2,3-Diferrocenylcyclopropenone: Synthesis, Structure, and Some Chemical and Electrochemical Properties

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Keywords: Cyclopropene / Ring opening / Electrochemistry / Ferrocene

Alkylation of ferrocene with tetrachlorocyclopropene in the presence of $AlCl_3$ followed by aqueous workup affords 2,3-diferrocenylcyclopropenone in high yield. We have studied some of this ketone's chemical transformations and electrochemical properties. 2,3-Diferrocenylcyclopropenone withstands thermolysis; it is stable in an acidic medium; the action of tetrafluoroboric acid–diethyl ether results in the formation of diferrocenyl(hydroxy)cyclopropenylium tetrafluoroborate; nucleophiles, including methyllithium and lithium aluminum hydride, react regioselectively with the three-membered ring by opening it to form the respective substituted *cis*-diferrocenylethenes. We present data from X-ray diffraction analyses of 2,3-diferrocenylcyclopropenone, isopropyl *cis*-2,3-diferrocenylacrylate, and *cis*-3,4-diferrocenyl-2-methylbut-3-en-2-ol.

Introduction

Recent investigations into the chemistry of 3-ferrocenylcyclopropenes[1−3] have made it possible to determine experimentally the geometrical parameters of the unsaturated three-membered ring, viz., the C=C and C−C bond lengths, the values of the angles at C(1), C(2), and C(3), and the steric orientation of substituents at C(3). Some characteristic features of the intramolecular transformations of 3-ferrocenylcyclopropenes have been elucidated, including their dependence on the spatial arrangement of the ferrocene group and the mutual effects of the ferrocene and cyclopropene fragments.

The preparation of arylcyclopropenones and their ketals, as well as studies on their reactivities and use in organic synthesis, has been the topic of many publications dealing with aryl-substituted cyclopropenes.[4−9] We note that the considerable theoretical interest in arylcyclopropenones stems from their strained, highly planar, and pseudoaromatic nature.

Virtually no studies on ferrocenyl-substituted analogs of arylcyclopropenones have been carried out so far, despite the fact that 2,3-diferrocenylcyclopropenone (**1**) was first isolated in ca. 7% yield by Agranat et al.[10,11] The analysis of the effects of the ferrocene fragments on the stability of the pseudoaromatic cyclopropenone system, as well as regio- and stereoselectivities of chemical transformations of ferrocenylcyclopropenones, is clearly of interest. Provided that the latter compounds are accessible, they may serve as the starting materials for the synthesis of various useful compounds of the ferrocene series that comprise functionalized olefin fragments.

The study of ferrocene derivatives having olefinic architectures and bearing functional groups has gained prominence by virtue of their exciting structures, chemical reactivities, and potential for use as molecular building blocks and in the realm of supramolecular chemistry as redox switching receptors.[12−15]

Diferrocenes that have their units separated by unsaturated carbon−carbon bonds constitute a classic example of molecules that are able to exhibit intramolecular electron mobility because their one-electron oxidation products usually are partially or completely delocalized mixed-valence derivatives; typical examples are provided by diferrocenylethene and diferrocenylethyne.[16,17] In this regard, electrochemical investigations on diferrocenes having cyclopropene units as spacers are rather scanty. To the best of our knowledge, the only electrochemical results reported concern 1,2,3-triferrocenylcyclopropenes.[18]

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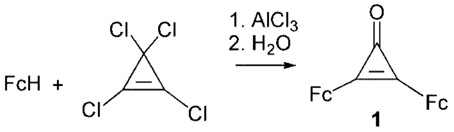
DOI: 10.1002/ejoc.200300318

This paper is devoted to the synthesis of the simplest representative of ferrocenylcyclopropenones, viz., 2,3-diferrocenylcyclopropenone (**1**), and to studies of some of its chemical transformations.

Results and Discussion

We have found that 2,3-diferrocenylcyclopropenone is formed smoothly upon conventional alkylation of ferrocene with tetrachlorocyclopropene in the presence of $AlCl_3$ at ambient temperature (Scheme 1).



Scheme 1

2,3-Diferrocenylcyclopropenone (**1**) is a storage-stable, orange, crystalline compound. Its structure was established by ^1H and ^{13}C NMR spectroscopy and by X-ray diffraction analysis of single crystals of **1** prepared by crystallization from benzene.

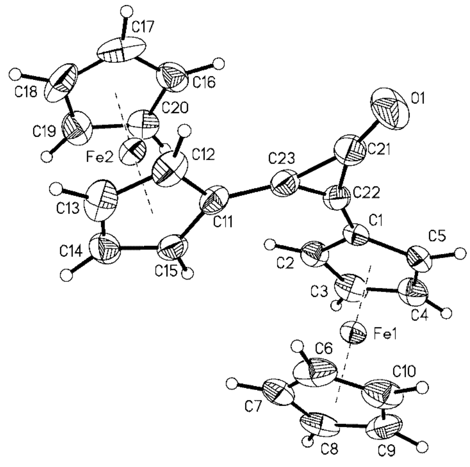


Figure 1. Crystal structure of **1**

A general view of **1** is depicted in Figure 1 and selected bond lengths and angles are listed in Table 1. In the molecule of compound **1**, the substituted cyclopentadienyl rings of the ferrocene fragments are coplanar with, and the ferrocene sandwiches oriented in opposite directions with respect to, the central planar three-membered ring. The differences between the lengths of the formally single C−C bonds and the double C=C bond are 0.051 and 0.054 Å, which are similar to the analogous length differences in 2,3-diphenylcyclopropenone.[19] The C=O, Fe−C, and carbon−carbon bonds of the cyclopentadienyl rings, as well as the geometrical parameters of the ferrocene sandwiches, are close to standard values.[20]

Table 1. Selected bond lengths and angles for compounds **1**, **5**, and **10**

	Selected bond lengths (Å)		Selected bond angles (°)	
1	C(21)−C(22)	1.409(3)	C(22)−C(21)−C(23)	57.54(15)
	C(21)−C(23)	1.412(3)	C(23)−C(22)−C(21)	61.33(16)
	C(23)−C(22)	1.358(3)	C(22)−C(23)−C(21)	61.13(17)
	O(1)−C(21)	1.215(3)	O(1)−C(21)−C(22)	151.4(3)
			O(1)−C(21)−C(23)	151.0(3)
5	O(1)−C(1)	1.342(3)	C(1)−C(2)−C(3)	117.1(2)
	O(2)−C(1)	1.205(3)	C(14)−C(2)−C(3)	124.0(2)
	C(1)−C(2)	1.481(3)	C(14)−C(2)−C(1)	118.9(2)
	C(2)−C(3)	1.333(3)	C(2)−C(3)−C(4)	125.8(2)
	C(3)−C(4)	1.462(3)	O(1)−C(1)−C(2)	113.1(2)
	C(2)−C(14)	1.473(3)	O(2)−C(1)−O(1)	122.3(2)
10	C(21)−C(22)	1.329(7)	C(23)−C(21)−C(22)	119.1(5)
	O(1)−C(23)	1.439(7)	C(22)−C(21)−C(1)	120.7(4)
	C(21)−C(23)	1.545(6)	C(21)−C(22)−C(11)	130.9(5)
	C(22)−C(11)	1.479(6)	C(24)−C(23)−C(21)	109.3(4)
	C(1)−C(21)	1.488(7)	C(24)−C(23)−C(25)	113.2(2)
	C(23)−C(24)	1.531(8)		

Electrochemistry

Figure 2 displays the cyclic- and square-wave voltammetric profiles exhibited by diferrocenylcyclopropenone (**1**) at a platinum electrode in a CH_2Cl_2 solution containing $[NBu_4][PF_6]$ as the supporting electrolyte.

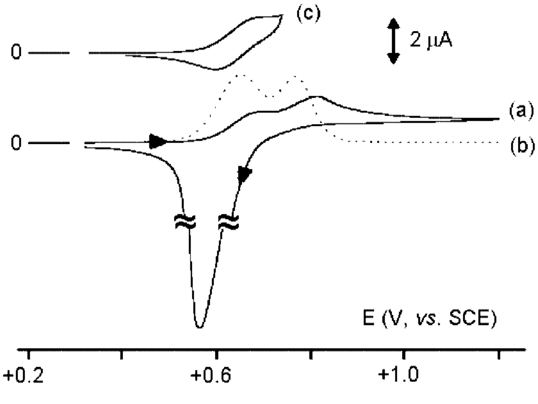


Figure 2. Cyclic- (−−) and osteryoung square-wave (− − −) voltammograms recorded at a platinum electrode in CH_2Cl_2 solution of **1** ($1.0 \cdot 10^{-3}$ mol·dm^{-3}) containing $[NBu_4][PF_6]$ (0.2 mol·dm^{-3}) as the supporting electrolyte. Scan rate: 0.1 V·s^{-1}

Two separate oxidations are observed, the second of which is affected by adsorption phenomena at the electrode surface. Unfortunately, the use of different electrode materials (such as glassy carbon or gold) did not modify the voltammetric profile. It is quite conceivable that the two anodic processes might correspond to the sequential oxidation of the two ferrocene subunits.

Attempts to generate the monocation **1**/[**1**]$^+$ by controlled potential coulometry in correspondence of the first anodic step (E_w = +0.70 V) were partially successful in that the closeness of the subsequent adsorption process prevented completion of exhaustive oxidation (the electrolysis current disappears substantially after consumption of ca. 0.4 electrons/molecule). As a consequence of such partial oxidation, the original orange solution (λ_{max} = 470 nm, very intense) turned brown-violet (λ_{max} = 510 nm, weak and broad), but, importantly, hydrodynamic voltammetry (at an electrode with periodical renewal of the diffusion layer) on the resulting solution indicated the presence of a catho-anodic wave at the same values of potential as the original first oxidation, which indicates the chemical reversibility of the **1**/[**1**]$^+$ electron removal process.

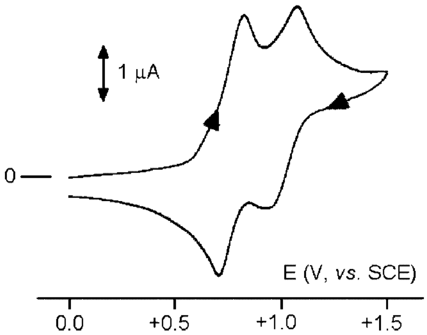


Figure 3. Cyclic voltammogram recorded at a platinum electrode in CH_2Cl_2 solution of **1** ($0.5\cdot10^{-3}$ mol·dm^{-3}) containing $[NBu_4][B(C_6F_5)_4]$ (0.1 mol·dm^{-3}) as the supporting electrolyte. Scan rate: 0.1 V·s^{-1}

As illustrated in Figure 3, the use of the poorly coordinating supporting electrolyte $[NBu_4][B(C_6F_5)_4]$, which is known to be able to make highly charged cations soluble,[21] allowed us to find evidence that the second oxidation is also chemically reversible, at least on the cyclic voltammetric time scale.

Step-by-step controlled potential electrolysis caused the original orange solution to turn progressively browner and then green. Cyclic voltammetric tests after exhaustive two-electron oxidation, however, revealed the presence not only of the [**1**]$^{2+}$/[**1**]$^+$ and [**1**]$^+$/**1** reductions, but also of significant amounts of a new species that reduces reversibly at lower potential values ($E^{o\prime}$ = +0.31 V). This observation implies that the dication [**1**]$^{2+}$ is not completely stable during the long times required for macroelectrolysis.

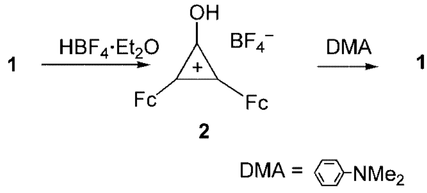
The formal electrode potentials of these redox processes are compiled in Table 2.

It is interesting to note that because $[B(C_6F_5)_4]^-$ possesses low ion-pairing capacity — notably lower than that of $[PF_6]^-$ — it commonly increases the separation between sequential oxidations of multiferrocenes by increasing the electrostatic repulsion between progressively electrogenerated charged cations.[21,22] This phenomenon implies that the classification of the mixed valent species according to the comproportionation constant K_{com}, as routinely derived from electrochemical measurements,[23] varies with the supporting electrolyte. Even if the value of K_{com} is contributed by different factors (such as electrostatic repulsion, statistical effects, inductive effects, and magnetic exchanges),[24] it follows that [**1**]$^+$ in the presence of $[NBu_4][PF_6]$ would belong to the localized Robin−Day[25] Class I mixed-valence species, whereas in the presence of $[NBu_4][B(C_6F_5)_4]$ it would belong to the partially delocalized Class II.

Chemical Transformations

The pseudoaromatic character of 2,3-diferrocenylcyclopropenone (**1**) is manifested in its stability towards thermolysis (boiling in mesitylene) and the action of acids (AcOH, HCl). This compound does not form Diels−Alder adducts with dienes such as 1,3-diphhenylisobenzofuran, tetraphenylcyclopentadienone, tetraphenylcyclopentadiene, and cyclohexa-1,3-diene.

Treatment of the cyclopropenone **1** with tetrafluoroboric acid−diethyl ether affords crystalline diferrocenyl(hydroxy)-cyclopropenylium tetrafluoroborate (**2**), which can be stored in a dry inert atmosphere (Scheme 2)



Scheme 2

The signals for the protons of the cyclopentadienyl rings of ferrocene in the ^1H NMR spectrum of the salt **2** are shifted to noticeably lower fields (δ_{C5H5} = 4.42 ppm, δ_{C5H4} = 4.90 and 5.12 ppm) relative to those of the original 2,3-diferrocenylcyclopropenone (**1**) (δ_{C5H5} = 4.25 ppm, δ_{C5H4} = 4.58 and 4.84 ppm). In addition, the NMR spectrum of the salt **2** contains a broad signal for the hydroxyl group (δ = 4.72 ppm). Data from the ^{13}C NMR spectrum corroborate the structure of the salt **2**.

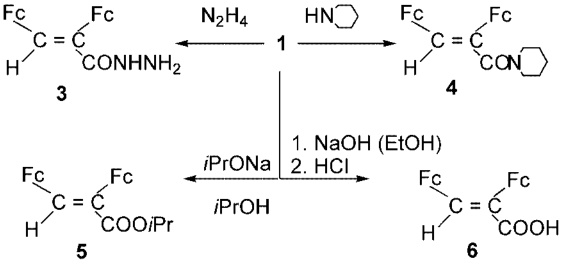
Table 2. Formal electrode potentials (V vs. SCE), peak-to-peak separations (mV), and separation between the two sequential oxidations (V) of **1** in CH_2Cl_2 solution.

Complex	$E^{o\prime}_{(0/+)}$	ΔE_p[a]	$E^{o\prime}_{(+/2+)}$	ΔE_p[a]	$\Delta E^{o\prime}$	K_{com}	Supporting electrolyte
1	+0.66	60	+0.81[a,b]	–	≈ 120	≈ $1.1\cdot10^2$	$[NBu_4][PF_6]$ (0.2 mol·dm^{-3})
	+0.75	91	+1.01	115	260	$2.5\cdot10^4$	$[NBu_4][B(C_6F_5)_4]$ (0.1 mol·dm^{-3})
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.

Unlike aryl- and ferrocenylcyclopropenyl cations, which give 3-substituted cyclopropenes upon the action of nucleophiles,[18] the cation **2** undergoes deprotonation to reform the starting 2,3-diferrocenylcyclopropenone (**1**) upon treatment with bases (*N*,*N*-dimethylaniline, pyridine) (Scheme 2).

We have found further that compound **1** reacted readily with different nucleophiles, e.g., hydrazine hydrate, piperidine, sodium isopropoxide, and sodium hydroxide (refluxing the reactants in ethanol or propan-2-ol), to give 2,3-diferrocenylacrylic acid derivatives in high yields (Scheme 3).



Scheme 3

The structures of compounds **3**−**6** were established based on their ^{1}H and ^{13}C NMR spectroscopic and elemental analysis data.

According to their ^{1}H NMR spectra, 2,3-diferrocenylacrylic acid (**6**) and its derivatives **3**−**5** are formed as single isomers, presumably with cis configurations. This assumption was confirmed by X-ray diffraction analysis of a single crystal of isopropyl 2,3-diferrocenylacrylate (**5**) prepared by crystallization from dichloromethane. The unit cells of the monoclinic crystals of compound **5** contained molecules closely arranged in pairs of cis isomers. A general view of the molecule **5** is given in Figure 4 and selected bond lengths and angles are shown in Table 1.

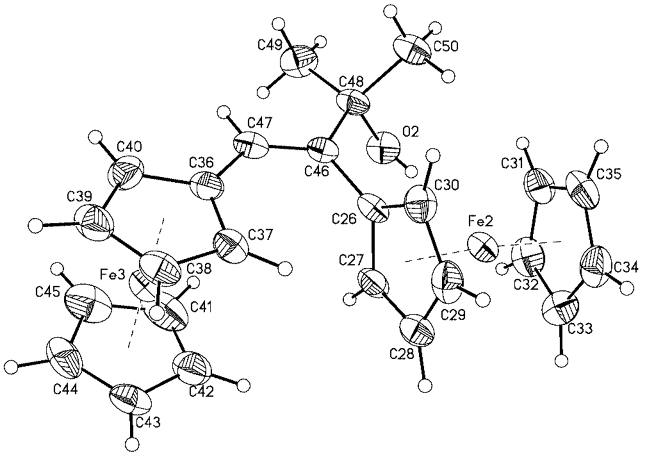


Figure 4. Crystal structure of **5**

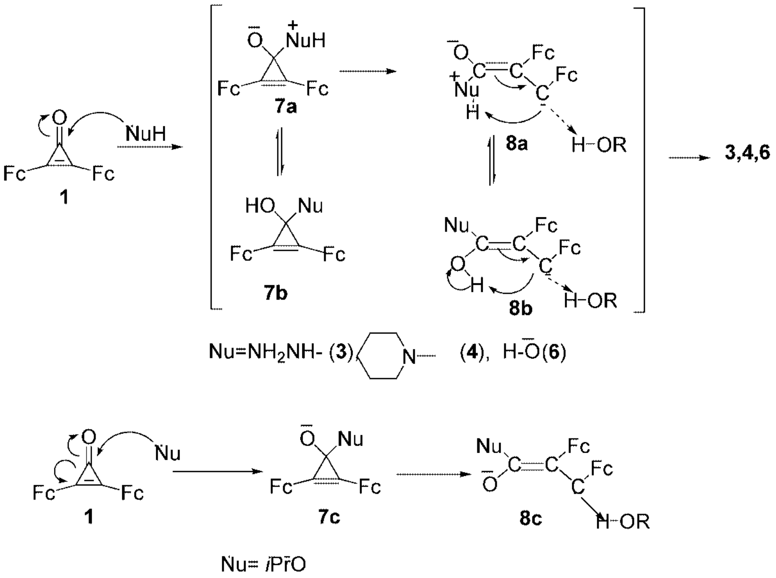
The three-membered ring opening of 2,3-diferrocenylcyclopropenone (**1**) can occur by two pathways:

1. The nucleophiles add to the carbonyl group to give intermediates **7a**−**c**, which undergo ring-opening into carbenoid (**8a**,**b**) or anionic carbenoid (**8c**) species (Scheme 4).

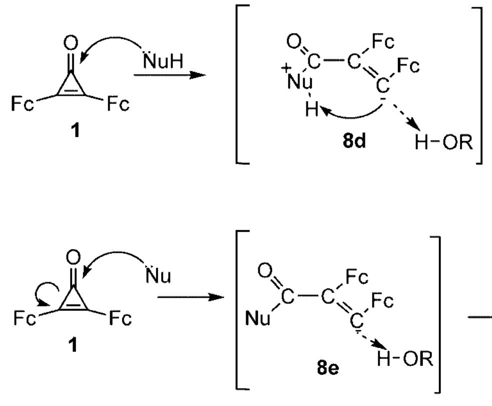
2. The nucleophiles attack the carbonyl carbon atom with concomitant heterolysis of a σ-bond of the cyclopropenone ring to give vinyl anionic intermediates (**8d**,**e**) (Scheme 5).

To understand the mechanisms, we must take into account the mesomeric character of the carbenoid, anionic carbenoid and vinyl anionic species **8a** ⇄ **8d** and **8c** ⇄ **8e** and interconversions of all of these species **8a**−**e** during protonation/deprotonation processes (Scheme 6).

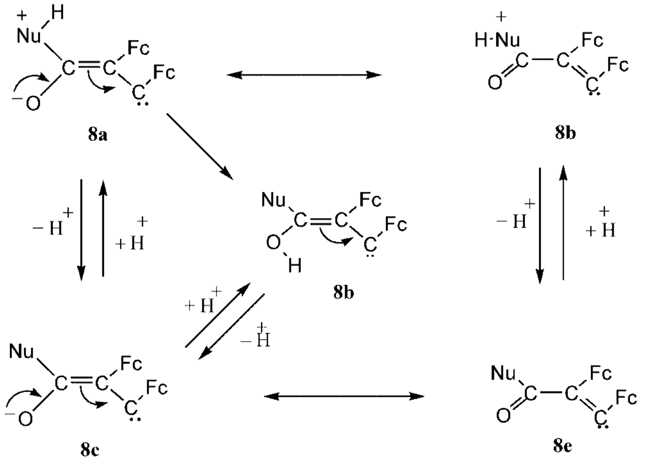
The transformations of the intermediates **8a**,**b**,**d** into the final products **3**, **4**, and **6**, respectively, can follow both the intra- and intermolecular mechanisms (Schemes 4 and 5).



Scheme 4



Scheme 5



Scheme 6

The intermediates **8c** and **8e** can yield the final product **5** only upon abstraction of a proton from a solvent, i.e., in an intermolecular fashion.

Our results do not allow us to make an unambiguous choice between the two possible pathways of the ring opening in cyclopropenone **1** and the two possible pathways of the transformation of the intermediates **8a**,**b**,**d** into the final products.

We believe, however, that we have data that favors the intermolecular transformation of the intermediates **8c** $\rightleftarrows$ **8e** into the final product. Thus, the cyclopropenone **1** also undergoes smooth opening of the small ring when treated with potassium *tert*-butoxide in benzene as an aprotic solvent. Quenching of the reaction mixture with D_2O resulted in *tert*-butyl *cis*-2,3-diferrocenylacrylate (**9**) containing ca. 85% deuterium as judged by the ^{1}H NMR spectroscopic data (Scheme 7).

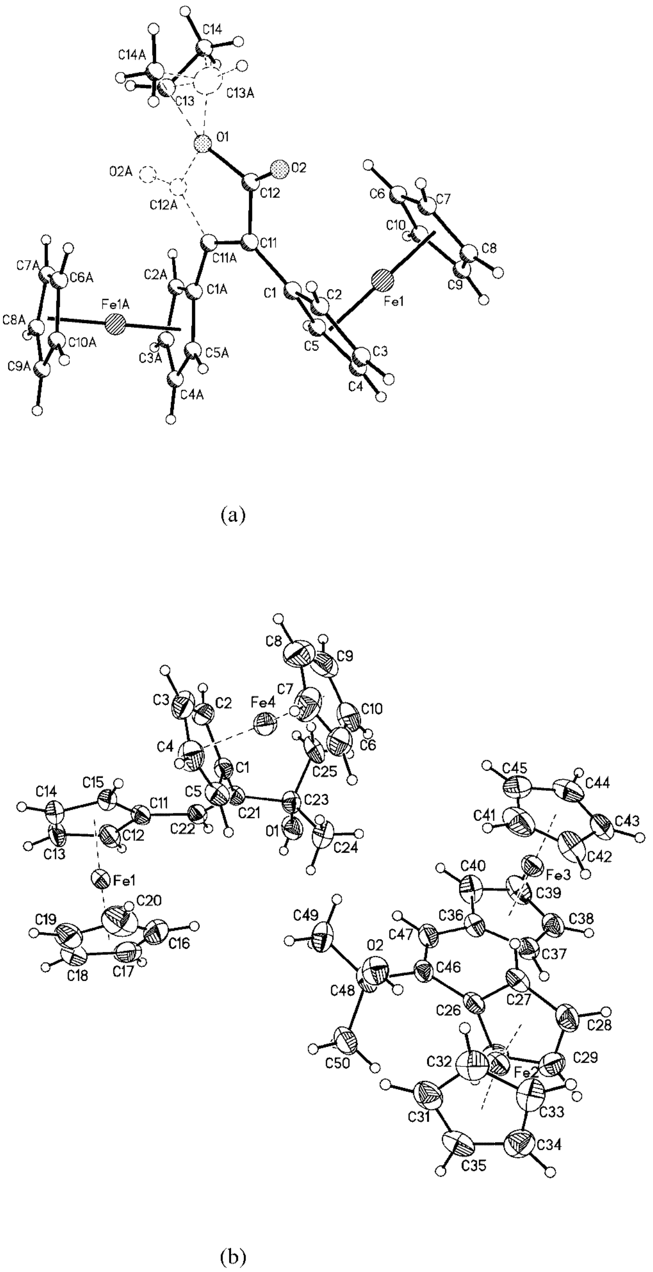
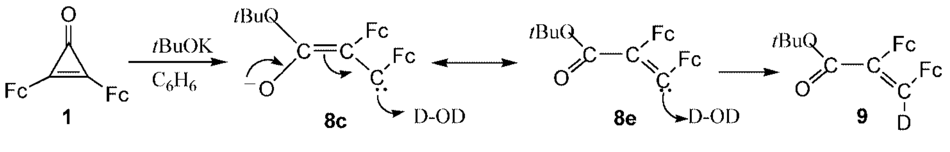


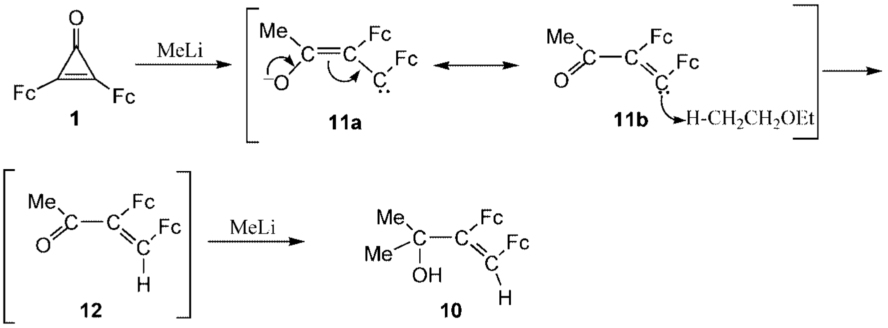
Figure 5. (a) Crystal structure and (b) twinned molecules of **10**

The reaction of 2,3-diferrocenylcyclopropenone (**1**) with methyllithium affords several products, the major one being 3,4-diferrocenyl-2-methylbut-3-en-2-ol (**10**) (yield: ca. 60%). We have not yet established the structures of the accompanying high-molecular mass reaction products.

The structure of the alcohol **10** was deduced from ^{1}H and ^{13}C NMR spectroscopic data and by X-ray diffraction



Scheme 7

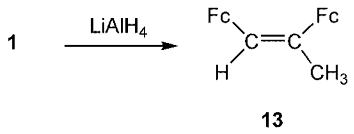


Scheme 8

analysis of a single crystal prepared by crystallization from a 3:1 mixture of hexane/diethyl ether. A general view of **10** is given in Figure 5(a) and selected bond lengths and angles are shown in Table 1. These data require no special comments. A characteristic feature of the crystal structure of compound **10** is the presence in the unit cell of twinned molecules having cis orientations of the ferrocenyl substituents (Figure 5, b).

Obviously, the reaction of 2,3-diferrocenylcyclopropenone (**1**) with methyllithium can follow the same pathways as those with heteronucleophiles (see Schemes 4 and 5). It seems probable that the abstraction of a proton from the solvent (ether) gives rise to a ketone **12**, which is followed by 1,2-addition of the second MeLi molecule to the conjugated system (Scheme 8).

We have also demonstrated that reduction of cyclopropenone **1** occurs upon reaction with $LiAlH_4$, which results in opening of the three-membered ring and formation of 1,2-diferrocenylpropene (**13**) (Scheme 9).



Scheme 9

We ascribed a *cis*-configuration to compound **13** by analogy with the reaction products **3**−**6** and **9** described above.

Conclusion

We have established experimentally a characteristic feature of the pseudoaromatic system of 2,3-diferrocenylcyclopropenone (**1**), viz., its ability to undergo nucleophilic opening of the cyclopropene ring under mild conditions with the regioselective formation of compounds incorporating *cis*-1,2-diferrocenylethene fragments. We have also demonstrated the presence of intramolecular electronic communication between the two ferrocenyl subunits of **1**.

Experimental Section

All the solvents were dried according to standard procedures[25] and were freshly distilled before use. Column chromatography was carried out on alumina (Brockmann activity III). The ^1H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$, with Me_4Si as the internal standard; the ^1H NMR spectrum of the tetrafluoroborate **2** was recorded as a solution in CD_2Cl_2. An Elemental Analysis system GmbH was used for elemental analyses.

The materials and apparatus for electrochemistry have been described elsewhere.[26] The $[NBu_4][B(C_6F_5)_4]$ supporting electrolyte was prepared according to a published procedure.[21] All the potential values are referred to the saturated calomel electrode (SCE).

The following reagents were purchased from Aldrich: tetrachlorocyclopropene, 98%; ferrocene, 98%; aluminum chloride, 99.99%; hydrazine monohydrate, 98%; piperidine, 99%; methyllithium, 1.6 M solution in diethyl ether; ethylmagnesium chloride, 2.0 M solution in diethyl ether; lithium aluminum hydride, powder, 95%; potassium *tert*-butoxide, 95%; deuterium oxide, 100.00 atom% D. Tetrafluoroboric acid−diethyl ether (50−52%) was purchased from Alfa AESAR.

2,3-Diferrocenylcyclopropenone (1): Aluminum chloride (0.67 g, 0.005 mol) was added portionwise over 30 min 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). The mixture was stirred for 1 h at 20 °C and then quenched by addition of 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 (Al_2O_3; hexane/dichloromethane, 3:1) to give compound **1**, yield 5.8 g (92%), orange crystals, m.p. 182−183 °C (ref.[5] m.p. 181 °C). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.25$ (s, 10 H, 2 C_5H_5), 4.58 (m, 4 H, C_5H_4), 4.84 (m, 4 H, C_5H_4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 65.16$ (2 C_{ipso}Fc), 70.00 (2 C_5H_5), 70.89, 71.93 (2 C_5H_4), 144.85 (2 C), 152.31 (C=O) ppm. $C_{23}H_{18}Fe_2O$ (422): calcd.C 65.58, H 4.28, Fe 26.36; found C 65.71, H 4.09, Fe, 26.54.

The Action of Tetrafluoroboric Acid−Diethyl Ether on Cyclopropenone 1: Tetrafluoroboric acid−diethyl ether (0.5 mL) was added dropwise with stirring at 20 °C in an atmosphere of dry nitrogen to a solution of compound **1** (0.21 g, 0.5 mmol) in dry dichloromethane (30 mL). The mixture was stirred for 1 h at 20 °C and then dry diethyl ether (150 mL) was added. The crystals that formed were filtered off, washed on a filter with several portions of dry diethyl ether, and then dried in a vacuum desiccator over

$CaCl_2$. The yield of diferrocenyl(hydroxy)cyclopropenylium tetrafluoroborate (**2**) was 0.22 g (88%), black crystals, m.p. ca. 205 °C (decomp.). ^1H NMR (300 MHz, CD_2Cl_2): δ = 4.42 (s, 10 H, 2 C_5H_5), 4.72 (br. s, 1 H, OH), 4.90 (m, 4 H, C_5H_4), 5.12 (m, 4 H, C_5H_4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 72.43 (2 C_5H_5), 74.07, 76.42 (2 C_5H_4), 85.00 (2 C_{ipso}Fc), 141.47 (2 C), 151.38 (C-OH) ppm. $C_{23}H_{19}BF_4Fe_2O$ (510): calcd. 54.17, H 3.76, B 2.12, F 14.91, Fe 21.90; found C 54.29, H 3.55, F 15.03, Fe 22.03.

***cis*-2,3-Diferrocenylacrylohydrazide (3):** A solution of compound **1** (0.42 g, 1 mmol) and hydrazine hydrate (2 mL) in ethanol (100 mL) was heated under reflux for 3 h. The reaction mixture was cooled, the ethanol was evaporated in vacuo, and the residue was chromatographed (Al_2O_3; hexane/dichloromethane, 2:1) to give the hydrazide **3**, yield 0.36 g (80%), orange crystals, m.p. 168−169 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.07 (s, 5 H, C_5H_5), 4.21 (s, 5 H, C_5H_5), 4.10 (m, 2 H, C_5H_4), 4.22 (m, 2 H, C_5H_4), 4.29 (m, 2 H, C_5H_4), 4.35 (m, 2 H, C_5H_4), 7.54 (s, 1 H, CH=), 9.40 (br. s, 3 H, $NHNH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 68.38, 69.32, 70.01, 70.41 (2 C_5H_4), 69.36, 69.40 (2 C_5H_5), 79.45, 80.42 (2 C_{ipso}Fc), 124.43 (C), 138.11 (CH=), 167.85 (C=O) ppm. $C_{23}H_{22}Fe_2N_2O$ (454): calcd. C 60.97, H 4.87, Fe 24.51, N, 6.14; found C 61.08, H 4.69, Fe 24.73, N 5.98.

***cis*-2,3-Diferrocenylacrylic Acid Piperidide (4):** Analogously to the procedure above, the reaction of cyclopropenone **1** (0.42 g, 1 mmol) with piperidine (2 mL) in ethanol (100 mL) and subsequent workup afforded compound **4**, yield 0.4 g (78%), orange crystals, m.p. 159−160 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.69 (m, 6 H, 3 CH_2), 3.44 (m, 2 H, CH_2), 3.78 (m, 2 H, CH_2), 4.09 (s, 5 H, C_5H_5), 4.13 (s, 5 H, C_5H_5), 4.16 (m, 2 H, C_5H_4), 4.175 (m, 2 H, C_5H_4), 4.19 (m, 2 H, C_5H_4), 4.23 (m, 2 H, C_5H_4), 6.27 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.67, 25.65, 26.37, 42.24, 48.61 (5 CH_2), 68.60, 68.66, 69.27, 69.67 (2 C_5H_4), 69.05, 69.28 (2 C_5H_5), 80.43, 80.74 (2 C_{ipso}Fc), 126.98 (CH=), 131.47 (C), 170.11 (C=O) ppm. $C_{28}H_{29}Fe_2NO$ (507): calcd. C 66.30, H 5.76, Fe 22.02, N 2.76; found C 66.44, H 5.58, Fe 21.89, N 2.58.

Isopropyl *cis*-2,3-Diferrocenylacrylate (5): Cyclopropenone **1** (0.42 g, 1 mmol) was added to a solution of sodium isopropoxide (formed from 0.2 g of metallic Na) in anhydrous propan-2-ol (100 mL) and then the mixture was heated under reflux for 3 h with stirring. Water (100 mL) was then added and the reaction product was extracted with benzene (3 × 50 mL). The combined extracts were washed with water (3 × 50 mL), the benzene was evaporated in vacuo, and the residue was chromatographed (Al_2O_3; hexane/dichloromethane, 3:1) to give the ester **5**, yield 0.36 g (75%), orange crystals, m.p. 173−174 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.45 (d, J = 6.3 Hz, 6 H, 2 CH_3), 4.06 (s, 10 H, 2 C_5H_5), 4.21 (m, 2 H, C_5H_4), 4.23 (m, 2 H, C_5H_4), 4.25 (m, 2 H, C_5H_4), 4.48 (m, 2 H, C_5H_4), 5.21 (m, J = 6.3 Hz, 1 H, CH), 7.23 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.12 (2 CH_3), 67.93 (CH), 67.86 (2 C), 69.42 (2 C), 70.52 (4 C) (2 C_5H_4), 69.22, 69.38 (2 C_5H_5), 79.80, 79.84 (2 C_{ipso}Fc), 127.26 (C), 136.06 (CH=), 167.34 (C=O) ppm. $C_{26}H_{26}Fe_2O_2$ (482): calcd. C 64.76, H 5.44, Fe 23.16; found C 64.58, H 5.59, Fe 23.37.

***cis*-2,3-Diferrocenylacrylic Acid (6):** A mixture of the cyclopropenone **1** (0.42 g, 1 mmol) and NaOH (0.5 g) in anhydrous ethanol (100 mL) was heated under reflux for 4 h with stirring. The ethanol was evaporated in vacuo and the residue was dissolved in water (50 mL) and acidified with 10% HCl to pH ≈ 1. The reaction product was extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed with water (3 × 20 mL), the ethyl acetate was evaporated in vacuo, and the residue was chromatographed (Al_2O_3; hexane/dichloromethane, 2:1) to give the acid **6**, yield 0.31 g (70%), orange crystals, m.p. 208−209 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.10 (s, 5 H, C_5H_5), 4.17 (s, 5 H, C_5H_5), 4.26 (m, 2 H, C_5H_4), 4.29 (m, 2 H, C_5H_4), 4.32 (m, 2 H, C_5H_4), 4.44 (m, 2 H, C_5H_4), 6.98 (br. s, 1 H, OH), 7.65 (s, 1 H, CH=) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 68.54, 69.70, 70.25, 70.44 (2 C_5H_4), 69.28, 69.53 (2 C_5H_5), 79.90, 80.51 (2 C_{ipso}Fc), 128.50 (C), 134.68 (CH=), 168.80 (C=O) ppm. $C_{23}H_{20}Fe_2O_2$ (440): calcd. C 62.90, H 4.57, Fe 25.29; found C 63.14, H 4.35, Fe 25.38.

***tert*-Butyl *cis*-3-Deuterio-2,3-diferrocenylacrylate (9):** A mixture of cyclopropenone **1** (0.42 g, 1 mmol) and potassium *tert*-butoxide (0.22 g, 2 mmol) in dry benzene (100 mL) was stirred with heating under reflux in an inert atmosphere for 4 h. The reaction mixture was cooled to 20 °C, quenched with D_2O (50 mL), and then stirring was continued for an additional 20 min. The organic layer was separated, concentrated in vacuo, and the residue was chromatographed (Al_2O_3; hexane/dichloromethane, 3:1) to give the ester **9**, yield 0.34 g (70%), orange crystals, m.p. 177−179 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.63 (s, 9 H, 3 CH_3), 4.00 (s, 5 H, C_5H_5), 4.05 (s, 5 H, C_5H_5), 4.16 (m, 2 H, C_5H_4), 4.23 (m, 2 H, C_5H_4), 4.27 (m, 2 H, C_5H_4), 4.46 (m, 2 H, C_5H_4), 7.18 (s, 0.17 H, CH=) ppm. $C_{27}H_{28}Fe_2O_2$: calcd. C 65.22, H 5.88, Fe, 22.46; found C.65.03, H 6.09, Fe 22.27.

***cis*-3,4-Diferrocenyl-2-methylbut-3-en-2-ol (10):** Methyllithium (4.0 mL of 1.6 M solution in diethyl ether) was added to a solution of compound **1** (0.42 g, 1 mmol) in dry benzene (100 mL). The mixture was stirred under an inert atmosphere for 3 h at 20 °C and then quenched by addition of water (100 mL). The organic layer was separated, washed with water (2 × 20 mL), the solvent was evaporated in vacuo, and the residue was chromatographed (Al_2O_3; hexane/diethyl ether, 2:1) to give the alcohol **10**, yield 0.28 g (62%), orange crystals, m.p. 132−133 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.64 (s, 6 H, 2 CH_3), 3.98 (s, 5 H, C_5H_5), 4.26 (s, 5 H, C_5H_5), 3.67 (m, 2 H, C_5H_4), 4.00 (m, 2 H, C_5H_4), 4.08 (m, 2 H, C_5H_4), 4.43 (m, 2 H, C_5H_4), 5.04 (br. s, 1 H, OH), 6.28 (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) ppm. $C_{25}H_{26}Fe_2O$ (454): calcd. C 66.11, H 5.77, Fe 24.60; found C 65.97, H 5.93, Fe 24.38.

***cis*-1,2-Diferrocenylpropene (13):** Lithium aluminum hydride (0.3 g) was added to a solution of compound **1** (0.42 g, 1 mmol) in dry diethyl ether (100 mL), the mixture was stirred in an atmosphere of dry nitrogen for 5 h at 20 °C, and then it was quenched by addition of ethyl acetate. Water (50 mL) was added, the organic layer was separated and washed with water (2 × 20 mL), and then it was dried with $MgSO_4$. The solvent was evaporated in vacuo, and the residue was chromatographed (Al_2O_3; hexane) to give compound **13**, yield 0.29 g (70%), orange finely crystalline powder, m.p. 167−168 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, CH_3), 4.16 (s, 5 H, C_5H_5), 4.19 (s, 5 H, C_5H_5), 4.08 (m, 1 H, C_5H_4), 4.15 (m, 1 H, C_5H_4), 4.21 (m, 2 H, C_5H_4), 4.34 (m, 2 H, C_5H_4), 4.55 (m, 2 H, C_5H_4), 6.02 (s, 1 H, CH=) ppm. $C_{23}H_{22}Fe_2$ (410): calcd. C 67.48, H 5.39, Fe 27.13; found C 67.27, H 5.53, Fe 26.91.

Determining the Crystal Structure: The unit cell parameters and the X-ray diffraction intensities were recorded on a Bruker Smart Apex CCD area detector/ω diffractometer (compounds **1** and **5**) and a Siemens P4/PC/ω diffractometer (compound **9**). The structures of compounds **1**, **5**, and **9** were solved by the direct method (SHELXS) and refined using a full-matrix least-squares method on F^2.

Crystal data for $C_{23}H_{18}Fe_2O$ (1): M = 422.07 g·mol^{-1}, monoclinic $P2_1/c$, a = 12.4586(7), b = 10.7003(6), c = 14.4277(8) Å, α = 90, β = 115.598(1), γ = 90°, V = 1734.58(17) Å^3, T = 291(2) K, Z = 4, ρ = 1.616 Mg/m^3, λ (Mo-K_α) = 0.71073 Å, F(000) = 864, absorption correction − analytical, index ranges $-14 \le h \le 14$, $-12 \le k \le 12$, $-17 \le l \le 17$, scan range $1.81 \le \theta \le 25.00°$, 3062 independent reflections, R_{int} = 0.0838, 13902 total reflections, 235 refinable parameters, final R indices [$I > 2\sigma(I)$] R_1 = 0.0292, wR_2 = 0.0668, R indices (all data) R_1 = 0.0369, wR_2= 0.0688, goodness-of-fit on F^2 0.956, largest difference peak and hole 0.254/−0.369 e·Å^{-3}.

Crystal data for $C_{26}H_{26}Fe_2O_2$ (5): M = 482.17 g·mol^{-1}, monoclinic $P2_1/n$, a = 12.9639(7), b = 11.0728(6), c = 15.3241(8) Å, α = 90, β = 93.6570(10), γ = 90°, V = 2195.2(2) Å^3, T = 291(2) K, Z = 4, ρ = 1.459 g/cm^3, λ (Mo-K_α) = 0.71073 Å, F(000) = 1000, absorption coefficient 1.341 mm^{-1}, index ranges $-15 \le h \le 15$, $-13 \le k \le 13$, $-18 \le l \le 18$, scan range $2.00 \le \theta \le 25.00°$, 3871 independent reflections, R_{int} = 0.0436, 17594 total reflections, 273 refinable parameters, final R indices [$I > 2\sigma(I)$] R_1 = 0.0317, wR_2 = 0.0630, R indices (all data) R_1 = 0.0456, wR_2= 0.0650, goodness-of-fit on F^2 0.998, largest difference peak and hole 0.414/−0.259 e·Å^{-3}.

Crystal data for $2C_{25}H_{26}Fe_2O$ (9): M = 908.32 g·mol^{-1}, triclinic $P\bar{1}$, a = 7.982(2), b = 9.9779(9), c = 25.943(2) Å, α = 100.004(7), β = 94.211(12), γ = 91.165(11)°, V = 2028.1(6) Å^3, T = 291(2) K, Z = 2, ρ = 1.487 g/cm^3, λ (Mo-K_α) = 0.71073 Å, F(000) = 944, absorption correction − integration, index ranges $0 \le h \le 9$, $-11 \le k \le 11$, $-30 \le l \le 30$, scan range $2.07 \le \theta \le 25.00°$, 7137 independent reflections, R_{int} = 0.0387, 7694 total reflections, 515 refinable parameters, final R indices [$I > 2\sigma(I)$] R_1 = 0.0484, wR_2 = 0.0948, R indices (all data) R_1 = 0.1007, wR_2= 0.1087, goodness-of-fit on F^2 0.843, largest difference peak and hole 0.509/−0.280 e·Å^{-3}.

CCDC-211051 (for **5**) and -211052 (for **1** and **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the grant CONACyT (Mexico, grant 34862-E). Thanks are due to M. L. Velasco, J. Perez, H. Rios, E. R. Patiño, and O. S. Yañez Muñoz for their technical assistance. P. Z. gratefully acknowledges the financial support from the University of Siena (PAR, 2003).

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Received June 2, 2003