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3,3-Diethyl- and 3,3-dibenzyl-1,2-diferrocenylcyclopropenes

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Reactions of 2,3-diferrocenylcyclopropenone **1** with ethyl- and benzylmagnesium chlorides afford 3,3-diethyl- and 3,3-dibenzyl-1,2-diferrocenylcyclopropenes **2** and **3**, respectively, and products of nucleophilic opening of the three-membered ring resulting from the addition of RMgCl to the carbonyl group, *viz.*, saturated ketones (4,5-diferrocenylheptan-3-ones **4a**,**b** and 3,4-diferrocenyl-1,5-diphenylpentan-2-ones **5a**,**b** as *ca.* 3 : 1 mixtures of two diastereomers) and other products. The spatial structures of compounds **2** and **4a** were established by X-ray diffraction analysis of single crystals. Protonation of the cyclopropenes **2** and **3** with tetrafluoroboric acid at −40 °C yields the corresponding 3,3-dialkyl-1,2-diferrocenylcyclopropylium tetrafluoroborates. Transformation of the latter into diferrocenylallylic cations upon increasing the temperature to 20 °C and their deprotonation under the action of *N*,*N*-dimethylaniline were studied. Electrochemical investigation of **1** and **2** shows that in both complexes the cyclopropene spacer allows electronic communication between the two outer ferrocenyl groups, this being notably greater for **2** than for **1**.

Introduction

The diverse and unusual chemistry associated with the cyclopropene ring system is well documented.[1,2] The reactivity of this system is dominated by its inherent ring strain, and reactions involving the cleavage of each of the bonds constituting the ring are known. Under thermal,[1–4] photochemical,[1–4] or metal-catalyzed[5] conditions, cyclopropenes undergo ring opening to vinylcarbene intermediates leading to a variety of different products. In the present work, we describe several transformations of 1,2-diferrocenylcyclopropenes with alkyl-(arylalkyl) substituents in position 3, which were prepared starting from 2,3-diferrocenylcyclopropenone.

It is known that the introduction of ferrocenyl substituents into the three-membered ring of cyclopropenes markedly changes their properties. This is most evident in the case of 3-ferrocenylcyclopropenes.[6–12] Thus 3-ferrocenyl-3-isopropylcyclopropene rearranges into 3-ferrocenyl-4-methylpenta-1,3-diene in solution at *ca.* 20 °C.[11] The small-ring opening of 3,3-diferrocenylcyclopropene at 20 °C results in 3-ferrocenyl-1*H*-cyclopentaferrocene.[12] Likewise, 3-aryl-1,2,3-triferrocenylcyclopropenes readily undergo rearrangements (50 °C, chloroform) to give the alkylation products of the aryl and ferrocenyl substituents.[7] Intramolecular stereoselective alkylation of only the aryl substituents occurs upon transformation of 3-phenyl- and 3-naphthyl-3-ferrocenylcyclopropenes into the corresponding ferrocenylindenes at higher temperatures (*ca.* 80 °C). Data on the properties of cyclopropenes containing ferrocenyl substituents only in positions 1 and 2 of the small ring are extremely scarce. Only 2-ferrocenyl-1,3-diphenyl-[13] and 1-ferrocenyl-1,3-diphenylcyclopropenes[14] have been described so far. The latter has been employed for the preparation of the 1-ferrocenylcyclopropyl cation[14,15] and the ability of the ferrocene ring to stabilize the carbocationic centre in the three-carbon ring has been examined.[16,17]

Diferrocenes separated by unsaturated carbon–carbon bonds constitute a classical example of molecules able to exhibit intramolecular electron mobility in that their one-electron oxidation products are usually partially or completely delocalised mixed-valent derivatives. A typical example is offered by diferrocenylethene and diferrocenylethyne.[18,19] In this connection, electrochemical investigations on diferrocenes having cyclopropenes as spacers are rather scanty. To the best of our knowledge, the only electrochemical results are concerned with 1,2,3-triferrocenylcyclopropenes.[13]

Given the considerable and often highly selective effect of ferrocenyl groups introduced into the small ring, we are interested in elucidating the specific features of the electronic interactions of the ferrocenyl substituent at the multiple bond of cyclopropene. This is of both theoretical and practical interest in relation to the search for selective reactions of ferrocene compounds in organic synthesis.

Results and discussion

2,3-Diferrocenylcyclopropenone **1** served as the starting material for the synthesis of 3,3-diethyl- and 3,3-dibenzyl-1,2-diferrocenylcyclopropenes. Compound **1** was first isolated as a side product (*ca.* 7%) upon alkylation of ferrocene with tetrachlorocyclopropene in the presence of $AlCl_3$ at a low temperature back in 1975.[8] The 1,2,3-triferrocenylcyclopropenylium salt was the main reaction product in that case. No studies of the minor 2,3-diferrocenylcyclopropenone **1** have been carried out.

We managed to simplify the procedure for the alkylation of ferrocene with tetrachlorocyclopropene by conducting the reaction in dichloromethane at 20 °C and using a smaller amount of aluminium chloride. The yield of 2,3-diferrocenylcyclopropenone **1** was *ca.* 90% (Scheme 1).

In this work we have studied the reactions of the cyclopropenone **1** with organomagnesium compounds (EtMgCl, BnMgCl). It was found that 1,2-diferrocenylcyclopropenes **2** and **3** and saturated diferrocenylalkyl ketones **4a**,**b** and **5a**,**b** were formed along with other products (Scheme 2).

The structures of compounds **2**–**5** were established from ^1H and ^{13}C NMR spectroscopic data.

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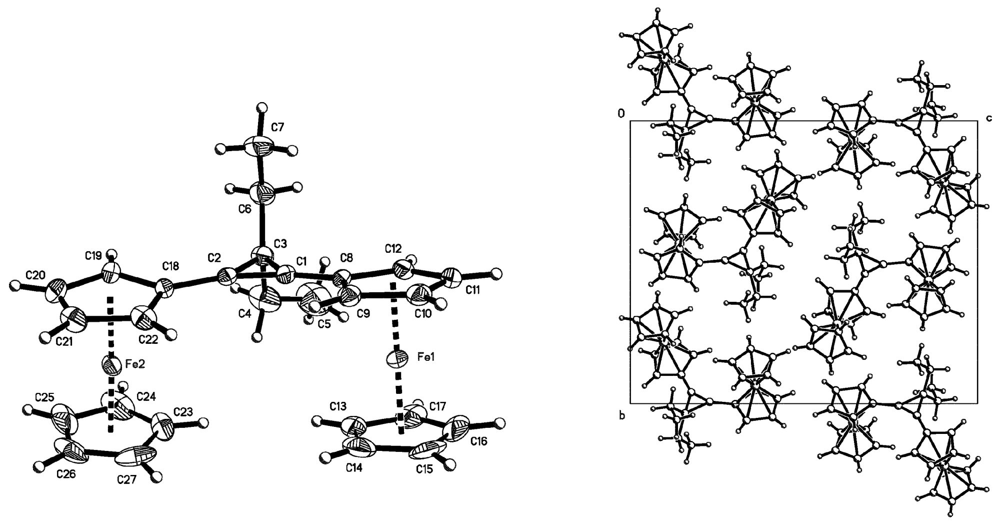
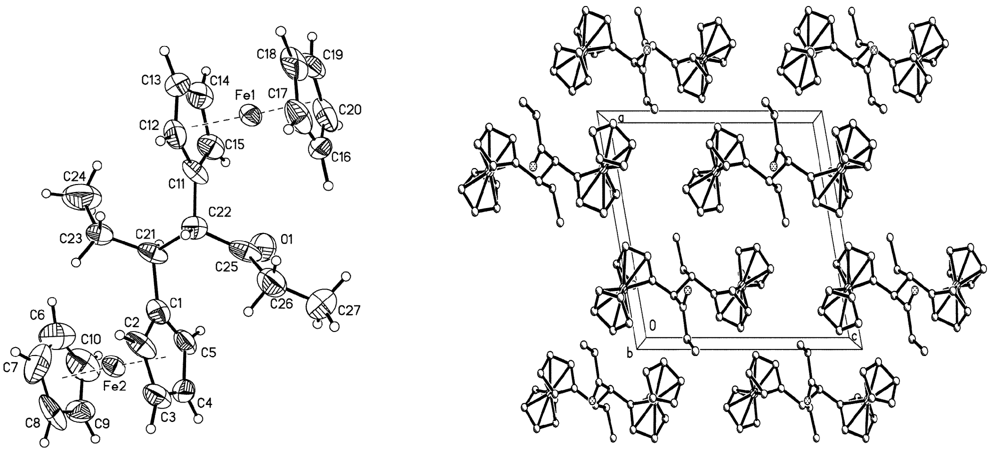


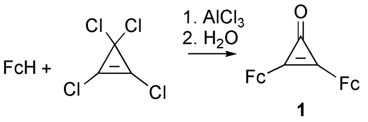
(a) **(b)**

Fig. 1 (a) Crystal structure of **2**. Selected bond lengths (Å): C(1)–C(2) = 1.285(11), C(1)–C(3) = 1.508(12), C(3)–C(2) = 1.494(11). Selected bond angles (°): C(2)–C(1)–C(3) = 64.1(6), C(1)–C(2)–C(3) = 65.2(6), C(2)–C(3)–C(1) = 50.7(5), C(6)–C(3)–C(4) = 112.8(9), C(6)–C(3)–C(1) = 121.5(8). (b) Crystal packing of **2**.



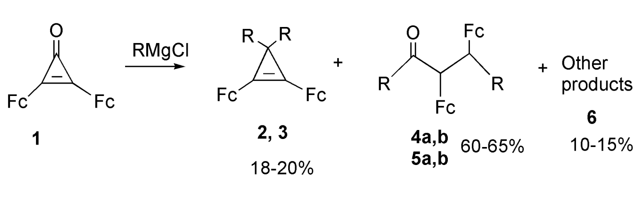
(a) **(b)**

Fig. 2 (a) Crystal structure of **4a**. Selected bond lengths (Å): C(1)–C(21) = 1.570(7), C(21)–C(22) = 1.567(5), C(21)–C(23) = 1.539(8), C(25)–O(1) = 1.191(6), C(25)–C(26) = 1.469(7), C(22)–C(11) = 1.468(7). Selected bond angles (°): C(22)–C(21)–C(1) = 107.4(4), C(11)–C(22)–C(25) = 112.4(5), C(25)–C(22)–C(21) = 110.5(5), O(1)–C(25)–C(22) = 120.4(5), O(1)–C(25)–C(26) = 120.9(7). (b) Crystal packing of **4a**.



Fc = $C_5H_5FeC_5H_4$

Scheme 1



R = Et (**2**; **4a,b**); R = $PhCH_2$ (**3**; **5a,b**)

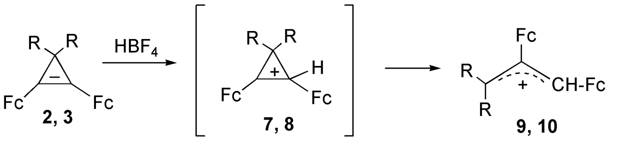
Scheme 2

The relative configuration of one of the cyclopropenes, *viz.*, 3,3-diethyl-1,2-diferrocenylcyclopropene **2**, was deduced from the NMR spectroscopic data and confirmed by X-ray diffraction analysis. The general view of a molecule of compound **2** is shown in Fig. 1a, and the crystal packing is given in Fig. 1b. A specific feature of the crystal structure of **2** is the presence, in the unit cell, of cyclopropene molecules closely arranged in pairs (Fig. 1b).

The three-membered ring in molecule **2** is a scalene triangle extended towards C(3). The C=C bond length [d = 1.285(11) Å] and the acute angle at C(3) ω = 50.7(5)° are similar to those of 3-aryl-3-ferrocenylcyclopropenes.[9,10] The substituted cyclopentadienyl rings of the ferrocene fragments are coplanar with, and the ferrocene sandwiches are oriented in opposite directions with respect to, the central planar small ring (Fig. 1a). The Fe–C bonds and geometrical parameters of the ferrocene sandwiches are similar to standard values.[9–11]

^{1}H and ^{13}C NMR spectroscopic data suggest that compounds **4**,**5** are formed as mixtures of two diastereomers (**4a**,**5a**, and **4b**,**5b**), respectively, in a ratio of *ca.* 3 : 1. The diastereomeric 4,5-diferrocenylheptan-3-ones (**4a** and **4b**) could be separated by preparative TLC on silica gel. The spatial structure of the major isomer **4a** was established by X-ray diffraction analysis of single crystals prepared by crystallization from hexane. The general view of a molecule of **4a** is shown in Fig. 2a, the crystal packing is shown in Fig. 2b; no special comments are needed. As follows from the X-ray diffraction data, compound **4a** has the structure of 4R*,5S*-diferrocenylheptan-3-one. By analogy, *erythro*-configurations were ascribed to the major isomer **5a**. No difficulties were encountered in the spectroscopic identification of ketones **4a**,**b** and **5a**,**b** since the positions of all the signals in the ^{1}H and ^{13}C NMR spectra, their multiplicities and integral intensities were distinctly different (see Experimental section).

We have demonstrated that the protonation of the cyclopropenes **2** and **3** with tetrafluoroboric acid etherate at −40 °C afforded tetrafluoroborates of 3,3-diethyl- and 3,3-dibenzyl-1,2-diferrocenylcyclopropyl cations **7** and **8**, respectively (Scheme 3).

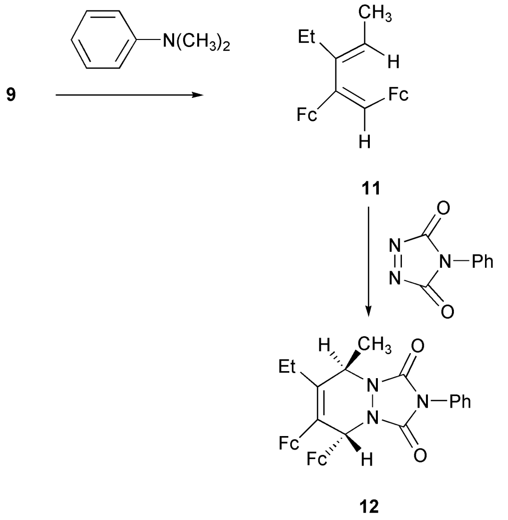


R = Et (**7**, **9**), PhCH$_2$ (**8**, **10**)

Scheme 3

The tetrafluoroborates **7** and **8** are finely crystalline, almost black compounds which can be stored unaltered for several hours in a dry inert atmosphere at low temperatures (−30 °C to −40 °C). The ^{1}H NMR spectra of the salts **7** and **8** (in CD_2Cl_2 solution) confirm completely their structures, since they each contain one singlet for an alicyclic proton at δ 3.37 and 3.56 ppm, respectively. As the solution temperature was gradually increased to *ca.* 20 °C, the tetrafluoroborates **7** and **8** converted into tetrafluoroborates of diferrocenylallylic cations **9** and **10**, respectively. Recording the ^{1}H NMR spectra at intervals allows this process to be monitored by following the appearance of the low-field singlets of the protons of the allylic cations **9** and **10** and the decrease in intensities of the more high-field alicyclic protons of the cations **7** and **8**. Complete conversions of the latter into the allylic cations **9** and **10** takes *ca.* 4 h.

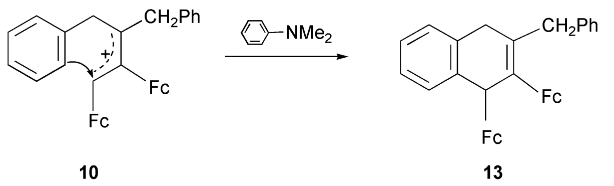
1,1-Diethyl-2,3-diferrocenylallylium tetrafluoroborate **9** undergoes deprotonation upon treatment with *N*,*N*-dimethylaniline to give 3-ethyl-1,2-diferrocenylpenta-1,3-diene **11**. This was characterized by ^{1}H and ^{13}C NMR spectra and by the Diels–Alder adduct (**12**) formed by its reaction with 4-phenyl-3,5-dihydro-1,2,4-triazole-3,5-dione (Scheme 4).



Scheme 4

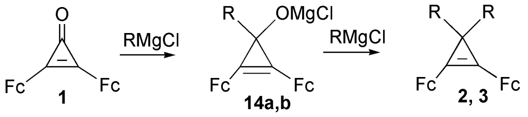
Unlike the cation **9**, its benzyl analogue **10** undergoes *N*,*N*-dimethylaniline-promoted intramolecular cyclization due to *ortho*-alkylation of one of the phenyl groups of the benzyl fragments to yield 3-benzyl-1,2-diferrocenyl-1,4-dihydronaphthalene **13** (Scheme 5).

Similar alkylation of the aryl fragments in arylferrocenylallylic cations prepared by acid-catalyzed ring opening of 3-aryl-3-ferrocenylcyclopropenes has often been observed previously,[9,10] but this resulted in ferrocenylindenes. The formation of naphthalene derivatives is the first example of this kind of reaction in ferrocenylallylic cations.



Scheme 5

The formation of 3,3-diethyl- and 3,3-dibenzyl-1,2-diferrocenylcyclopropenes **2** and **3** is an unusual outcome of the reaction of 2,3-diferrocenylcyclopropenone **1** with ethyl- and benzylmagnesium chlorides, respectively, which probably occurs *via* intermediate magnesium enolates **14a**,**b** and their reaction with a second molecule of RMgCl (Scheme 6).



R = Et (**a**), PhCH$_2$(**b**)

Scheme 6

Similar processes in which the carbonyl group has been completely replaced by two alkyl radicals are known only for the reactions of ferrocenyl ketones with alkylmagnesium iodides.[20,21]

It is quite obvious that the diferrocenylalkyl ketones **4a**,**b** and **5a**,**b** resulted from small-ring opening of one of the two possible products arising from the addition of the Grignard reagents to the carbonyl group (**14a**,**b**) or to the C$_1$ carbon atom (**16a**,**b**) of cyclopropenone **1**. In the first case, vinylcarbene intermediates **15a**,**b** are formed, and in the second one, carbanionic intermediates **17a**,**b** are obtained (Scheme 7).

The addition of the second RMgCl molecule to the intermediates **15a**,**b** or **17a**,**b** gives rise to the same carbanions **18a**,**b**, which, when treated with water, abstract protons from the water molecules resulting in the formation of the final products **4** and **5**.

In order to corroborate the reaction mechanism proposed in Scheme 7, the reaction mixture of cyclopropenone **1** and EtMgCl was treated with deuterium oxide (D_2O). ^{1}H NMR spectroscopic data show that 4,5-dideuterioheptanone **4-D** was formed as a mixture of two isomers **4a-D** and **4b-D** (~3 : 1, respectively) (Scheme 8).

This result confirms the formation of ferrocenyl(vinyl) anionic intermediates **18a**,**b** in the course of the reaction and their further transformation into saturated ketones **4** and **5** upon treatment with a protic solvent (water). However, which of the two possible routes of small-ring opening (Scheme 7) is preferable for the formation of **18a**,**b** cannot be defined yet.

Low deuterium content in position 4 of the compounds **4a**,**b-D** seems to be due to isotopic exchange during chromatographic purification of the products on Al_2O_3 (Brockmann activity III).

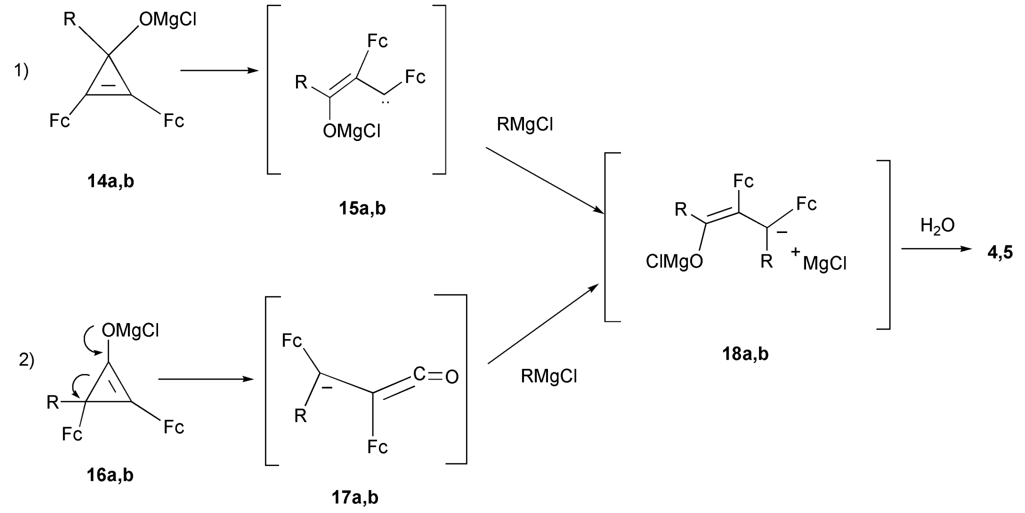
Electrochemistry

In a previous paper we discussed the electrochemical behaviour of **1** in CH_2Cl_2 solution.[23] Depending upon the coordinating as well as the ion-pairing abilities of the supporting electrolyte, compound **1** afforded two reversible, more or less separated, one-electron oxidations. In fact, in the presence of the classical [NBu$_4$][PF$_6$] the separation of the two processes is notably lower than that in the presence of the (relatively) new [NBu$_4$][B(C$_6$F$_5$)$_4$],[24] Table 1.

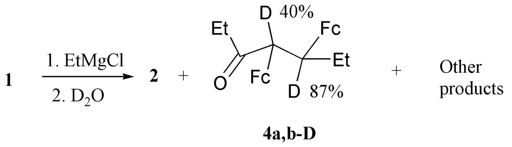
Table 1 Formal electrode potentials (V, *vs.* SCE), peak-to-peak separations (mV), and separation between the two sequential oxidations (V) of complexes **1** and **2** in CH_2Cl_2 solution

Complex	$E^{\circ'}_{(0/+)}$/V	ΔE_p[a]	$E^{\circ'}_{(0/+)}$/V	ΔE_p[a]/mV	$\Delta E^{\circ'}$/V	K_{com}	Supporting electrolyte	Proposed nature of the corresponding mixed-valent monocation[c]
1	+0.66	60	+0.81[a,b]	—	≈120	≈$1.1 \cdot 10^2$	$[NBu_4][PF_6]$ (0.2 mol dm^{-3})	Class I
	+0.75	91	+1.01	115	260	$2.5 \cdot 10^4$	$[NBu_4][B(C_6F_5)_4]$ (0.1 mol dm^{-3})	Class II
2	+0.38	79	+0.63	85	250	$1.7 \cdot 10^4$	$[NBu_4][PF_6]$ (0.2 mol dm^{-3})	Class II
	+0.45	139	+0.83	145	380	$2.6 \cdot 10^6$	$[NBu_4][B(C_6F_5)_4]$ (0.1 mol dm^{-3})	Class III
FcH	+0.39	80					$[NBu_4][PF_6]$ (0.2 mol dm^{-3})	
	+0.42	145					$[NBu_4][B(C_6F_5)_4]$ (0.1 mol dm^{-3})	

[a] Measured at 0.1 V s^{-1}. [b] Affected by electrode adsorption. [c] See text



Scheme 7



4a,b-D

Scheme 8

Since such separation is directly linked[25] to the value of the comproportionation constant, K_{com}:

$$\mathbf{1} + [\mathbf{1}]^{2+} \overset{K_{com}}{\rightleftharpoons} 2[\mathbf{1}]^{+}$$

which in turn reflects in part[26] the extent of charge delocalisation present in the mixed-valent monocation $[\mathbf{1}]^+$, it follows that this latter, under the appropriate conditions (or, in the presence of the low coordinating and low ion-pairing anion $[B(C_6F_5)_4]^-$) would possess a partially delocalised extra charge (Robin–Day[27] Class II).

By way of comparison, let us hence discuss the electrochemical behaviour of 1,1-diethyl-2,3-diferrocenylcyclopropene, **2**. Fig. 3 illustrates its redox ability in CH_2Cl_2 solutions containing $[NBu_4][PF_6]$ and $[NBu_4][B(C_6F_5)_4]$, respectively, as supporting electrolytes.

As seen, independent of the nature of the supporting electrolyte, two separated anodic steps are also displayed, both possessing features of chemical reversibility.

As Fig. 4 shows, exhaustive one-electron oxidation corresponding to the first anodic process (E_w = +0.5 V; $[NBu_4][PF_6]$ as supporting electrolyte) causes the red solution of **2** (λ_{max} = 460 nm, very intense) to generate the stable green monocation $[\mathbf{2}]^+$ (λ_{max} = 680 nm, broad); subsequent oxidation (E_w = +0.8 V) in turn affords the stable grey–green dication $[\mathbf{2}]^{2+}$ (λ_{max} = 690 nm, broad).

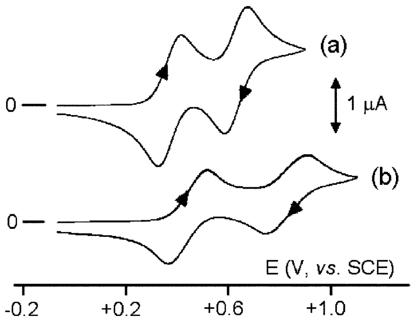


Fig. 3 Cyclic voltammograms recorded at a platinum electrode in CH_2Cl_2 solutions of **2** (0.8 × 10^{-3} mol dm^{-3}) containing: (a) $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) as supporting electrolyte; (b) $[NBu_4][B(C_6F_5)_4]$ (0.1 mol dm^{-3}) as supporting electrolyte. Scan rate 0.1 V s^{-1}.

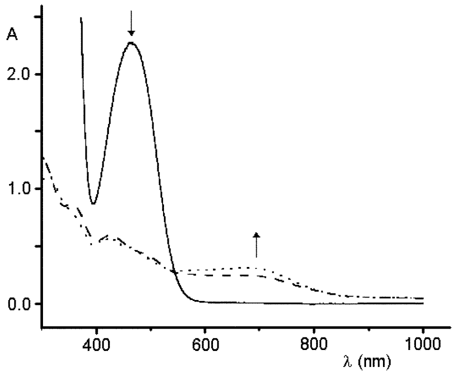


Fig. 4 Spectrophotometric behaviour of **2** (0.8 × 10^{-3} mol dm^{-3}) after step-by-step exhaustive oxidation in CH_2Cl_2 solution ($[NBu_4][PF_6]$ (0.2 mol dm^{-3}) as supporting electrolyte). (—) Initial; (- - -) after about one-electron oxidation; (. . . . . .) after about two-electron oxidation (see text).

As can be deduced from Table 1, the use of the low coordinating anion $[B(C_6F_5)_4]^-$ in this case significantly increases the electronic communication between the two ferrocenyl units. In fact, $[\mathbf{2}]^+$ looks like a partially delocalized Class II mixed valent species in the presence of $[NBu_4][PF_6]$, whereas it can be classified as a completely delocalized Class III species in the presence of $[NBu_4][B(C_6F_5)_4]$.

It is noted that comparison between $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ shows that the presence of the two electron-donating ethyl units in **2** enhances the intramolecular electron mobility, thus allowing us to hypothesize that in both the diferrocenylcyclopropene complexes the electronic communication between the two ferrocene subunits is not only due to through space (or electrostatic) interactions, but it is likely to also involve a through bond contribution.

Experimental

All the solvents were dried according to standard procedures and used freshly distilled. IR spectra were obtained for samples as KBr pellets on a Specord IR-75 instrument. The mass spectrum of compound **4b** was obtained on a Varian-MAT CH-6 instrument (EI, 70 eV). The ^1H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ and CD_2Cl_2 with Me_4Si as the internal standard. Chemical shifts are given in ppm and *J* values in Hz. Chromatographic separations were carried out on columns of alumina (Brockmann activity III) and on plates with a fixed SiO_2 layer.

The following reagents from Aldrich were employed: tetrachlorocyclopropene, 98%; ferrocene, 98%; aluminium chloride, 99.99%; ethylmagnesium chloride, 2.0 M solution in diethyl ether; benzylmagnesium chloride, 1.0 M solution in diethyl ether. Tetrafluoroboric acid etherate, 50–52%, was purchased from Alfa AESAR.

Materials and apparatus used in the electrochemistry experiments have been described elsewhere.[28] $[NBu_4][B(C_6F_5)_4]$ supporting electrolyte was prepared according to the published procedure.[24] All the potential values are referenced to the saturated calomel electrode (SCE).

Synthesis of 2,3-diferrocenylcyclopropenone 1

To a stirred solution of ferrocene (5.6 g, 0.03 mol) and tetrachlorocyclopropene (3.6 g, 0.02 mol) in dry dichloromethane (200 ml), aluminium chloride (0.67 g, 0.005 mol) was added portion-wise for 30 min. The mixture was stirred for 1 h at 20 °C and poured into cold water (200 ml). The organic layer was separated, washed with water (2 × 50 ml), and dried with $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was chromatographed on Al_2O_3 (hexane–dichloromethane, 3 : 1) to give compound **1**, yield 5.8 g (92%), as orange crystals, mp 182–183 °C (lit:[8] mp 181 °C) [Found: C, 65.71; H, 4.09; Fe, 26.54. Calc. for $C_{23}H_{18}Fe_2O$: C, 65.58; H, 4.28; Fe, 26.36%]; ν_{max} (KBr)/cm^{-1}: 729, 821, 850, 887, 1003, 1100, 1109, 1480, 1602, 1825, 1850, 2917, 3100; δ_H (300 MHz, $CDCl_3$): 4.25 (10 H, s, 2 C_5H_5), 4.58 (4 H, m, C_5H_4), 4.84 (4 H, m, C_5H_4); δ_C (75 MHz, $CDCl_3$): 65.16 (2 C_{ipso}Fc); 70.0 (2 C_5H_5); 70.85, 71.93 (2 C_5H_4); 144.85 (2 C); 152.312 (C=O).

The reaction of 2,3-diferrocenylcyclopropenone 1 with ethylmagnesium chloride

A 2 M solution of ethylmagnesium chloride in diethyl ether (4 ml) was added to a solution of compound **1** (0.42 g, 1 mmol) in dry benzene (100 ml). The mixture was stirred in an inert atmosphere for 3 h at 20 °C and quenched by addition of water (100 ml). The organic layer was separated, washed with water (2 × 20 ml) and benzene was evaporated *in vacuo*. The residue was chromatographed on Al_2O_3 (hexane–diethyl ether, 3 : 1) to give 3,3-diethyl-1,2-diferrocenylcyclopropene **2**, yield 0.10 g (22%), 4,5-diferrocenylheptan-3-one **4**, yield 0.26 g (58%), and 3-ethyl-4,5-diferrocenylheptan-3-ol **6**, yield 0.052 g (10%).

Compound **2**, orange crystals, mp 168–169 °C [Found: C, 69.74; H, 6.21; Fe, 23.87. Calc. for $C_{27}H_{28}Fe_2$: C, 69.86; H, 6.08; Fe, 24.06%]; ν_{max} (KBr)/cm^{-1}: 721, 824, 1004, 1120, 1267, 1464, 1609, 1643, 2859, 2920, 3095; δ_H (300 MHz, $CDCl_3$): 0.98 (6 H, t, *J* = 7.5, 2CH_3), 1.70 (4 H, q, *J* = 7.5, 2 CH_2), 4.15 (10 H, s, 2 C_5H_5), 4.33 (4 H, m, C_5H_4), 4.46 (4 H, m, C_5H_4); δ_C (75 MHz, $CDCl_3$): 12.46 (2 CH_3); 29.46 (2 CH_2); 32.16 (C); 68.61, 68.94 (2 C_5H_4); 69.28 (2 C_5H_5); 75.19 (2 C_{ipso}Fc); 117.03 (2 C).

Compound **4**, orange oil, represents a *ca.* 3 : 1 mixture of isomers **4a** and **4b** (^1H NMR data). The isomers were separated by preparative TLC (hexane–diethyl ether, 4 : 1).

Compound **4a**, 0.17 g (38%), orange crystals, mp 176–177 °C [Found: C, 67.41; H, 6.09; Fe, 23.31. Calc. for $C_{27}H_{30}Fe_2O$: C, 67.25; H, 6.27; Fe, 23.16%]; ν_{max} (KBr)/cm^{-1}: 762, 815, 1102, 1145, 1250, 1435, 1520, 1709, 2931, 3089; δ_H (300 MHz, $CDCl_3$): 0.75 (3 H, t, *J* = 7.5, CH_3), 0.92 (3 H, t, *J* = 7.2, CH_3), 1.80 (2 H, m, CH_2), 2.41 (2 H, q, *J* = 7.2, CH_2), 2.46 (1 H, m, CH), 3.22 (1 H, d, *J* = 9.0, CH), 3.99 (5 H, s, C_5H_5), 4.08 (5 H, s, C_5H_5), 3.85 (1 H, m, C_5H_4), 3.92 (2 H, m, C_5H_4), 4.02 (1 H, m, C_5H_4), 4.09 (2 H, m, C_5H_4), 4.16 (1 H, m, C_5H_4), 4.36 (1 H, m, C_5H_4); δ_C (75 MHz, $CDCl_3$): 6.88, 12.46 (2 CH_3); 26.45, 38.32 (2 CH_2); 45.99, 58.36 (2 CH); 66.25, 66.56, 66.86, 67.52, 68.27, 68.56, 69.34, 69.66 (2 C_5H_4); 68.35, 68.44 (2 C_5H_5); 84.12, 93.49 (2 C_{ipso}Fc); 210.95 (C=O).

Compound **4b**, 0.05 g (10%), orange crystals, mp 164–165 °C; MS: *m/z* 482 [M]$^+$; ν_{max} (KBr)/cm^{-1}: 768, 824, 1100, 1125, 1231, 1425, 1512, 1689, 2919, 3086; δ_H (300 MHz, $CDCl_3$): 0.94 (3 H, t, *J* = 7.3, CH_3), 1.05 (3H, t, *J* = 7.5, CH_3), 1.88 (2 H, m, CH_2), 2.45 (2 H, q, *J* = 7.5, CH_2), 2.49 (1 H, m, CH), 3.56 (1 H, d, *J* = 5.1, CH), 3.97 (5 H, s, C_5H_5), 4.04 (5 H, s, C_5H_5), 3.67 (1 H, m, C_5H_4), 3.76 (1 H, m, C_5H_4), 3.79 (1 H, m, C_5H_4), 3.94 (1 H, m, C_5H_4), 4.03 (2 H, m, C_5H_4), 4.08 (2 H, m, C_5H_4); δ_C (75 MHz, $CDCl_3$): 8.39, 13.61 (2 CH_3); 24.73, 37.33 (2 CH_2); 46.10, 56.56 (2 CH); 66.68, 67.03, 68.00, 68.74 (2 C); 68.92, 69.57, 69.72 (2 C_5H_4); 68.40, 68.46 (2 C_5H_5); 91.32, 94.00 (2 C_{ipso}Fc); 210.12 (C=O).

Compound **4-D**, 0.51 g (56%), orange oil, represents a *ca.* 3 : 1 mixture of isomers **4a-D** and **4b-D** (^1H NMR data). MS: *m/z* 483, 484 [M]$^+$.

Compound **4a-D**, δ_H (300 MHz, $CDCl_3$): 0.76 (3 H, t, *J* = 7.3, CH_3), 0.92 (3 H, t, *J* = 7.2, CH_3), 1.81 (2 H, q, *J* = 7.3, CH_2), 2.41 (2 H, q, *J* = 7.2, CH_2), 2.46 (0.13 H, m, CH), 3.22 (0.6 H, s, CH), 3.99 (5 H, s, C_5H_5), 4.06 (5 H, s, C_5H_5), 3.85 (1 H, m, C_5H_4), 3.92 (2 H, m, C_5H_4), 4.02 (1 H, m, C_5H_4), 4.09 (2 H, m, C_5H_4), 4.16 (1 H, m, C_5H_4), 4.36 (1 H, m, C_5H_4).

Compound **4b-D**, δ_H (300 MHz, $CDCl_3$): 0.95 (3 H, t, *J* = 7.2, CH_3), 1.04 (3 H, t, CH_3, *J* = 7.5, CH_3), 1.89 (2 H, q, *J* = 7.2, CH_2), 2.44 (2 H, q, *J* = 7.5, CH_2), 2.49 (0.12 H, m, CH), 3.56 (0.55 H, s, CH), 3.97 (5 H, s, C_5H_5), 4.04 (5 H, s, C_5H_5), 3.67 (1 H, m, C_5H_4), 3.76 (1 H, m, C_5H_4), 3.79 (1 H, m, C_5H_4), 3.94 (1 H, m, C_5H_4), 4.03 (2 H, m, C_5H_4), 4.07 (2 H, m, C_5H_4).

The reaction of 2,3-diferrocenylcyclopropenone 1 with benzylmagnesium chloride

This was carried out analogously using cyclopropenone **1** (0.42 g, 1 mmol) and benzylmagnesium chloride (1 M solution in diethyl ether, 6 ml). The reaction mixture was worked up as described above, subsequent chromatography on Al_2O_3 (hexane–diethyl ether, 2 : 1) gave 3,3-dibenzyl-1,2-diferrocenylcyclopropene **3**, yield 0.12 g (20%), and 3,4-diferrocenyl-1,5-diphenylpentanon-2-one **5**, yield 0.33 g (55%).

Compound **3**, 0.12 g (20%), orange crystals, mp 112–113 °C [Found: C, 75.39; H, 5.67; Fe, 19.20. Calc. for $C_{37}H_{32}Fe_2$: C, 75.53; H, 5.48; Fe, 18.99%]; ν_{max} (KBr)/cm^{-1}: 718, 821, 1003, 1105, 1258, 1470, 1589, 1623, 1645, 2883, 2936, 3085; δ_H (300 MHz, $CDCl_3$): 2.96 (4 H, s, 2 CH_2), 4.10 (10 H, s, 2 C_5H_5), 4.33 (4 H, m, C_5H_4), 4.39 (4 H, m, C_5H_4), 7.15–7.29 (10 H, m, 2 C_6H_5); δ_C (75 MHz, $CDCl_3$): 33.31 (C); 43.85 (2 CH_2); 68.85, 69.03 (2 C_5H_4); 69.34 (2 C_5H_5); 74.37 (2 C_{ipso}Fc); 117.69 (2 C); 125.66, 127.90, 129.91 (2 C_6H_5); 140.90 (2 C_{ipso}).

Compound **5**, 0.33 g (55%), orange powder, mp 183–188 °C, represents a *ca.* 3 : 1 mixture of isomers **5a** and **5b** (^{1}H NMR data). MS: *m/z* 606 $[M]^+$. [Found: C, 73.41; H, 5.39; Fe, 18.31. Calc. for $C_{37}H_{34}Fe_2O$: C, 73.29; H, 5.65; Fe, 18.42%]; ν_{max} (KBr)/cm^{-1}: 767, 823, 1021, 1110, 1233, 1448, 1525, 1536, 1654, 1710, 2921, 3098.

Compound **5a**, δ_H (300 MHz, $CDCl_3$): 2.61 (1 H, m, CH), 3.15 (2 H, d, *J* = 6.3, CH_2), 3.23 (2 H, s, CH_2), 3.54 (1 H, d, *J* = 8.4, CH), 4.09 (5 H, s, C_5H_5), 4.14 (5 H, s, C_5H_5), 4.05 (1 H, m, C_5H_4), 4.12 (2 H, m, C_5H_4), 4.15 (1 H, m, C_5H_4), 4.18 (2 H, m, C_5H_4), 4.21 (1 H, m, C_5H_4), 4.46 (1 H, m, C_5H_4), 6.89–7.54 (10 H, m, 2 C_6H_5).

Compound **5b**, δ_H (300 MHz, $CDCl_3$): 2.68 (1 H, m, CH), 3.10 (2 H, d, *J* = 6.6, CH_2), 3.30 (2 H, s, CH_2), 3.41 (1 H, d, *J* = 8.7, CH), 4.00 (5 H, s, C_5H_5), 4.10 (5 H, s, C_5H_5), 3.95 (1 H, m, C_5H_4), 4.02 (2 H, m, C_5H_4), 4.13 (1 H, m, C_5H_4), 4.15 (2 H, m, C_5H_4), 4.17 (1 H, m, C_5H_4), 4.32 (1 H, m, C_5H_4), 7.04–7.63 (10 H, m, 2 C_6H_5).

The action of tetrafluoroboric acid etherate on the cyclopropene 2

Tetrafluoroboric acid etherate (3 ml) was added dropwise in an atmosphere of dry nitrogen to a stirred solution of the cyclopropene **2** (0.32 g, 0.7 mmol) in dry diethyl ether (100 ml) at −40 to −50 °C and the mixture was stirred for 15 min at −40 °C. The black powder that formed was separated by decanting, washed with several portions of cold dry ether, and dried in a vacuum desiccator with external cooling. The yield of tetrafluoroborate **7**, a nearly black powder, was 0.25 g (64%), decomp. at *ca.* 183 °C; δ_H (300 MHz, CD_2Cl_2): 1.14 (3 H, t, *J* = 7.4, CH_3), 1.26 (3 H, t, *J* = 7.2, CH_3), 1.88–2.14 (4 H, m, 2 CH_2), 2.47 (1 H, s, CH), 4.13 (2 H, m, C_5H_4), 4.17 (2 H, m, C_5H_4), 4.58 (2 H, m, C_5H_4), 5.74 (2 H, m, C_5H_4), 4.22 (5 H, s, C_5H_5), 4.35 (5 H, s, C_5H_5).

A solution of the tetrafluoroborate **7** (0.22 g, 0.4 mmol) in dichloromethane (50 ml) was kept at ambient temperature for 4 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 desiccator to give 1,1-diethyl-2,3-diferrocenylallylium tetrafluoroborate **9** as a dark brown powder, yield 0.17g (80%), decomp. at *ca.* 200 °C [Found: C, 58.93; H, 5.12; F, 13.64; Fe, 23.45. Calc. for $C_{27}H_{29}BF_4Fe_2$: C, 58.74; H, 5.30; F, 13.77; Fe, 20.23%]; δ_H (300 MHz, CD_2Cl_2): 1.12 (3 H, t, *J* = 6.6, CH_3), 1.73 (3 H, t, *J* = 6.9, CH_3), 2.57–3.54 (4 H, m, 2 CH_2), 4.20 (2 H, m, C_5H_4), 4.70 (2 H, m, C_5H_4), 5.20 (1 H, m, C_5H_4), 6.22 (2 H, m, C_5H_4), 6.41 (1 H, m, C_5H_4), 4.27 (5 H, s, C_5H_5), 4.86 (5 H, s, C_5H_5) 8.57 (1 H, s, CH).

The action of tetrafluoroboric acid etherate on the cyclopropene 3

Analogous treatment of the cyclopropene **3** (0.44 g, 0.8 mmol) in dry ether (100 ml) with tetrafluoroboric acid etherate (4 ml) at −50 °C afforded tetrafluoroborate **8**, yield 0.41 g, 60%, as a black powder, decomp. at *ca.* 190 °C; δ_H (300 MHz, CD_2Cl_2): 2.86 (1 H, s, CH), 3.28 (2 H, d, *J* = 13.5, CH_2), 3.38 (2 H, d, *J* = 15.3, CH_2), 4.19 (2 H, m, C_5H_4), 4.29 (2 H, m, C_5H_4), 4.73 (2 H, m, C_5H_4), 5.61 (2 H, m, C_5H_4), 4.14 (5 H, s, C_5H_5), 4.48 (5 H, s, C_5H_5), 6.95–7.44 (10 H, m, 2 C_6H_5).

A solution of the tetrafluoroborate **8** (0.34 g, 0.5 mmol) in dry CH_2Cl_2 (50 ml) was kept at ambient temperature for 4 h and 1,1-dibenzyl-2,3-diferrocenylallylium tetrafluoroborate **10** was precipitated with dry ether, yield 0.25 g (72%), as a nearly black fine crystalline powder, decomp. at *ca.* 210 °C [Found: C, 65.89; H, 4.74; F, 11.42; Fe, 16.68. Calc. for $C_{37}H_{33}BF_4Fe_2$: C, 65.72; H, 4.92; F, 11.24; Fe, 16.52%]; δ_H (300 MHz, CD_2Cl_2): 3.71 (2 H, br s, CH_2), 3.99 (2 H, br s, CH_2), 4.70 (1 H, m, C_5H_4), 4.79 (1 H, m, C_5H_4), 4.92 (3 H, m, C_5H_4), 5.51 (1 H, m, C_5H_4), 6.05 (1 H, m, C_5H_4), 6.11 (1 H, m, C_5H_4), 4.87 (5 H, s, C_5H_5), 5.01 (5 H, s, C_5H_5), 7.21–7.47 (10 H, m, 2 C_6H_5), 8.59 (1 H, s, CH).

3-Ethyl-1,2-diferrocenylpenta-1,3-diene 11

N,*N*-Dimethylaniline (0.5 ml) was added dropwise to a solution of the tetrafluoroborate **9** (0.17 g, 0.3 mmol) in dichloromethane (50 ml). The mixture was stirred for 1 h at 20 °C, then the excess of the amine was removed by washing with 5% HCl (3 × 15 ml) and the solvent was evaporated *in vacuo*. The residue was chromatographed on Al_2O_3 (hexane) to give 0.11 g (80%) of the diene **11** as orange crystals, mp 142–143 °C [Found: C, 69.73; H, 5.91; Fe, 24.25. Calc. for $C_{27}H_{28}Fe_2$: C, 69.86; H, 6.08; Fe, 24.06%]; ν_{max} (KBr)/cm^{-1}: 738, 829, 1014, 1102, 1259, 1444, 1580, 1664, 2895, 2930, 3081; δ_H (300 MHz, $CDCl_3$): 0.92 (3 H, t, *J* = 7.5, CH_3), 1.82 (3 H, d, *J* = 6.9, CH_3), 2.30 (2 H, q, *J* = 7.5, CH_2), 4.10 (5 H, s, C_5H_5), 4.11 (5 H, s, C_5H_5), 4.18 (2 H, m, C_5H_4), 4.20 (2 H, m, C_5H_4), 4.34 (2 H, m, C_5H_4), 4.38 (2 H, m, C_5H_4), 5.59 (1 H, q, *J* = 6.9, CH=), 6.38 (1 H, s, CH=); δ_C (75 MHz, $CDCl_3$): 12.80, 23.81 (2 CH_3); 13.40 (CH_2); 66.54, 68.08, 68.37, 68.83 (2 C_5H_4); 69.03, 69.48 (2 C_5H_5); 83.21, 88.47 (2 C_{ipso}Fc); 121.06, 122.87 (2 CH=); 138.42, 140.48 (2 C).

3-Benzyl-1,2-diferrocenyl-1,4-dihydronaphthalene 13

Treatment of the tetrafluoroborate **10** (0.38 g, 0.5 mmol) with *N*,*N*-dimethylaniline and subsequent chromatography (Al_2O_3, hexane) afforded 0.20 g (65%) of compound **13** as a pale yellow powder, mp 184–186 °C [Found: C, 75.68; H, 5.24; Fe, 19.18. Calc. for $C_{37}H_{32}Fe_2$: C, 75.53; H, 5.48; Fe, 18.99%]; ν_{max} (KBr)/cm^{-1}: 723, 817, 1009, 1110, 1245, 1452, 1567, 1620, 1667, 2906, 2936, 3087; δ_H (300 MHz, $CDCl_3$): 3.12 (1 H, d, *J* = 18.0, CH_2), 3.24 (1 H, d, *J* = 18.0, CH_2), 3.66 (1 H, d, *J* = 15.6, CH_2), 3.97 (1 H, d, *J* = 15.6, CH_2), 3.95 (5 H, s, C_5H_5), 4.06 (5 H, s, C_5H_5), 3.90 (2 H, m, C_5H_4), 4.01 (2 H, m, C_5H_4), 4.18 (2 H, m, C_5H_4), 4.24 (2 H, m, C_5H_4), 7.01–7.33 (9 H, m, C_6H_4, C_6H_5).

7-Ethyl-5,6-diferrocenyl-8-methyl-2-phenyl-5,8-dihydro[1,2,4]-triazolo[1,2-*a*]pyridazine-1,3-dione 12

4-Phenyl-3,5-dihydro-1,2,4-triazole-3,5-dione (0.05 g, 0.3 mmol) was added to a solution of the diene **11** (0.12 g, 0.25 mmol) in benzene (20 ml). The mixture was stirred at 20 °C for 3 h, the solvent was evaporated *in vacuo*, and the residue was chromatographed on Al_2O_3 (hexane–dichloromethane, 2 : 1) to give 0.12 g (70%) of the adduct **12** as yellow crystals, mp 213–214 °C [Found: C, 65.84; H, 4.98; Fe, 17.73; N, 6.69. Calc. for $C_{35}H_{33}Fe_2N_3O_2$: C, 65.75; H, 5.20; Fe, 17.48; N, 6.57%]; ν_{max} (KBr)/cm^{-1}: 742, 834, 1014, 1025, 1140, 1280, 1463, 1620, 1665, 1712, 2915, 2930, 3078; δ_H (300 MHz, $CDCl_3$): 1.26 (3 H, t, *J* = 7.5, CH_3), 1.45 (3 H, d, *J* = 6.3, CH_3), 3.73 (2 H, q, *J* = 7.5, CH_2), 3.91 (5 H, s, C_5H_5), 4.14 (5 H, s, C_5H_5), 3.85 (1 H, m, C_5H_4), 4.01 (2 H, m, C_5H_4), 4.07 (1 H, m, C_5H_4), 4.35 (2 H, m, C_5H_4), 4.41 (1 H, m, C_5H_4), 4.56 (1 H, m, C_5H_4), 4.59 (1 H, q, *J* = 6.3, CH), 5.68 (1 H, s, CH), 7.33–7.50 (5 H, m, C_6H_5); δ_C (75 MHz, $CDCl_3$): 13.77, 16.34 (2 CH_3); 23.72 (CH_2); 52.52, 56.23 (2 CH); 66.87, 67.17, 67.58, 67.60, 67.76, 68.72, 69.15, 71.21 (2 C_5H_4); 69.00, 69.63 (2 C_5H_5); 84.30, 87.88 (2 C_{ipso}Fc); 125.46, 128.09, 129.16 (C_6H_5); 126.11, 131.35 (2 C); 135.11 (C_{ipso}); 152.66, 152.86 (2 C=O).

Crystal structure determination

The unit cell parameters and the X-ray diffraction intensities were recorded on a Siemens P4/PC/ω diffractometer (compound **2**) and on a Bruker Smart Apex CCD area detector/ω diffractometer (compound **4a**). The structures of compounds **2** and **4a** were solved by the direct method (SHELXS) and refined using full-matrix least-squares on F^2.

Crystal data for $C_{27}H_{28}Fe_2$ (**2**),† $M = 464.19$ g mol^{-1}, monoclinic $P2_1/c$, $a = 7.632(2)$, $b = 15.352(4)$, $c = 18.943(8)$ Å, $\alpha = 90$, $\beta = 94.83(3)$, $\gamma = 90°$, $V = 2211.6(12)$ Å^3, $T = 293(2)$ K, $Z = 4$, $\rho = 1.394$ Mg m^{-3}, λ(Mo-Kα) = 0.71073 Å, $F(000) = 968$, absorption coefficient 1.322 mm^{-1}, index ranges $0 \le h \le 9$, $0 \le k \le 18$, $-22 \le l \le 22$, scan range $2.16 \le \theta \le 25.01°$, 3884 independent reflections, $R_{int} = 0.0622$, 4195 total reflections, 264 refinable parameters, final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0711$, $wR_2 = 0.1517$, R indices (all data) $R_1 = 0.1389$, $wR_2 = 0.1872$, largest difference peak and hole 0.604/−0.384 e Å^{-3}.

Crystal data for $C_{27}H_{30}Fe_2O$ (**4a**),† $M = 482.21$ g mol^{-1}, monoclinic $P2_1$, $a = 11.0169(8)$, $b = 7.8226(5)$, $c = 13.1321(9)$ Å, $\alpha = 90$, $\beta = 102.3290(10)$, $\gamma = 90°$, $V = 1105.63(13)$ Å^3, $T = 291(2)$ K, $Z = 2$, $\rho = 1.448$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, $F(000) = 504$, absorption coefficient 1.328 mm^{-1}, index ranges $-13 \le h \le 13$, $-9 \le k \le 9$, $-15 \le l \le 15$, scan range $1.59 \le \theta \le 25.00°$, 3864 independent reflections, $R_{int} = 0.0351$, 9069 total reflections, 273 refinable parameters, final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0390$, $wR_2 = 0.0749$, R indices (all data) $R_1 = 0.0511$, $wR_2 = 0.0784$, largest difference peak and hole 0.478/−0.183 e Å^{-3}.

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