, 2H, C_5H_4), 3.97 (s, 5H, C_5H_5), 4.00 (m, 2H, C_5H_4), 4.07 (m, 2H, C_5H_4), 4.25 (s, 5H, C_5H_5), 4.42 (m, 2H, C_5H_4), 5.03 (br. s, 1H, OH), 6.27 (s, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 30.18 (2 CH_3), 68.24, 68.46, 69.50, 71.53 (2 C_5H_4), 68.97, 69.40 (2 C_5H_5), 72.47 (C), 81.74, 83.75 (2 C_{ipso}Fc), 125.52 (CH), 138.32 (C): Calc. for $C_{25}H_{26}Fe_2O$ (454): C 66.11; H 5.77; Fe 24.60. Found: C, 65.97; H, 5.93; Fe, 24.38%.

4.6. 3,3-Dibutyl-1,2-diferrocenylcyclopropene (*9b*)

A 2.5 M solution of butyllithium in hexane (5.0 ml) was added with stirring in an inert atmosphere to a solution of **8** (1.00 g, 1.85 mmol) in dry benzene (200 ml). The mixture was stirred for 3 h at ambient temperature and then water (100 ml) was added. The organic layer was separated, washed with water (250 ml), the solvent was removed in vacuum, and the residue was chromatographed on alumina (hexane–diethyl ether, 3:1) to give 3,3-dibutyl-1,2-diferrocenylcyclopropene **9b** as a red crystals, yield 0.832 g (86%), m.p. 113–114 °C. FTIR (KBr), ν/cm^{-1}: 3094, 2956, 2926, 2869, 1709, 1643, 1461, 1378, 1105, 1024,1001, 816: UV–Vis (CH_2Cl_2) $\lambda_{max} = 455$, 321, 279, 246 nm: ^{1}H NMR (300 MHz, $CDCl_3$)δ; 0.89–0.98 (m, 3H, CH_3), 1.50–1.05 (m, 3H, CH_3), 1.14–1.45 (m, 4H, CH_2), 1.48–1.82 (m, 4H, CH_2), 1.90–2.06 (m, 2H, CH_2), 2.41–2.67 (m, 2H, CH_2), 3.92 (s, 2H, C_5H_4), 4.00 (s, 5H, C_5H_5), 4.13 (s, 5H, C_5H_5), 4.21 (s, 2H, C_5H_4), 4.31 (s, 2H, C_5H_4), 4.45 (s, 2H, C_5H_4). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.03 (CH_3), 14.29 (CH_3), 22.73 (CH_2), 23.06 (CH_2), 23.58 (CH_2), 25.03 (CH_2), 29.94 (CH_2), 30.58 (CH_2), 37.5 (C), 68.23 (C_5H_4), 68.55 (C_5H_4), 68.76 (C_5H_4),

69.10 (C_5H_4), 69.06 (C_5H_5), 69.23 (C_5H_5), 73.59 (C_{ipso}Fc), 75.08 (C_{ipso}Fc),112.13 (C═), 133.59 (C═): Calc. for $C_{31}H_{36}Fe_2$ (520): C, 71.53; H, 6.92; Fe, 21.53. Found: C, 71.55; H, 6.95; Fe, 21.50%.

4.7. 2-sec-Butyl-1,3-diferrocenylcyclopropene (**9c**)

A 1.7 M solution of *sec*-butyllithium in cyclohexane (12.0 ml) was added with stirring in an inert atmosphere to a solution of **8** (1.00 g, 1.85 mmol) in dry benzene (200 ml). The mixture was stirred for 3 h at ambient temperature and then water (100 ml) was added. The organic layer was separated, washed with water (250 ml), the solvent was removed in vacuum, and the residue was chromatographed on alumina (hexane–diethyl ether, 3:1) to give **9c.** Red oil, yield 0.430 g (44%) FTIR (KBr), ν/cm^{-1}: 3094, 2956, 2926, 2869, 1709, 1643, 1461, 1378, 1105, 1024, 1001, 816: UV–Vis (CH_2Cl_2) $\lambda_{max} = 461$, 327, 280, 327, 247 nm: ^{1}H NMR (300 MHz, $CDCl_3$)δ: 0.86–0.92 (m, 6H, CH_3), 1.00–1.04 (m, 6H, CH_3), 1.25–1.39 (m, 2H, CH_2), 1.54–1.73 (m, 2H, CH_2), 1.88 (br, 2H, CH), 4.15 (s, 10H, C_5H_5), 4.33 (s, 4H, C_5H_4), 4.49 (s, 2H, C_5H_5), 4.54 (s, 2H, C_5H_4), ^{13}C NMR (75 MHz, $CDCl_3$) δ: 11.97 (CH_3), 12.78 (CH_3), 17.94 (CH_2), 18.96 (CH_2), 28.57 (CH), 29.94 (CH), 40.59 (C), 68.59 (C_5H_4), 68.78 (C_5H_4), 68.81 (C_5H_4), 68.98 (C_5H_5), 75.25 (C_{ipso}Fc), 111.66 (C═), 134.53 (C═): Calc. for $C_{31}H_{36}Fe_2$ (520): C, 71.53; H; 6.92; Fe, 21.53. Found: C, 71.54; H, 6.93; Fe, 21.52%.

4.8. Reaction of 1-ethoxy-2,3-diferrocenylcyclopropenylium tetrafluoroborate **8** with tert-butyllithium

A 1.7 M solution of *tert*-butyllithyum in pentane (9.0 ml) was added with stirring in an inert atmosphere to a solution of **8** (1.00 g, 1.85 mmol) in dry benzene (200 ml). The mixture was stirred for 3 h at ambient temperature and then water (100 ml) was added. The organic layer was separated, washed with water (250 ml), the solvent was removed in vacuum, and the residue was chromatographed on alumina (hexane–diethyl ether, 3:1) to give compounds **11** and **12**.

4.9. 2-tert-Butyl-1,3-diferrocenylcyclopropene (**11**)

Orange crystals, yield: 0.654 g (76%), m.p. 147–148 °C; FTIR (KBr), ν/cm^{-1}: 3093, 2960, 2925, 2899, 2863, 1850, 1717, 1649, 1556, 1411, 1359, 1105, 1001, 815: UV–Vis (CH_2Cl_2) $\lambda_{max} = 447$, 278, 236 nm: ^{1}H NMR (300 MHz, CD_2CI_2) δ_H: 1.28 (s, 9H, CH_3), 2.44 (s, 1H, CH), 4.04 (s, 10H, C_5H_5), 4.27 (s, 4H, C_5H_4), 4.41 (s, 4H, C_5H_4). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.36 (CH), 29.65 (CH_3), 31.68 (C), 67.09 (C_5H_4), 69.03 (C_5H_4), 69.13 (C_5H_5), 69.20 (C_5H_4), 69.22 (C_5H_4), 69.27 (C_5H_5), 73.11 (2 C_{ipso}Fc); 109.3 (C═); 120.9 (C═): Calc. for $C_{27}H_{28}Fe_2$ (464): C, 69.82; H, 6.03; Fe, 24.13. Found: C, 69.85; H, 6.09; Fe, 24.18%.

4.10. 1,3-Di-tert-butyl-2,3-diferrocenylcyclopropene (**12**)

Orange crystals, yield .231 g (24%), m.p. 135–136 °C; FTIR (KBr), ν/cm^{-1}: 3094, 2957,2927, 2865, 1647, 1477, 1389, 1361, 1219, 1105, 1027, 1001, 818, 756: UV–Vis (CH_2Cl_2) $\lambda_{max} = 447$, 278, 236 nm: ^{1}H NMR (300 MHz, CD_2CI_2) δ_H: 0.93 (s, 9H, CH_3), 1.29 (s, 9H, CH_3), 4.02 (s, 10H, C_5H_5), 4.07 (s, 4H, C_5H_4), 4.18 (s, 10H, C_5H_5), 4.23 (s, 4H, C_5H_4), 4.32–4.58 (m, 8H, C_5H_4). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 29.314 (CH_3), 29.34 (CH_3), 30.67 (2C), 35.11 (C), 68.84 (C_5H_4), 68.94 (C_5H_5), 69.04 (C_5H_4), 69.19 (C_5H_5), 69.39 (C_5H_4), 73.12 (2 C_{ipso}Fc), 111.4 (C═); 121.1 (C═): Calc. for $C_{31}H_{36}Fe_2$ (520): C, 71.53; H, 6.92; Fe, 21.53. Found: C, 71.56; H, 6.90; Fe, 21.58%.

5. Crystal structure determination

The unit cell parameters and X-ray diffraction intensities were recorded at room temperature with a Siemens P/4 diffractometer. The structures of compounds **9a**, **9b** and **11** were solved by the direct method (SHELXS-97) and refined using full-matrix least-squares in F^2. The crystallographic data, the experimental conditions and corrections are given in Table 1.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 279909 for compound **9a**, No. 279910 for compound **9b**, No. 279911 for compound **11**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] R. Breslow, R. Haynie, J. Mirra, J. Am. Chem. Soc. 81 (1959) 247–248.
[2] M.E. Vol'pin, Yu.D. Koreshkov, D.N. Kursanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk. (1959) 560.
[3] B.E. Zaitsev, Yu.D. Koreshkov, M.E. Vol'pin, Y.N. Sheinker, Dokl. Akad. Nauk SSSR. 136 (1961) 1090–1092.
[4] (a) S.W. Tobey, R. West, J. Am. Chem. Soc. 86 (1964) 1459;
(b) R. West, A. Sado, S.W. Tobey, J. Am. Chem. Soc. 88 (1966) 2488;
(c) R. West, D.C. Zecher, W. Goyart, J. Am. Chem. Soc. 92 (1970) 149.
[5] C.R. Kerber, H.C. Ming, J. Am. Chem. Soc. 95 (1973) 3239–3245.
[6] A.J. Fry, R.L. Krieger, I. Agranat, E. Aharon-Shalom, Tetrahedron Lett. 17 (52) (1976) 4803–4806.

[7] I. Agranat, E. Aharon-Shalom, J. Am. Chem. Soc. 35 (1975) 3829–3830.
[8] K. Komatsu, T. Kitagawa, Chem. Rev. 103 (2003) 1371–1427.
[9] E.I. Klimova, T.B. Klimova, L. Ruiz, M. Martinez, C. Alvarez, G. Espinosa, R.A. Toscano, J. Organomet. Chem. 545 (1997) 191–199.
[10] E.I. Klimova, M. Martinez, T. Klimova, C. Alvarez, R.A. Toscano, R. Moreno, L. Ruiz, J. Organomet. Chem. 566 (1998) 175–185.
[11] E.I. Klimova, M. Martinez, T. Klimova, C. Alvarez, R.A. Toscano, L. Ruiz, J. Organomet. Chem. 598 (2000) 254–261.
[12] E.I. Klimova, M. Martinez, T. Klimova, J.M. Mendez, S. Hernández, L. Ruiz, J. Organomet.Chem. 659 (2002) 56–63.
[13] E.I. Klimova, T.B. Klimova, A. Cinquantini, M. Corsini, P. Zanello, R.A. Toscano, S.O. Hernandez, M.G. Martinez Garcia, Org. Biomol. Chem. 1 (2003) 4458–4464.
[14] E.I. Klimova, T. Klimova, S.O. Hernandez, M.R. Esquivelzeta, L.R. Ruız, M.G. Martınez, J. Organomet. Chem. 689 (2004) 2395–2400.