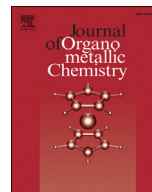




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journal homepage: www.elsevier.com/locate/jorganchemFrom diferrocenyl-cyclopropenone to diferrocenyl-cyclopropenylium cations and triferrocenylpropenones: An electrochemical study[☆]Steve W. Lehrich, Alexander Hildebrandt, Marcus Korb, Heinrich Lang^{*}

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ABSTRACT

The reaction of 2,3-diferrocenylcyclopropenone (**1**) with the electrophiles H[BF₄] and [Et₃O][BF₄], respectively, produced the corresponding cyclopropenylium cations [Fc₂C₃OH][BF₄] (**2**) and [Fc₂C₃OEt][BF₄] (**3**) (Fc = Fe(η⁵-C₅H₄)(η⁵-C₅H₅)). Reacting **3** with HNEt₂ afforded the NEt₂-functionalized species [Fc₂C₃NEt₂][BF₄] (**4**). However, when **2** was reacted with nucleophiles such as FcLi a ring opening of the C₃ cycle was observed and *E*- and *Z*-1,2,3-triferrocenylpropenones *Z*-**5** and *E*-**5** were formed. Crystallization of a dichloromethane solution containing **3**, layered with hexane, gave the BF₃ adduct of diferrocenylcyclopropenone **6** at the interphase. The molecular solid state structures of *Z*-**5**, *E*-**5** and **6** were determined by single crystal X-ray diffraction. Compound *E*-**5** possesses a helical chirality and crystallizes in an enantiopure form. The electronic properties of the ferrocenyl-substituted cyclopropenylium cations **2–4** and of the triferrocenyl- α,β -unsaturated ketones *Z*-**5** and *E*-**5** were studied by cyclic voltammetry and square wave voltammetry. In comparison to the cyclopropenone derivative **1**, the ferrocenyl oxidation processes of the cyclopropenylium cations **2** and **3** are shifted towards higher potentials, which is caused by the lower electron density of the strained C₃ rings. Compound **4** decomposes during the electrochemical measurements. Furthermore, it could be shown that *E/Z* isomerism has only small effects on the electronic properties of the triferrocenyl- α,β -unsaturated ketones. Spectroelectrochemical UV–Vis/NIR measurements carried out on **1** and *Z*-**5** and *E*-**5** confirmed electron-transfer interactions within the 2,3-diferrocenylcyclopropenone and the 1,2,3-triferrocenyl- α,β -unsaturated ketones. However, the cyclopropenylium cations **2** and **3** show no long time stability under oxidative conditions.

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1. Introduction

Since the first preparation of triphenylcyclopropenylium perchlorate [1], cyclopropenylium cations as the smallest member of Hückel aromatic systems have been studied intensively [2]. Cyclopropenylium ions possess a high reactivity due to their strained ring system. On the other hand, the aromatic stabilization induces a considerable thermodynamic stability [2,3]. The chemistry of cyclopropenones is followed by the presence of zwitterionic mesomeric structures that contain the aromatic cyclopropenylium motif (Fig. 1), which causes the high polarity of the molecule and enhances the stability of the strained system [2,4,5]. Thermolysis or nucleophilic attack at the C₃(=O) ring cause ring opening, allowing, for example, to prepare five- or six-membered nitrogen-containing

heterocycles [6,7]. Cyclopropenones can also act as a three-carbon building block to elongate the nucleophiles added [8].

Ferrocenyl-substituted cyclopropenones allow to introduce iron atoms in a large number of different organic compounds [8]. In this respect, especially extended conjugated metal-containing systems are of great interest because they can be used as model compounds for molecular wires [8–12]. Furthermore, the electron-donating nature of ferrocenyl functionalities on the cyclopropenone system enhances their stability by delocalizing the positive charge [3,13,14]. Another benefit of using ferrocenyls in cyclopropenone chemistry is the *in situ* generation of mixed-valent compounds through oxidation of one of the two ferrocenyl units and hence the possibility to study the charge transfer behaviour through the aromatic C₃ framework. This family of compounds can be considered as enrichment of well-studied diferrocenyl-functionalized 5-membered heterocycles [15–24].

Herein, we report the charge transfer between ferrocenyl/ferrocenium moieties via 2 π -aromatic strained C₃ ring systems in

[☆] Dedicated to Prof. Dr. John A. Gladysz on the occasion of his 65th birthday.

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respective mixed-valent compounds. In addition, the reaction chemistry of differrocenylcyclopropenone towards FcLi to give 1,2,3-triferrocenylprop-2-enones and their electrochemical and spectroelectrochemical characteristics are discussed.

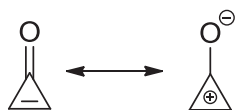


Fig. 1. Mesomeric structures of cyclopropenones [2].

2. Results and discussion

2.1. Synthesis

Diferrocenylcyclopropenone (**1**) (Scheme 1) was prepared by Friedel–Crafts alkylation of ferrocene with tetrachlorocyclopropane in the presence of AlCl_3 [3,13]. The synthesis of the cyclopropenylium salts **2–4** (Scheme 1) was performed according to published procedures [4,5,25]. During crystallization of **3** from a hexane/dichloromethane mixture at ambient temperature it was observed that at the hexane ad-layer a minor number of single crystals of **6** grew, most likely due to a trace of BF_3 present in the Et_3OBF_4 reagent. The solid state molecular structure of **6** is discussed in the Supporting Information (Fig. S15). To prepare **6** in a straightforward manner, differrocenylcyclopropenone (**1**) was subsequently treated with trifluoroborane etherate in tetrahydrofuran. However, instead of neutral **1**· BF_3 , cationic **2** was isolated (Scheme 1), tracing the *in situ* formation of HBF_4 .

Klimova et al. described the nucleophilic attack of phenyl- or methyl-lithium on differrocenyl-substituted cyclopropenes [26]. In this respect, compound **1** was treated with ferrocenyllithium, producing *Z*- and *E*-1,2,3-triferrocenylprop-2-enone (*Z*-**5**, *E*-**5**) (Scheme 1).

Compounds **1** and *Z*/*E*-**5** are stable towards air, light and moisture both in the solid state and in solution. The cyclopropenylium cations **2–4** are best isolated using anhydrous solvents under inert conditions and are preferably stored under argon atmosphere, whereas aerobic conditions led to a slow decomposition of the respective compounds.

2.2. Characterization

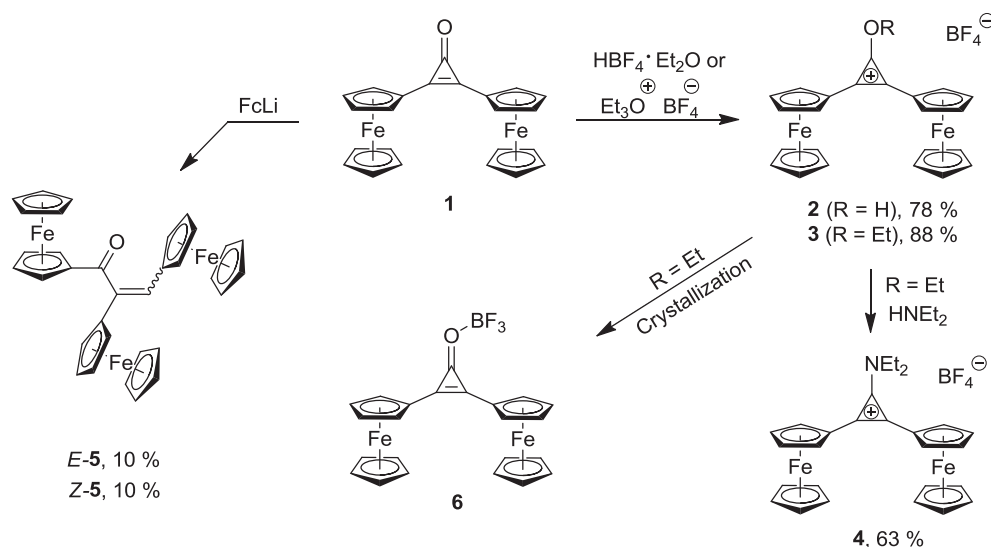
The identity of organometallic compounds **1–5** was confirmed by IR and NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$) spectroscopy. The observed infrared bands of **1** at 1849 cm^{-1} , 1817 cm^{-1} and 1614 cm^{-1} are diagnostic for the cyclopropenone structure motif [3]. The change of the characteristic carbonyl stretching vibrations in **1** as well as the occurrence of $\nu_{\text{B-F}}$ vibrations ($1060 - 1170\text{ cm}^{-1}$) in IR spectroscopy could be used to monitoring the progress of the reactions.

1,2,3-Triferrocenylprop-2-enones *Z*/*E*-**5** were additionally characterized by high resolution mass spectrometry, elemental analysis (Materials and Methods) and single crystal X-ray structure analysis (Fig. 2).

The electrochemical behavior of **1–5** was studied by cyclic voltammetry (CV) and square wave voltammetry (SWV). In addition, for compounds **1** and *Z*/*E*-**5** *in situ* UV–Vis/NIR spectroelectrochemistry measurements were carried out.

The molecular structures of *Z*-**5** and *E*-**5** (Fig. 2) in the solid state have been determined by single crystal X-ray diffraction analysis. Suitable crystals of *Z*/*E*-**5** were obtained by solvent evaporation at ambient temperature. They crystallize in the *non*-centrosymmetric orthorhombic space group $Pca2_1$ (*Z*-**5**) (absolute structure parameter [27] = 0.022(16)) and the *non*-centrosymmetric *Sohncke* space group [28] $P2_1$ (*E*-**5**) (absolute structure parameter [27] = 0.06(4)) with one molecule in the asymmetric unit.

The ferrocenyl groups of *Z*-**5** and *E*-**5** are attached to the carbonyl carbon atom and the α - and β -position of the ethylene unit (Fig. 2, Scheme 1). The C1–O1, C1–C2 and C2–C3 bond lengths are in the range for related compounds, i. e. 2,3-diferrocenyl-1-phenyl-prop-2-enone or [Fc-COCH=CH-Anth] derivatives (Anth = antracenyl) [29–41]. Due to the steric interaction for a *cis*-substitution pattern, the ferrocenyls at the olefin group resulted in an increased bending out of the vinylic plane by $10.5(7)^\circ$ for *Z*-**5**, in contrast to $173.2(19)^\circ$ for *E*-**5**, as evidenced by the C14–C2–C3–C24 torsion angle. To avoid an interaction of the hydrogen atoms of the Fe2- and Fe3-labeled ferrocenyls in *Z*-**5**, they are rotated out of plane of the C–C=C vinyl unit by $31.9(5)^\circ$ for the Fe2 entity and by $47.2(4)^\circ$ for the Fe3 moiety. For *E*-**5**, the *trans*-substitution avoids the steric interaction between the two ferrocenyls and reduces the rotation out of the olefin plane to $22.8(14)$ and $21.3(17)^\circ$, respectively. In contrast to *Z*-**5** with an *anti*-orientation, the ferrocenyls in *E*-**5** are rotated in a *syn*-coplanar fashion towards each other with a plane



Scheme 1. Synthesis of cyclopropenylium salts **2–4**, differrocenylcyclopropenone BF_3 complex **6** and 1,2,3-triferrocenylprop-2-enones *Z*-**5** and *E*-**5**.

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