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Diferrocenylcyclopropenyl cations. Synthesis, structures, and some chemical properties

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Abstract

Synthesis of diferrocenylcyclopropenyl tetrafluoroborates with hetero-substituents in the three-membered ring, viz., ethoxy, trityloxy, ferrocenyl(phenyl)methoxy, *N*,*N*-diethylamino, piperidino, and morpholino, is described. The spatial structure of diferrocenyl(morpholino)cyclopropenyl tetrafluoroborate was established based on the data from X-ray diffraction analysis. Under the action of potassium *tert*-butoxide, all the diferrocenylcyclopropenyl tetrafluoroborates undergo three-membered ring-opening with formation of the corresponding 2,3-diferrocenylacrylic acid derivatives. A mechanism of the ring-opening is suggested.

Keywords: Ferrocene; Diferrocenylcyclopropenes; Diferrocenylcyclopropenyl tetrafluoroborates; Derivatives of 2,3-diferrocenylacrylic acid; Ring opening; X-ray structural analysis

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1. Introduction

According to the Hückel rule [1], the cyclopropenyl cation represents the simplest aromatic system, this is built of three carbon atoms with two π electrons delocalized over three 2p orbitals. The first representative of this class of compounds, viz., triphenylcyclopropenyl tetrafluoroborate, was synthesized by Breslow in 1957 [2]. It manifested high thermodynamic stability; neither ring-opening reactions typical of cyclopropane, viz., brominolysis or catalytic hydrogenolysis, nor addition to the double bond typical of cyclopropenes, could be effected. In 1959, Vol'pin et al. [3] reported the preparation of hydroxydiphenylcyclopenylium.

Cyclopropenyl cations are the subject of many studies in theoretical, physical, and synthetic organic chemistry [4,5]. The possibility of the use of cyclopropenyl cations in the synthesis of organic compounds with unusual structural fragments accounts for the theoretical and practical interest in these species [4].

The first syntheses of metallocenyl-substituted cyclopropenylium derivatives, viz., ferrocenyldiphenyl- and triferrocenylcyclopropenyl tetrachloroaluminates (**1** and **2**), starting from tetrachlorocyclopropene were described in 1967 [6] and 1975 [7], respectively. Their reactions with nucleophilic reagents afforded ferrocenyl-substituted cyclopropenes (**3**–**5**) [8] (Scheme 1).

No detailed studies dealing with the preparation and application of ferrocenylcyclopropenyl cations were carried out. Hitherto, no ferrocenylcyclopropenylium with hetero-substituents in the three-membered ring was reported.

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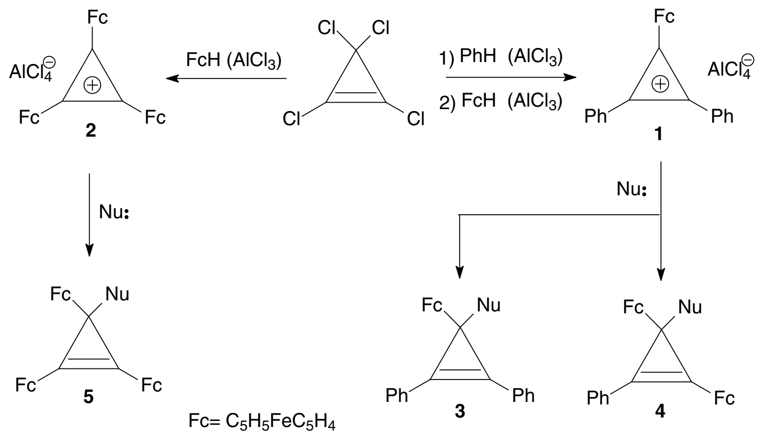


Scheme 1.

In the present work, we describe synthesis of alkoxy- and dialkylamino-diferrocenylcyclopropenyl cations and studies of some of their chemical properties.

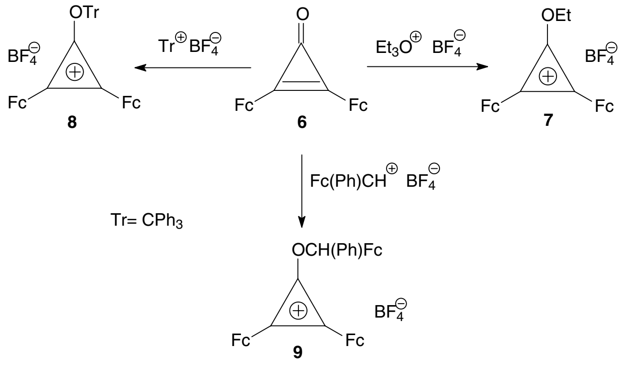
2. Results and discussion

Diferrocenylcyclopropenone **6** easily obtainable by alkylation of ferrocene with tetrachlorocyclopropene in the presence of $AlCl_3$ in ca. 90% yield [9] was used as the starting compound for the preparation of hetero-substituted diferrocenylcyclopropenyl tetrafluoroborates.

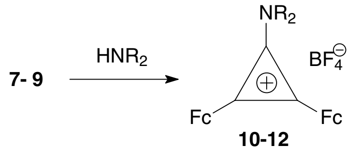
We have found that diferrocenylcyclopropenone **6** reacts with triethyloxonium, triphenylmethylium, and ferrocenyl(phenyl)methylium tetrafluoroborates to give crystalline alkoxy(diferrocenyl)cyclopropenylium tetrafluoroborates (**7**–**9**) (Scheme 2).

These dark violet salts are stable on storage in a dry inert atmosphere, they are characterized by ^1H and ^{13}C NMR spectra and data from elemental analyses.

In reactions with secondary amines, compounds **7**–**9** produce amino(diferrocenyl)cyclopropenylium tetrafluoroborates **10**–**12** (Scheme 3).



Scheme 2.



Scheme 3.

N,*N*-diethylamino- (**10**), piperidino- (**11**), and morpholino-diferrocenylcyclopropenylium (**12**) tetrafluoroborates are red-violet crystalline compounds that are storage-stable under ordinary conditions for a long time. Their structures were determined based on the data from ^1H and ^{13}C NMR spectra and elemental analyses.

The spatial configuration of compound **12** was established by X-ray diffraction analysis of a single crystal prepared by crystallization from ethanol. The general view of the molecule of diferrocenyl(morpholino)cyclopropenylium tetrafluoroborate **12** is shown in Fig. 1(a), the crystal packing, in Fig. 1(b), and selected bond lengths and bond angles are listed in Table 1. The three-membered ring in the structure **12** represents a virtually equilateral triangle with the carbon–carbon bond lengths of 1.351–1.381 Å and bond angles of 59.1–61.3°. The C(1)–N(1) bond length ($d = 1.288(7)$ Å) is close to the C═N double bond length ($d = 1.29$ Å) [10,11], which suggests the considerable contribution of the free electron pair on the nitrogen atom to the delocalization of the positive charge of the three-membered ring. Hence, the equilibrium between the mesomeric forms **12a** and **12b** is largely shifted towards the iminium salt **12b** (Scheme 4).

The substituted cyclopentadienyl rings of the ferrocenyl fragments in compound **12** are coplanar with the small ring, the ferrocenyl sandwiches are oppositely oriented (Fig. 1(b)). The morpholine substituent has the chair conformation. The Fe–C bond lengths and the

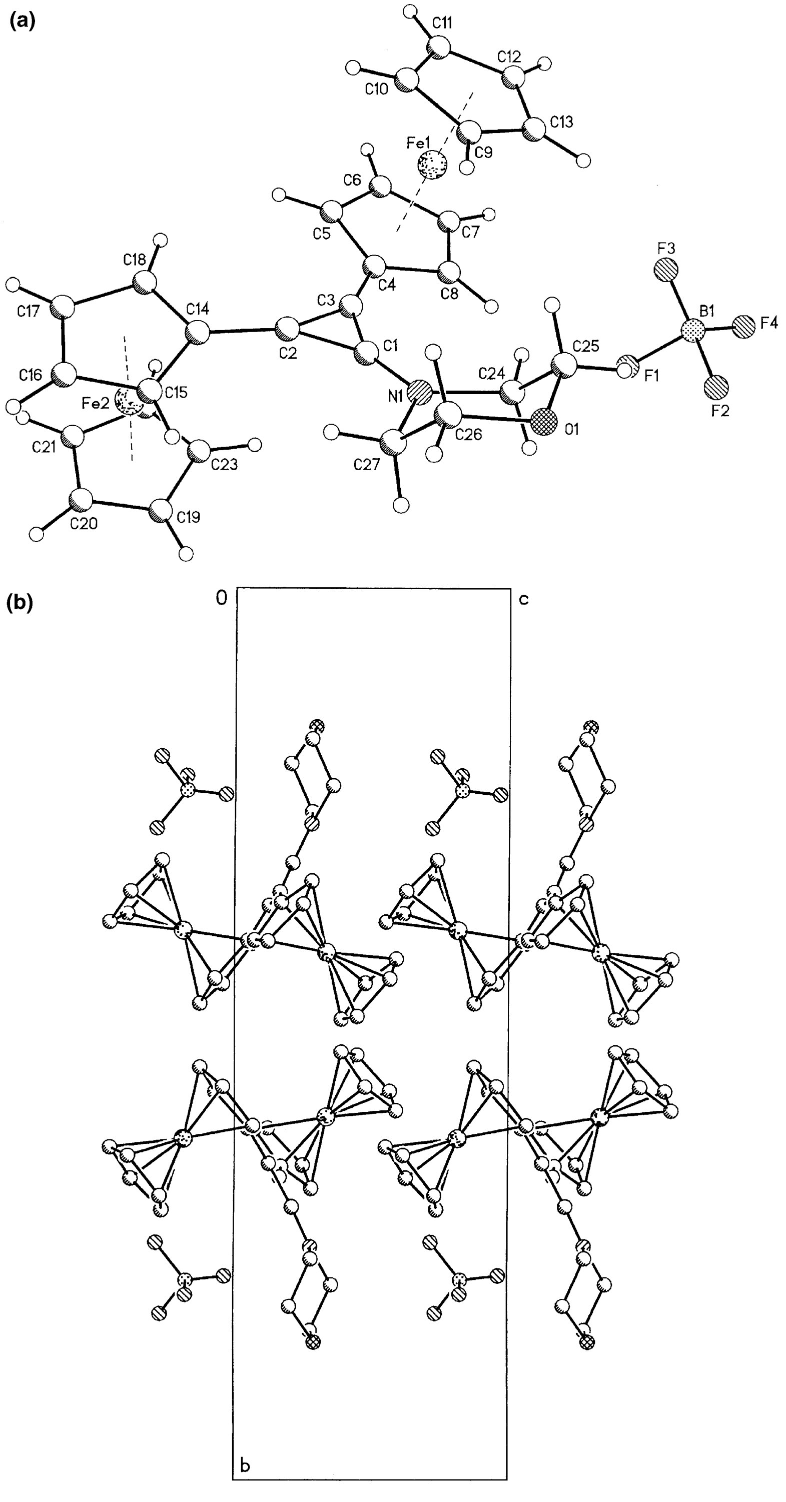


Fig. 1. (a) Crystal structure of compound 12; (b) crystal packing of **12**.

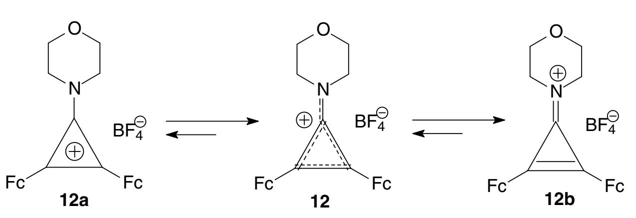
geometry of the ferrocene sandwiches are close to standard characteristics [10,12].

Apparently, the structures of cyclopropenylium tetrafluoroborates **7**–**11** are similar to those of compound **12** (Scheme 5).

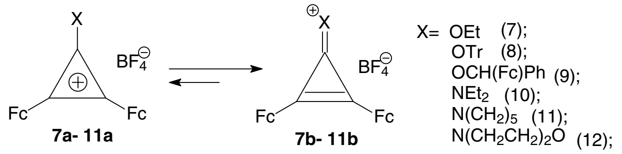
This follows from the ^{13}C NMR spectra of the cations **7**–**12**, where the signals for the C_{ipso}Fc carbon atoms resonate in a high-field region (δ = 60–69 ppm), which is uncommon for compounds of the ferrocene series [9,11,13,14].

Table 1
Selected bond lengths and bond angles for **12**

Selected bond lengths, *r* (Å)		Selected bond angles, *ω* (°)	
C(1)–C(2)	1.381(8)	C(3)–C(1)–C(2)	59.1(4)
C(1)–C(3)	1.359(7)	C(3)–C(2)–C(1)	59.6(4)
C(2)–C(3)	1.351(8)	C(2)–C(3)–C(1)	61.3(4)
C(1)–N(1)	1.288(7)	N(1)–C(1)–C(3)	150.4(6)
C(24)–N(1)	1.497(8)	N(1)–C(1)–C(2)	150.6(6)
C(27)–N(1)	1.499(7)	C(1)–N(1)–C(24)	122.8(5)
C(2)–C(14)	1.464(8)	C(1)–N(1)–C(27)	122.0(6)
C(4)–C(3)	1.404(8)	C(3)–C(4)–C(5)	126.6(6)
B(1)–F(1)	1.375(16)	C(1)–C(3)–C(4)	152.1(6)



Scheme 4.

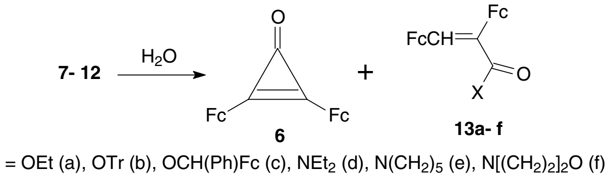


Scheme 5.

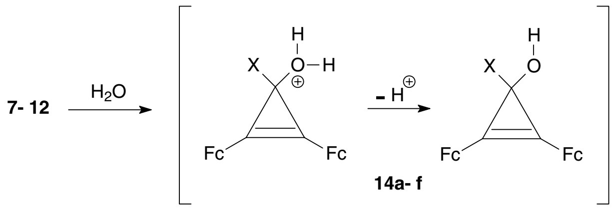
Studies of the chemical properties of the salts **7**–**12** revealed, that upon contact with water or moist solvents (on heating) they decompose to form 2,3-diferrocenylcyclopropene **6** (60–70%) together with the corresponding 2,3-diferrocenylacrylic acid derivatives **13a**–**f** (8–10%) (Scheme 6).

In our opinion, this reaction involves the nucleophilic addition of water to the electron-deficient carbon atom of the three-membered ring bearing the heteroatom to afford unstable addition products **14a**–**f** (Scheme 7).

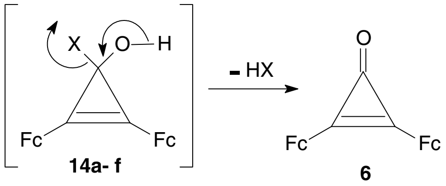
These undergo intramolecular transformations with retention of the small ring leading to cyclopropenone **6** (Scheme 8) or with small-ring opening into carbenoid intermediates **15a**–**f** resulting in 2,3-diferrocenylacrylic acid derivatives **13a**–**f** (Scheme 9).



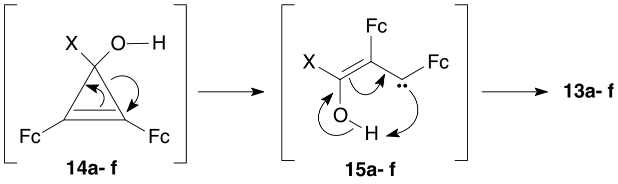
Scheme 6.



Scheme 7.



Scheme 8.



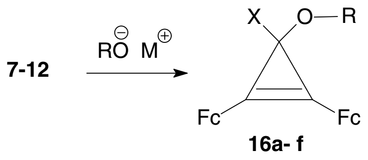
Scheme 9.

To exclude the formation of cyclopropenone **6** one should presumably employ nucleophiles, e.g., metal alkoxides, which would afford the intermediate addition products **16a**–**f** (Scheme 10).

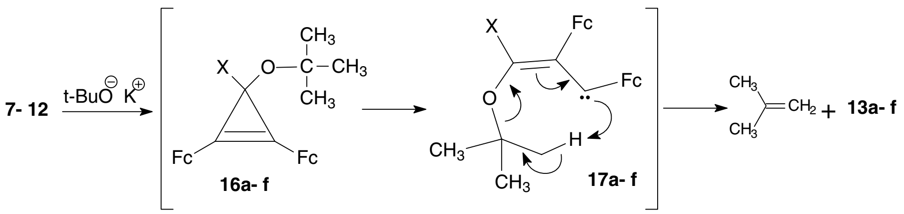
Presumably, in this case it would be possible to isolate either the nucleophilic addition products (e.g., diferrocenylcyclopropenone ketals) or intramolecular transformation products resulting from the small-ring opening.

To check this assumption, we studied the reactions of the salts **7**–**12** with potassium *tert*-butoxide. It was found that the reactions occur with evolution of isobutylene (this followed from decoloration of bromine water and appearance of heavy oil droplets) and formation of the corresponding 2,3-diferrocenylacrylates and -acrylamides **13a**–**f** in high yields (Scheme 11).

According to the data from ^{1}H and ^{13}C NMR spectroscopy, these derivatives were formed as single geometrical isomers, presumably, with *cis*-arranged ferrocenyl groups, which is in keeping with the spatial



Scheme 10.



Scheme 11.

orientation of the ferrocenyl sandwiches in the molecule of isopropyl 2,3-diferrocenylacrylate [9]. However, we could not obtain crystals of compounds **13a**–**f** suitable for unambiguous determination of their absolute configurations by X-ray diffraction analysis.

Table 2
Crystal data, data collection and refinement parameters for **12**

Data	**12**
Molecular formula	$C_{27}H_{26}BF_4Fe_2NO$
Formula weight (g mol^{-1})	579.00
Temperature (K)	291(2)
Crystal system	Orthorhombic
Space group	$P2_12_12$
a (Å)	14.721(1)
b (Å)	24.683(2)
c (Å)	7.6412(6)
α (°)	90.0
β (°)	90.0
γ (°)	90.0
V (Å^3)	2776.4(4)
Z	4
D_{calc}(Mg mm^{-3})	1.385
Absorption coefficient (mm^{-1})	1.091
F(0 0 0)	1184
Radiation, λ (Å)	Mo Kα, 0.71073
Monochromator	Graphite
θ Range (°)	2.67–25.00
Reflections collected	22,796
Reflections independent	4879
R_{int}	0.0653
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0485$, $wR_2 = 0.1095$
R indices (all data)	$R_1 = 0.0744$, $wR_2 = 0.1149$
Data/restraints/parameters	6373/0/479
Refinement method	Full-matrix-least-squares on F^2
Goodness-of-fit	0.943
Minimum/maximum residual electron density (e Å^{-3})	−0.280/0.566

3. Experimental

All the solvents were dried according to standard procedures [14] and were freshly distilled before use. Column chromatography was carried out on alumina (Brockmann activity III). The ^{1}H and ^{13}C NMR spectra of the tetrafluoroborates **7**–**12** were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in CD_2Cl_2 with Me_4Si as the internal standard. The ^{1}H and ^{13}C NMR spectra of the compounds **13a**–**f** were recorded for solutions in $CDCl_3$. An Elemental Analysis System GmbH was used for elemental analyses. Mass spectra (EI, 70 eV) were obtained on a Varian MAT CH-6 mass spectrometer. The unit cell parameters and the X-ray diffraction intensities were recorded on a Bruker Smart Apex CCD area detector/ω diffractometer. The crystallographic data, parameters of the X-ray experiment, and refinements for **12** are listed in Table 2.

Diferrocenylcyclopropenone **6** was prepared by alkylation of ferrocene with tetrachlorocyclopropene in the presence of $AlCl_3$ [9]; ferrocenyl(phenyl)methylium tetrafluoroborate was obtained by treatment of ferrocenyl(phenyl)methanol with tetrafluoroboric acid etherate [13,14].

The following reagents were purchased from Aldrich: ferrocene, 98%; aluminum chloride, 99.99%; tetrachlorocyclopropene, 98%; triethyloxonium tetrafluoroborate, 1.0 M solution in dichloromethane; triphenylcarbenium tetrafluoroborate; diethylamine, 99.5%; piperidine, 99%; morpholine, 99+%; potassium *tert*-butoxide, 95%. Tetrafluoroboric acid etherate (50–52%) was purchased from Alfa AESAR.

3.1. *Ethoxy(diferrocenyl)cyclopropenylium tetrafluoroborate (7)*

Triethyloxonium tetrafluoroborate (1.0 M solution in dichloromethane, 5 mmol) was added in a dry inert atmosphere with stirring to a solution of diferrocenylcyclopropenone **6** (0.85 g, 2 mmol) in dichloromethane (50 ml). Stirring was continued for 2 h and dry diethyl ether (100 ml) was added. The violet precipitate was filtered off, washed with dry ether, and dried in vacuo. The yield of the title compound was 0.88 g (82%), m.p. 209–211 °C; MS *m*/*z* (%): 538 (71), 452 (100); δ_H (300 MHz, CD_2Cl_2): 2.96 (3H, t, $J = 7.2$ Hz, CH_3), 6.12 (10H, s, $2C_5H_5$), 6.48 (2H, q, $J = 7.2$ Hz, CH_2), 6.62 (4H, m, C_5H_4), 6.83 (4H, m, C_5H_4). Found: C, 55.73; H, 4.50; F, 14.09; Fe, 20.93%. Calc. for $C_{25}H_{23}BF_4Fe_2O$: C, 55.81; H, 4.31; F, 14.13; Fe, 20.77.

3.2. *Diferrocenyl(trityloxy)cyclopropenylium tetrafluoroborate (**8**)*

A solution of triphenylcarbenium tetrafluoroborate (0.99 g, 3 mmol) in CH_2Cl_2 (20 ml) was added to a solution of diferrocenylcyclopropenone **6** (0.85 g, 2 mmol) in dichloromethane (50 ml). The mixture was stirred in an atmosphere of dry nitrogen for 1 h at 20 °C and dry diethyl ether (100 ml) was added. The precipitate was filtered off, washed with dry ether, and dried in vacuo. The yield of the title compound was 1.3 g (85%), violet crystals, m.p. 314–317 °C; MS *m/z* (%): 752 (68), 666 (98); δ_H (300 MHz, CD_2Cl_2): 5.66 (10H, s, $2C_5H_5$), 6.42 (4H, m, C_5H_4), 6.53 (4H, m, C_5H_4), 7.38–7.99 (15H, m, 3Ph). Found: C, 66.84; H, 4.49; F, 10.25; Fe, 15.01%. Calc. for $C_{42}H_{33}BF_4Fe_2O$: C, 87.06; H, 4.42; F, 10.10; Fe, 14.85.

3.3. Diferrocenyl(ferrocenyl(phenyl)methoxy)-cyclopropenylium tetrafluoroborate (*9*)

Analogously, the reaction of diferrocenylcyclopropenone **6** (0.42 g, 1 mmol) in CH_2Cl_2 (30 ml) with ferrocenyl(phenyl)methylium tetrafluoroborate (0.54 g, 1.5 mmol) in dichloromethane (25 ml) (1 h, 20 °C) afforded the title salt, yield 0.61 g (81%), dark violet crystals, m.p. 323–325 °C; MS *m/z* (%): 784 (74), 698 (96); δ_H (300 MHz, CD_2Cl_2): 4.28 (5H, s, C_5H_5), 4.65 (2H, m, C_5H_4), 5.43 (10H, s, $2C_5H_5$), 4.76 (2H, m, C_5H_4), 6.36 (4H, m, C_5H_4), 6.44 (4H, m, C_5H_4), 5.62 (1H, s, CH), 7.15–7.48 (5H, m, Ph). Found: C, 61.38; H, 4.13; F, 9.52; Fe, 21.49%. Calc. for $C_{40}H_{33}BF_4Fe_3O$: C, 61.27; H, 4.24; F, 9.70; Fe, 21.37.

3.4. N,N-diethylamino(diferrocenyl)cyclopropenylium tetrafluoroborate (*10*)

Diethylamine (3.0 ml) was added drop wise to a solution of salt **7** (0.54 g, 1 mmol) in dichloromethane (50 ml) and the mixture was stirred for 2 h at 20 °C in an inert atmosphere. Then dry ethanol (100 ml) was added, the mixture was stirred for 30 min, concentrated in vacuo to 30 ml, and left overnight at 20 °C. The precipitate that formed was filtered off, washed with dry ethanol, and dried in a vacuum desiccator over P_2O_5. The yield of the title compound was 0.37 g (74%), red-violet crystals, m.p. 182–184 °C; MS *m/z* (%): 565 (86), 479 (100); δ_H (300 MHz, CD_2Cl_2): 1.50 (6H, t, $J = 7.2$ Hz, $2CH_3$), 3.84 (4H, q, $J = 7.2$ Hz, $2CH_2$), 4.35 (10H, s, $2C_5H_5$), 4.83 (4H, m, C_5H_4), 4.90 (4H, m, C_5H_4); δ_C (75 MHz, CD_2Cl_2): 14.62 ($2CH_3$), 49.04 ($2CH_2$), 60.45 ($2C_{ipso}$Fc), 70.82 ($2C_5H_5$), 71.81, 74.39 ($2C_5H_4$), 132.04 (2C), 139.40 (C–N). Found: C, 57.54; H, 4.73; F, 13.61; Fe, 19.63; N, 2.52%. Calc. for $C_{27}H_{28}BF_4Fe_2N$: C, 57.39; H, 5.00; F, 13.45; Fe, 19.77; N, 2.48.

3.5. Diferrocenyl(piperidino)cyclopropenylium tetrafluoroborate (*11*)

The title compound was obtained analogously, yield 77%, red-violet crystals, m.p. 204–205 °C; MS *m/z* (%): 577 (89), 491 (100); δ_H (300 MHz, CD_2Cl_2): 1.76 (2H, m, CH_2), 2.75 (2H, m, CH_2), 2.95–3.41 (4H, m, $2CH_2$), 3.64 (2H, m, CH_2), 4.26 (10H, s, $2C_5H_5$), 4.31 (2H, m, C_5H_4), 4.49 (2H, m, C_5H_4), 4.69 (2H, m, C_5H_4), 4.87 (2H, m, C_5H_4); δ_C (75 MHz, CD_2Cl_2): 30.87, 43.58, 48.93 ($5CH_2$), 60.31 ($2C_{ipso}$Fc), 70.72 ($2C_5H_5$), 71.68, 74.20 ($2C_5H_4$), 130.19 (2C), 138.89 (C–N). Found: C, 58.44; H, 4.68; F, 13.29; Fe, 19.18; N, 2.59%. Calc. for $C_{28}H_{28}BF_4Fe_2N$: C, 58.28; H, 4.89; F, 13.17; Fe, 19.36; N, 2.43.

3.6. Diferrocenyl(morpholino)cyclopropenylium tetrafluoroborate (*12*)

The title compound was obtained analogously, yield 78%, red-violet crystals, m.p. 210–212 °C; MS *m/z* (%): 579 (82), 493 (100); δ_H (300 MHz, CD_2Cl_2): 3.91(4H, m, $2CH_2$), 3.99 (4H, m, $2CH_2$), 4.37 (10H, s, $2C_5H_5$), 4.87 (4H, m, C_5H_4), 4.91 (4H, m, C_5H_4); δ_C (75 MHz, CD_2Cl_2): 51.97, 66.61 ($4CH_2$), 60.61 ($2C_{ipso}$Fc), 71.42 ($2C_5H_5$), 72.23, 75.23 ($2C_5H_4$), 132.51 (2C), 139.47 (C–N). Found: C, 55.86; H, 4.68; F, 13.24; Fe, 19.40; N, 2.34%. Calc. for $C_{27}H_{26}BF_4Fe_2NO$: C, 56.01; H, 4.53; F, 13.12; Fe, 19.29; N, 2.42.

3.7. Ethyl 2,3-diferrocenylacrylate (*13a*)

A stirring mixture of salt **7** (0.54 g, 1 mmol) and t-BuOK (0.22 g, 2.2 mmol) in dry benzene (50 ml) was boiled under reflux in an inert dry atmosphere for 3 h. The solvent was evaporated and the residue was chromatographed on alumina (hexane–ether, 4:1) to yield 0.33 g (70%) of the title compound, red powder, m.p. 141–142 °C; MS *m/z* (%): 468 (100); δ_H (300 MHz, $CDCl_3$): 1.47 (3H, t, $J = 7.2$ Hz, CH_3), 4.06 (5H, s, C_5H_5), 4.07 (5H, s, C_5H_5), 4.21 (2H, m, C_5H_4), 4.24 (4H, m, C_5H_4), 4.36 (2H, q, $J = 7.2$ Hz, CH_2), 4.47 (2H, m, C_5H_4), 7.28 (1H, s, CH=); δ_C (75 MHz, $CDCl_3$): 14.47 (CH_3), 60.45 (CH_2), 69.47, 69.66 ($2C_5H_5$), 70.56, 71.24, 71.32, 71.89 ($2C_5H_4$), 79.72, 82.20 ($2C_{ipso}$Fc), 136.74 (CH=), 126.77 (–C=), 167.51 (C=O). Found: C, 64.29; H, 5.23; Fe, 24.06%. Calc. for $C_{25}H_{24}Fe_2O_2$: C, 64.14; H, 5.17; Fe, 23.86.

3.8. Triphenylmethyl 2,3-diferrocenylacrylate (*13b*)

This compound was obtained analogously, yield 68%, brown powder, m.p. 173–175 °C; MS *m/z* (%): 682 (100); δ_H (300 MHz, $CDCl_3$): 4.09 (5H, s, C_5H_5), 4.13 (5H, s, C_5H_5), 4.28 (2H, m, C_5H_4), 4.36 (2H, m, C_5H_4), 4.48 (2H, m, C_5H_4), 4.59 (2H, m, C_5H_4), 7.89 (1H, s, CH=), 7.01–7.15 (3H, m), 7.32–7.64 (12H, m, 3Ph). Found: C, 74.09; H, 4.88; Fe, 16.48%. Calc. for $C_{42}H_{34}Fe_2O_2$: C, 73.92; H, 5.02; Fe, 16.37.

3.9. Ferrocenyl(phenyl)methyl 2,3-diferrocenylacrylate (**13c**)

The title compound was obtained as described for the synthesis of **13a**, yield 0.50 g (70%), dark red fine crystalline powder, m.p. 213–215 °C; MS *m/z* (%): 714 (100); δ_H (300 MHz, $CDCl_3$): 4.02 (1H, s, CH), 4. 08 (5H, s, C_5H_5), 4.12 (5H, s, C_5H_5), 4.19 (5H, s, C_5H_5), 4.22 (4H, m, C_5H_4), 4.27 (2H, m, C_5H_4), 4.35 (2H, m, C_5H_4), 4.38 (2H, m, C_5H_4), 4.42 (2H, m, C_5H_4), 7.16 (1H, s, CH=), 7.19–7.38 (5H, m, Ph). Found: C, 67.39; H, 4.63; Fe, 23.61%. Calc. for $C_{40}H_{34}Fe_3O_2$: C, 67.27; H, 4.80; Fe, 23.46.

3.10. N,N-diethyl 2,3-diferrocenylacrylamide (**13d**)

Yield 65%, orange powder, m.p. 171–172 °C; MS *m/z* (%): 495 (100); δ_H (300 MHz, $CDCl_3$): 1.30 (6H, t, $J = 7.2$ Hz, $2CH_3$), 4.08 (5H, s, C_5H_5), 4.14 (5H, s, C_5H_5), 4.17 (2H, m, C_5H_4), 4.20 (4H, m, C_5H_4), 4.27 (4H, q, $J = 7.2$ Hz, $2CH_2$), 4.49 (2H, m, C_5H_4), 6.29 (1H, s, CH=); δ_C (75 MHz, $CDCl_3$): 12.97, 14.23 ($2CH_3$), 38.54, 43.24 ($2CH_2$), 69.07, 69.32 ($2C_5H_5$), 68.03, 68.55, 69.04, 69.65 ($2C_5H_4$), 80.59, 80.79 ($2C_{ipso}$Fc), 126.27 (CH=),132.57 (C), 171.02 (C=O). Found: C, 65.35; H, 6.07; Fe, 22.69; N, 2.76%. Calc. for $C_{27}H_{29}Fe_2NO$: C, 65.48; H, 5.91; Fe, 22.56; N, 2.82.

3.11. N-(2,3-diferrocenylacryloyl)piperidine (**13e**)

Yield 70%, dark red powder, m.p. 159–160 °C; MS *m/z* (%): 507 (100); δ_H (300 MHz, $CDCl_3$): 1.69 (6H, m, $3CH_2$), 3.44 (2H, m, CH_2), 3.78 (2H, m, CH_2), 4.09 (5H, s, C_5H_5), 4.13 (5H, s, C_5H_5), 4.16 (2H, m, C_5H_4), 4.17 (2H, m, C_5H_4), 4.19 (2H, m, C_5H_4), 4.23 (2H, m, C_5H_4), 6.27 (1H, s, CH=); δ_C (75 MHz, $CDCl_3$): 24.67, 25.64, 26.36, 42.24, 48.60 ($5CH_2$), 69.05, 69.28 ($2C_5H_5$), 68.60, 68.65, 69.30, 69.68 ($2C_5H_4$), 80.43, 80.74 ($2C_{ipso}$Fc), 126.98 (CH=), 131.47 (C), 170.11 (C=O). Found: C, 66.17; H, 5.93; Fe, 21.86; N, 2.69%. Calc. for $C_{28}H_{29}Fe_2NO$: C, 66.30; H, 5.76; Fe, 22.02; N, 2.76.

3.12. N-(2,3-diferrocenylacryloyl)morpholine (**13f**)

Yield 77%, red-brown powder, m.p. 190–192 °C; MS *m/z* (%): 509 (100); δ_H (300 MHz, $CDCl_3$): 3.76 (4H, m, $2CH_2$), 3.82 (4H, m, $2CH_2$), 4.08 (5H, s, C_5H_5), 4.14 (5H, s, C_5H_5), 4.19 (6H, m, C_5H_4), 4.25 (2H, m, C_5H_4), 6.28 (1H, s, CH=); δ_C (75 MHz, $CDCl_3$): 49.04 ($2CH_2$), 66.87 ($2CH_2$), 69.15, 69.34 ($2C_5H_5$), 68.88, 69.17, 69.75, 69.92 ($2C_5H_4$), 80.05, 80.26 ($2C_{ipso}$Fc), 128.06 (CH=), 130.57 (C), 170.35 (C=O). Found: C, 63.78; H, 5.44; Fe, 22.07; N, 2.63%. Calc. for $C_{27}H_{27}Fe_2NO_2$: C, 63.68; H, 5.35; Fe, 21.93; N, 2.75.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 264421 for compound **12**. 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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