

# Ferrocenylmethyl-functionalized 5-membered heterocycles: Synthesis, solid-state structure and electrochemical investigations

Deeb Taher<sup>a,\*</sup>, Asma Ghazzy<sup>a</sup>, Firas F. Awwadi<sup>a</sup>, Wissam Helal<sup>a</sup>, Khaled Al Khalyfeh<sup>b</sup>, Marcus Korb<sup>c</sup>, Alexander Hildebrandt<sup>c</sup>, Eduard Kovalski<sup>c</sup>, Heinrich Lang<sup>c</sup>

<sup>a</sup> Department of Chemistry, The University of Jordan, Amman 11942, Jordan

<sup>b</sup> Al-Hussein Bin Talal University, Faculty of Natural Sciences, Department of Chemistry, P.O. Box 20, Ma'an, Jordan

<sup>c</sup> Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry, Inorganic Chemistry, D-09107 Chemnitz, Germany

## ARTICLE INFO

### Article history:

Received 12 April 2018

Accepted 11 June 2018

Available online 30 June 2018

### Keywords:

Ferrocenylmethyl

Heterocycle

Solid state structure

Electrochemistry

DFT calculation

## ABSTRACT

Treatment of  $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{OH})_2$  (**1**) with two equivalents of  $\text{ClC(O)R}$  (**2**) (**a**,  $\text{R} = 2\text{-}^i\text{C}_4\text{H}_3\text{O}$ ; **b**,  $\text{R} = 2\text{-}^i\text{C}_4\text{H}_3\text{S}$ ; **c**,  $\text{R} = 2\text{-}^i\text{C}_4\text{H}_3\text{Se}$ ; **d**,  $\text{R} = 3\text{-}^i\text{C}_4\text{H}_3\text{S}$ ) produced the corresponding ferrocenylmethyl carboxylates  $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{OC(O)R})_2$  (**3a–d**), while the reaction of  $\text{FcCH}_2\text{OLi}$  ( $\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)$ ) with 2,5- $(\text{ClC(O)})_2\text{-}^i\text{C}_4\text{H}_2\text{X}$  (**5**) (**a**,  $\text{X} = \text{O}$ ; **b**,  $\text{X} = \text{S}$ ; **c**,  $\text{X} = \text{Se}$ ) in a 2:1 molar ratio gave 2,5- $(\text{FcCH}_2\text{OC(O)})_2\text{-}^i\text{C}_4\text{H}_2\text{X}$  (**6a–c**). Compounds **3a–d** and **6a–c** were characterized by elemental analysis, NMR ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ ) and IR spectroscopy. The molecular structures of **3a,b,d** in the solid state were determined by single crystal X-ray structure analysis. Compound **3a** crystallizes in the monoclinic space group  $P2_1/c$ , while **3b,d** crystallize in the triclinic space group  $P\bar{1}$ . The ester groups and the heteroatoms are in an *anti* arrangement with respect to each other. Cyclic voltammetry measurements for **3a–d** and **6a–c** show reversible electrochemical processes ( $\text{Fc}/\text{Fc}^+$ ) between 165 and 176 mV for **3a–d**, and 94 and 116 mV for **6a–cb**, using  $[\text{N}^i\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$  as the supporting electrolyte. It was found that for **3a**, a somewhat higher  $\text{Fc}/\text{Fc}^+$  redox potential ( $E^0$ ) is observed when compared with the more electron-rich systems **3b,c,d**. The molecular electronic structures of the title compounds were additionally investigated by DFT calculations, revealing different degrees of HOMO–LUMO energy gaps within the series, due to a lowering of the LUMO energy, depending on the nature of the heterocyclic ring.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

During the last few decades, ferrocene-derivatives have gained great importance [1]. For example, ferrocene has been demonstrated to be a useful building block in transition metal-containing oligomers and polymers due to its reversible one-electron redox behavior [2]. Due to the favorable electronic properties of ferrocene and its easy functionalization, ferrocene derivatives have found many useful applications, for example, in homogeneous catalysis, [3] as high-burning rate catalysts [4], as active components in anticancer drugs [5] and as model systems for molecular wires [6]. Ferrocenyl-functionalized  $\pi$ -conjugated hydrocarbons, *i.e.* arenes or five- and six-membered heterocycles, have gained interest towards their use in electronic communications in their mixed-valent state [7–12].

Carbochalcogenates are of potential interest regarding their applications as antioxidants or antitumor apoptosis inducers for

effective chemo-prevention of cancer in a variety of organs [13], as liquid crystalline materials [14] and as building blocks in organic chemistry [15]. The electronic properties of their ferrocenyl-substituted derivatives have been investigated, as recently discussed [9,16–19].

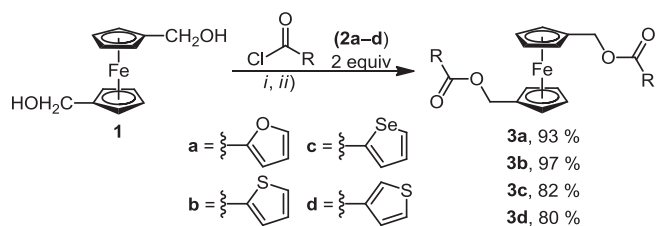
Herein, we report on the design, synthesis, solid state structure, electrochemical behavior and molecular orbital electronic structure calculations of a series of 5-membered heterocyclic compounds, such as furan, thiophene and selenophene, featuring  $\text{FcCH}_2\text{OC(O)}$  units as terminal groups. The studies described herein are a continuation of recently reported results obtained in this area [9,16–18].

## 2. Results and discussion

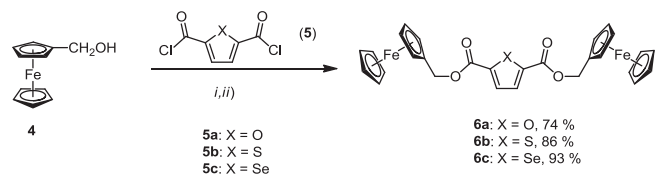
Treatment of 1,1'-bis(hydroxymethyl)ferrocene,  $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-CH}_2\text{OH})_2$  (**1**), with acid chlorides  $\text{ClC(O)R}$  (**2**) (**a**,  $\text{R} = 2\text{-}^i\text{C}_4\text{H}_3\text{O}$ ; **b**,  $\text{R} = 2\text{-}^i\text{C}_4\text{H}_3\text{S}$ ; **c**,  $\text{R} = 2\text{-}^i\text{C}_4\text{H}_3\text{Se}$ ; **d**,  $\text{R} = 3\text{-}^i\text{C}_4\text{H}_3\text{S}$ ) in a 1:2 molar ratio in dichloromethane in the presence of 2 equivalents of  $\text{NEt}_3$  at ambient temperature gave the appropriate compounds  $\text{Fe}(\eta^5\text{-C}_5\text{-}$

\* Corresponding author.

E-mail address: [d.taher@ju.edu.jo](mailto:d.taher@ju.edu.jo) (D. Taher).



**Scheme 1.** Synthesis of **3a–d**. (i) Treatment of **1** with 2 equivalents of Et<sub>3</sub>N in dichloromethane at 25 °C; (ii) 2 equivalents of ClC(O)R, 0 °C, 18 h. Yields are based on **1**.



**Scheme 2.** Synthesis of **6a–c**. (i) Treatment **4** with MeLi (ratio 1:1), diethyl ether, 0 °C; (ii) 1 equivalent of 2,5-(ClC(O))<sub>2</sub>-C<sub>4</sub>H<sub>2</sub>X, –78 °C, 18 h. Yields are based on **4**.

H<sub>4</sub>CH<sub>2</sub>OC(O)R)<sub>2</sub> (**3a–d**) in very good yields (Scheme 1, Experimental). After appreciable workup, **3a–d** could be isolated as yellow solids.

In an analogous manner, the reaction of 2,5-(ClC(O))<sub>2</sub>-C<sub>4</sub>H<sub>2</sub>X (**5**) (a, X = O; b, X = S; c, X = Se) with FcCH<sub>2</sub>OLi (**4**) afforded the corresponding ferrocenylmethyl compounds 2,5-(FcCH<sub>2</sub>C(O))<sub>2</sub>-C<sub>4</sub>H<sub>2</sub>X (**6**) (a, X = O; b, X = S; c, X = Se) as yellow solids in good yields (Scheme 2, Experimental).

Compounds **3a–d** and **6a–c** do not require elaborate purification procedures (Experimental). For **3a–d**, extraction with a water/

CH<sub>2</sub>Cl<sub>2</sub> mixture in a 1:5 ratio (*v/v*) is adequate, while for **6a–c**, filtration of the reaction mixture through a pad of Celite is satisfactory. Recrystallization of both families of compounds from CHCl<sub>3</sub>/hexane mixtures in a 3:1 ratio (*v/v*) at –18 °C afforded analytically pure samples.

Compounds **3a–d** and **6a–c** are stable towards moisture and air in solution, as well as in the solid state. They dissolve in polar organic solvents like dichloromethane, chloroform and tetrahydrofuran, however, in hexane they are insoluble. The molecular structures of **3a**, **b** and **d** in the solid state are reported, as are the electrochemical behaviors for **3a–d** and **6a–c**.

Compounds **3a–d** and **6a–c** were identified by elemental analysis, IR and NMR (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H}) spectroscopy and high-resolution ESI TOF mass-spectrometry.

The most characteristic feature in the IR spectra of all the compounds is the appearance of one strong ν(CO) stretching vibration between 1690 and 1715 cm<sup>–1</sup>, which is typical for C(O)OCH<sub>2</sub>Fc units [20].

The <sup>1</sup>H NMR spectra of **3a–d** and **6a–c** are consistent with their molecular structures, showing resonances with the expected coupling patterns for the C<sub>5</sub>H<sub>4</sub>, C<sub>5</sub>H<sub>5</sub> and the heterocyclic moieties (Experimental) [9,16–18,21,22]. As expected, solely pseudo-triplets for the cyclopentadienyl C<sub>5</sub>H<sub>4</sub> ring protons with J<sub>HH</sub> = 1.8 Hz are observed. The CH<sub>2</sub> protons appear as singlets at ca. δ 5.1 ppm for all compounds [23]. For **6a–c**, an additional singlet at δ 4.22 ppm is found for the C<sub>5</sub>H<sub>5</sub> protons [9,16–18]. The resonance signal of the HO functionality in **1** and **4** disappears during treatment of **1/4** with **2a–d/5a–c** and hence NMR spectroscopy can be used to monitor the progress of the reaction (Experimental).

Most representative in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **3a–d** and **6a–c** are the signals for the carbonyl carbon atom of the C(O)OCH<sub>2</sub>-Fc group, which were observed between δ 159 and 163 ppm [20]. All the other organic groups show the anticipated signals without any peculiarities [9,16–18].

**Table 1**  
Crystallographic data and refinement details for **3a,b** and **3d**.

	<b>3a</b>	<b>3b</b>	<b>3d</b>
Empirical formula	C <sub>22</sub> H <sub>18</sub> FeO <sub>6</sub>	C <sub>22</sub> H <sub>18</sub> FeO <sub>4</sub> S <sub>2</sub>	C <sub>22</sub> H <sub>18</sub> FeO <sub>4</sub> S <sub>2</sub>
Formula weight (g/mol)	434.21	466.33	466.33
T (K)	115.3(6)	120.00(10)	116.9(2)
Wavelength (Å)	0.71073	0.71073	116.9(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P2 <sub>1</sub> /c	P-1	P-1
<i>Unit cell dimensions</i>			
a (Å)	11.531(2)	7.7297(6)	6.0750(9)
b (Å)	7.6333(8)	7.8362(8)	8.3178(14)
c (Å)	10.4844(14)	8.6370(5)	9.7058(11)
α (°)		110.077(7)	84.819(12)
β (°)	79.871(5)	91.644(6)	89.444(11)
γ (°)		101.409(7)	83.124(13)
V (Å <sup>3</sup> )	889.8	479.00	484.92(12)
Z	2	1	1
D <sub>calc</sub> (Mg/m <sup>3</sup> )	1.621	1.617	1.597
Absorption coefficient (mm <sup>–1</sup> )	0.888	1.033	8.485
F(0 0 0)	448	240	240
Crystal size (mm)	0.4 × 0.35 × 0.01	0.4 × 0.3 × 0.2	0.4 × 0.35 × 0.02
θ range (°)	3.237–24.992	3.054–24.993	4.574–64.927
Index ranges	–13 ≤ h ≤ 10, –9 ≤ k ≤ 9, –12 ≤ l ≤ 12	–9 ≤ h ≤ 9, –9 ≤ k ≤ 7, –8 ≤ l ≤ 10	–7 ≤ h ≤ 7, –9 ≤ k ≤ 8, –8 ≤ l ≤ 11
Reflections collected	2300	3123	2521
Independent reflections	2300 (R <sub>int</sub> = 0.0406)	1679 (R <sub>int</sub> = 0.0225)	1634 (R <sub>int</sub> = 0.0225)
Data completeness	98.8%	99.6%	98.7%
Data/restraints/parameters	2300/0/134	1679/86/170	1634/213/211
Goodness-of-fit (GOF) on F <sup>2</sup>	0.880	1.069	1.069
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0412, wR <sub>2</sub> = 0.0777	R <sub>1</sub> = 0.0310, wR <sub>2</sub> = 0.0763	R <sub>1</sub> = 0.0545, wR <sub>2</sub> = 0.1389
R indices (all data)	R <sub>1</sub> = 0.0735, wR <sub>2</sub> = 0.0932823	R <sub>1</sub> = 0.0350, wR <sub>2</sub> = 0.0763	R <sub>1</sub> = 0.0553, wR <sub>2</sub> = 0.1411
Largest difference in peak and hole (e Å <sup>–3</sup> )	0.583 and –0.279	0.263 and –0.420	0.711 and –0.794

<sup>a</sup>R<sub>1</sub> = Σ||F<sub>o</sub>| – |F<sub>c</sub>||/Σ|F<sub>o</sub>|.

<sup>b</sup>wR<sub>2</sub> = [Σ[w(F<sub>o</sub><sup>2</sup> – F<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ [w(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>.

Download English Version:

<https://daneshyari.com/en/article/7762402>

Download Persian Version:

<https://daneshyari.com/article/7762402>

[Daneshyari.com](https://daneshyari.com)