ELECTROCHEMICAL GENERATION OF A CATALYST FOR MICHAEL ADDITION OF DICARBONYL COMPOUNDS AND CYANIDE ANION TO ACRYLOYLFERROCENE [†, ‡]

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Abstract. *Michael addition of diethyl malonate, ethyl acetoacetate, acetylacetone, and cyanide anion to acryloylferrocene promoted by a catalyst* in situ *generated from a sacrificial zirconium anode is described. Most of the obtained compounds were identified by comparison of their spectral and physical data with those published elsewhere, whereas the only newly synthesized compound - diethyl 2,2-bis(3-ferrocenyl-3-oxopropyl)malonate - was completely characterized by spectral (IR, ^{1}H- and ^{13}C-NMR), physical and crystallographic (single-crystal X-ray) data.*

Key words: *electrolysis, zirconium, sacrificial anode, Michael addition,
acryloylferrocene, dicarbonyls, cyanides*

1. INTRODUCTION

Zirconium compounds have been widely used in organic synthesis, since they are commercially available (or well described in the literature), easily handled, of low toxicity, and of high catalytic activity in many reactions. They are known to catalyze different organic reactions, such as Ferrier rearrangement (Swamy et al., 2004; Smitha and Sanjeeva Reddy, 2004), Fries rearrangement (Harrowven and Dainty, 1996), Friedel-

Crafts acylation (Heine et al., 1946), sodium borohydride reduction (Itsuno et al., 1988, 1990; Purushothama Chary et al. 1999, 2000), multicomponent condensations affording dihydropyrimidinones (Venkateshwar Reddy et al, 2002) and β-aryl-β-mercaptoketones (Kumar and Akanksha, 2007), Pechmann reactions (Karami and Kiani, 2011) etc. (Curini et al., 2004; Firouzabadi and Jafarpour, 2008; Zhang and Li, 2009). Catalytic activity of different zirconium compounds in Michael conjugate addition of nucleophiles to α,β-unsaturated carbonyls has also been recognized by organic chemists and used in organic synthesis. In this regard, both types of nucleophiles - those with a heteroatom as the nucleophilicity carrier and *C*-nucleophiles were successfully used (Curini et al., 2004; Firouzabadi and Jafarpour, 2008; Zhang and Li, 2009). In continuation of our permanent interest in both the electrochemical generation of catalysts (Vukićević et al., 1991, 1998) and ferrocene chemistry (Vukićević et al., 2002; Damljanović et al., 2014), we recently reported on a new and versatile method for the electrochemical generation of a catalyst capable of promoting the Ferrier rearrangement and hetero-Michael conjugate addition of *N*- and *S*-nucleophiles to methyl vinyl ketone, using a sacrificial zirconium anode (Stevanović et al., 2012). Now, we decided to examine whether this technique is suitable for the formation of new C-C bonds by Michael addition of *C*-nucleophiles to a conjugate enone. For this purpose we have chosen acryloylferrocene (**1**, Scheme 1) as the Michael acceptor and diethyl malonate (**2a**), ethyl acetoacetate (**2b**), acetylacetone (**2c**), and the cyanide anion as the Michael donors.

2. RESULTS AND DISCUSSION

The present investigations were initiated having in mind the experience gained in performing hetero-Michael addition and Ferrier rearrangement promoted by a catalyst generated *in situ* from a zirconium sacrificial anode (Stevanović et al., 2012). Thus, we have chosen an acetonitrile solution of lithium perchlorate as the reaction medium and submitted a 1:1 mixture (one mmol scale) of enone **1** and diethyl malonate (**2a**) (Scheme 1) to a constant current electrolysis (20 mA) in an undivided electrolytic cell, using a zirconium spiral as the anode and a platinum spiral as the cathode. Initial experiments revealed that the electrochemical oxidation of zirconium produced species insoluble in acetonitrile which coated the anode and passivated it, causing an uncontrolled increase of the electrode voltage and heating of the solution (up to boiling) due to the electrical resistance increase. However, the cell was afterwards placed in an ultrasonic bath and in this way the species generated by the anode were simultaneously removed from the electrode surface.

a) R = R^1 = OC$_2$H$_5$; b) R = CH$_3$, R^1 = OC$_2$H$_5$; c) R = R^1 = CH$_3$,
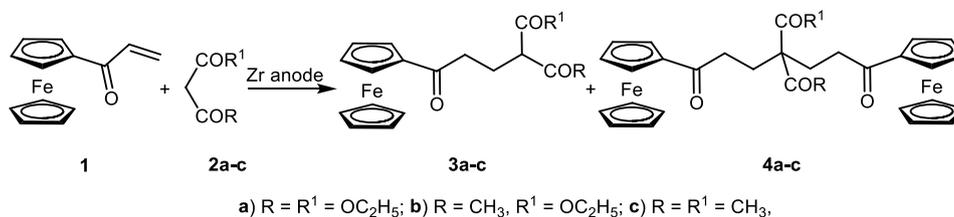
Scheme 1 Michael addition of dicarbonyls **2a-c** to enone **1**
             catalyzed by an electrochemically generated zirconium catalyst

Knowing that the reactions promoted by zirconium compounds were usually performed using up to 10 mol% of the catalyst (Smitha and Sanjeeva Reddy, 2004), the electrolysis time was estimated to provide 0.4 F·mol^{-1} charge consumption, i.e., to provide the generation of 0.1 mmol of a certain compound of tetravalent zirconium in a one mmol scale experiment. After the electrolysis, the mixture was additionally stirred for half an hour at room temperature and worked up in a usual way. The raw reaction mixture was chromatographed (SiO$_2$/hexane-ethyl acetate, 8:2, v/v) to give two products, which, on the basis of spectral data (IR, ^{1}H- and ^{13}C-NMR), were identified as compounds **3a** and **4a** (Scheme 1). Compounds **3a** and **4a** were isolated in 34% and 11% yield, respectively (Run 1, Table 1).

Table 1 Michael addition of dicarbonyls **2a-c** to enone **1**
catalyzed by an electrochemically generated zirconium catalyst

Run	Dicarbonyl	Solvent	Electrolyte	Reaction conditions	Reactants ratio (1/2)[a]	Yield of products (%)[b]		
						3	4	Ratio 3/4[a]
1	2a	MeCN	0.1 M LiClO$_4$	A	1:1	34	11	76:24
2	2a	MeCN	0.1 M LiClO$_4$	A	2:1	17	5	72:28
3	2a	MeCN	0.1 M LiClO$_4$	B	1:1	36	10	78:22
4	2a	MeCN	0.1 M LiClO$_4$	A	1:2	38	9	81:19
5	2a	MeCN	0.1 M LiClO$_4$	C	1:1	33	10	77:23
6	2a	EtOH	0.1 M NaClO$_4$	A	1:1	23	3	88:12
7	2a	EtOH	0.1 M NaClO$_4$	B	1:1	25	4	86:14
8	2a	EtOH	0.1 M NaClO$_4$	C	1:1	24	5	83:17
9	2a	EtOH	0.1 M NaClO$_4$	B	1:2	39	2	95:5
10	2a	EtOH	0.05 M NaClO$_4$, 0.05 M AcONa	D	1:2	70	6	92:8
11	2b	EtOH	0.05 M NaClO$_4$, 0.05 M AcONa	D	1:2	32	Traces	-
12	2c	EtOH	0.05 M NaClO$_4$, 0.05 M AcONa	D	1:2	56	Traces	-

[a] mol/mol;
[b] Yield of isolated products;
Reaction conditions: A) 0.4 F·mol^{-1}; 0.5 h stirring after the electrolysis.
B) 0.4 F·mol^{-1}; overnight stirring after the electrolysis. C) 0.8 F·mol^{-1}; 0.5 h stirring after the electrolysis.
D) 0.4 F·mol^{-1}; 0.5 h irradiation in an ultrasonic bath after the electrolysis.

Since compound **4a** is, apparently, a product of Michael addition of **3a** to **1**, in the following experiment, we performed electrolysis under the same reaction conditions, but using reactants in the ratio **1/2a** = 2:1, expecting an increased yield of **4a**. However, the result was an almost doubled decrease of the yields of both **3a** and **4a** (see Run 2, Table 1).

Due to the failure of our effort to improve the yield of compound **3a** [by stirring the reaction mixture after the electrolysis overnight (Run 3, Table 1), using a double amount of malonate **2a** (Run 4, Table 1) and introducing a double amount of the catalyst (Run 5, Table 1)], we decided to change the solvent/supporting electrolyte system. Ethanol and sodium perchlorate were chosen and the next four experiments (runs 6-9, Table 1) were conducted under the same conditions as those with the acetonitrile/lithium perchlorate system. As the data listed in Table 1 show, the results were similar, except that the ratio of products (**3a/4a**) was somewhat higher.

The highest yield of compound **3a** (69.5%) was achieved when the reaction was performed in an ethanol solution of sodium perchlorate and sodium acetate (0.05 M each) (Run 10, Table 1). Afterwards, the other two dicarbonyl compounds were submitted to the same reaction conditions and yielded ketoester **3b** and dione **3c**. However, the yields of the corresponding Michael adducts were considerably lower than in the case of malonate **2a** (compare runs 11 and 12 with run 10, Table 1). Interestingly, compounds **4b** and **4c** were not isolated from the mixtures obtained by reacting **2b** and **2c** with enone **1**; TLC analysis of the reaction mixtures revealed trace-bands of compounds more polar than compounds **3b** and **3c**, that we attributed to compounds **4b** and **4c**.
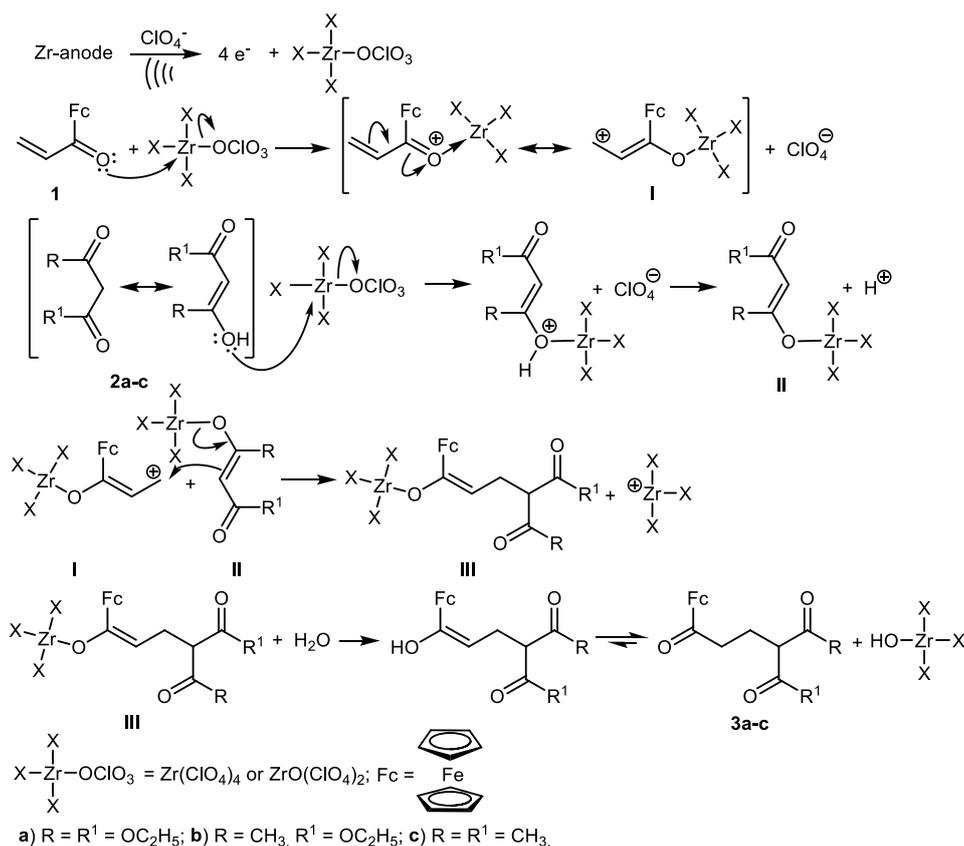
Scheme 2 The plausible mechanism of Michael addition dicarbonyls **2a-c** to enone **1** catalyzed by an electrochemically generated zirconium catalyst

The proposed mechanism of the Michael reaction described in the present paper is depicted in Scheme 2. First of all, after establishing an electrical circuit, an oxidative dissolution of zirconium took place, since this metal is the most susceptible system component to oxidation. We do not know (at this moment) the exact nature of the generated catalyst, but from an organic chemist point of view that is for the time being

less important than the fact that it acts as a successful catalyst. Electrolyses were performed without the electrode potential control; therefore this oxidation should give the most stable zirconium cation, i.e., some species of tetravalent zirconium. It might be either zirconium or zirconyl perchlorate ($Zr(ClO_4)_4$, or $ZrO(ClO_4)_2$, respectively). Due to the known susceptibility of $Zr(ClO_4)_4$ to hydrolysis (Babaeva and Rosolovskii, 1977), we believe that the catalyst was more likely to be $ZrO(ClO_4)_2$, since all experiments were performed with non-dried solvents. Once generated, the zirconium compound (whatever it is) acts as a Lewis acid and plays an important role in the prearrangement of both enone **1** and dicarbonyls **2** for the Michael addition (by establishing of intermediates **I** and **II**, as depicted in Scheme 2). The reaction of these species leads to the formation of a new C-C bond, i.e., to the formation of intermediate **III**, which smoothly undergoes hydrolysis to final products **3**.
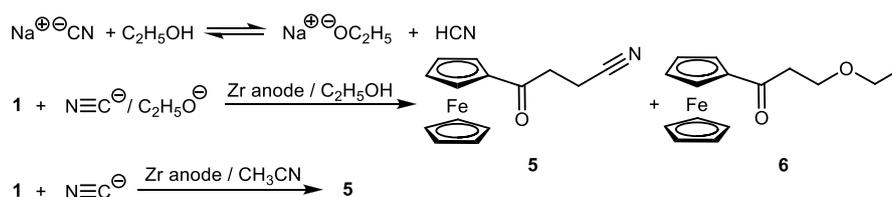
Scheme 3 Michael addition of cyanide anion to enone **1** in ethanol, catalyzed by an electrochemically generated zirconium catalyst

Additionally, we decided to investigate the reaction of acryloylferrocene (**1**) with cyanides under the conditions allowing an *in situ* generation of a zirconium catalyst, expecting an addition of this anion to the enone system of **1**, i.e. ferrocene-containing ketonitrile **5** (Scheme 2) as the product.

Table 2 Michael addition of cyanide anion to enone **1** catalyzed by an electrochemically generated zirconium catalyst

Run	Solvent	Electrolyte	Reaction conditions	Reactants ratio $(1/CN^{\ominus})^{a)}$	Yield of products (%)[b]		
					5	**6**	Ratio **5/6**[a]
1	EtOH	0.05 M $NaClO_4$, 0.05 M AcONa	D	1:2	24	48	33:67
2	EtOH	0.05 M $NaClO_4$, 0.05 M AcONa	D	1:0	-	-	-
3[c]	EtOH	0.05 M $NaClO_4$, 0.05 M AcONa	D	1:2	33	41	46:54
4	EtOH	0.05 M $NaClO_4$, 0.05 M AcONa	B	1:2	34	44	46:54
5	MeCN	0.1 M $LiClO_4$	A	1:2	41	-	-

[a] mol/mol;
[b] Yield of the isolated products;
[b] Sodium cyanide was added after the electrolysis was completed;
Reaction conditions: For reaction conditions, see Table 1.

For the first experiment we chose the conditions found to be the best for the Michael addition of malonate **2a** to enone **1**. Thus, a 1:2 mixture of **1** and sodium cyanide in an ethanol solution of sodium perchlorate and sodium acetate was electrolyzed and the obtained mixture ultrasonicated for additional 30 min. After the usual work-up, the expected product, ketonitrile **5**, was obtained, but it turned out that the addition of the cyanide anion to the conjugate enone system of **1** was not the only reaction that proceeded under these conditions. In addition to that, the main part of the consumed enone **1** underwent the oxa Michael addition, i.e., the addition of ethanol, giving ketoether **6**, so that the ratio **5**/**6** amounted to 33:67 (see Run 1, Table 2). In a subsequent experiment, we performed the electrolysis without sodium cyanide, ultrasonicated the obtained mixture for 30 min and, under these conditions, the addition of ethanol to the enone **1** did not take place (see Run 2, Table 2). When, however, sodium cyanide was added to the mixture obtained in this way and ultrasonicated for 30 min, the mixture containing both **5** and **6** was obtained again, but the abundance of **5** was slightly higher (36%; **5**/**6** = 46:54; see Run 3, Table 2). Almost the same result was obtained when the reaction was performed by electrolysis of the mixture of enone **1** and sodium acetate, and after that the obtained reaction mixture stirred at room temperature overnight (see Run 4, Table 2).

The mechanism of this reaction could be similar to that presented in Scheme 2 for the addition of carbonyls **2a-c**. The key event is the formation of intermediate **I** (Scheme 2), which readily undergoes the addition of cyanide anion and, of course, the addition of ethanol. However, it seems strange, at the first glance, that the addition of ethanol to enone **1** did not proceed in the presence of only the generated catalyst (see Run 2, Table 1), but took place when, in addition to the catalyst, cyanides were present. This could be rationalized by the fact that sodium cyanide is highly susceptible to protolysis, and that ethanol is a protic, polar solvent in which this process can proceed readily (see Scheme 3). The ethoxide formed in this way must compete with cyanide as the Michael donor.

Most of the obtained products are previously known compounds and their spectral data were in complete agreement with those published elsewhere (Pejović et al., 2013). The only new compound obtained by these investigations was **4a**, and its spectral data were in good agreement with the proposed structure. In addition, this compound was a crystalline solid, and its crystal and molecular structures were determined by single-crystal X-ray analysis. The molecule of **4a** contains two halves which are equal in composition and they are denoted by suffixes A and B in the atomic labels (Fig. 1). Some of the corresponding structural fragments exhibit significant conformational differences. The largest difference in the C1−C11−C12−C13−C17 chain is in the value of C1−C11−C12−C13 torsion angle [173.9(2) and 141.6(3)° for A and B fragments, respectively]. As a consequence, two ferrocene units display different spatial orientations with respect to the rest of the molecule, as well as different intermolecular interactions in the crystal packing. However, both ferrocene units in **4a** adopt the same eclipsed conformation. The two terminal C15−C16 ethyl groups also exhibit significantly different orientations [The C14−O3−C15−C16 torsion angle is 78.6(4) and 159.2(4)° for A and B, respectively]. The corresponding bond distances and angles in the two halves of **4a** have very similar values (Table 3). As expected the central carbon atom C17 forms the longest C−C bonds in the molecules [1.536(4), 1.548(4), 1.538(4) and 1.528(4) Å for C17−C13a, C17−C13b, C17−C14a and C17−C14b, respectively].
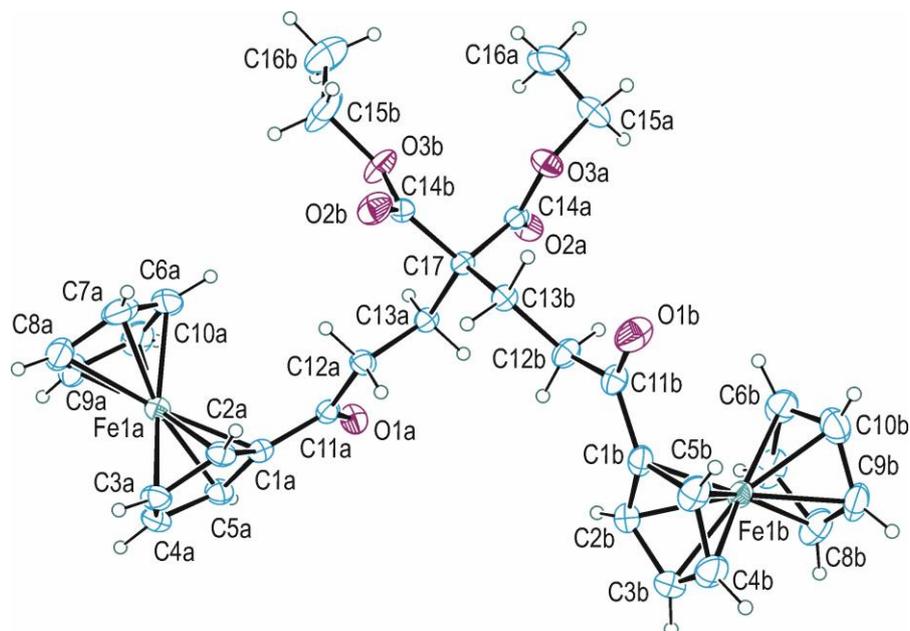
Fig. 1 The molecular structure of **4a**. Displacement ellipsoids are drawn at 30% probability level. CCDC 1411212 contains the supplementary crystallographic data for this compound, which can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Table 3 Selected bond distances (Å) in the crystal structure of **4a**

Bond	Fragment A	Fragment B
C1−C11	1.477(4)	1.472(4)
C14A−C17	1.538(4)	1.528(4)
O1−C11	1.213(3)	1.210(4)
O2−C14	1.189(3)	1.189(4)
O3−C14	1.341(3)	1.342(4)
O3−C15	1.463(4)	1.461(4)

In conclusion, herein we presented an original protocol for the formation of new C-C bonds by a Michael addition of dicarbonyl compounds **2a-c** and cyanide anion to the enone system of acryloylferrocene (**1**) promoted by a catalyst generated *in situ* from a sacrificial zirconium anode. Although the number of substrates used as Michael donors was rather limited, our investigations clearly showed that this method is a good alternative for the existing catalytic protocols, since it represents an easy procedure that does not require expensive or complex equipment.

3. EXPERIMENTAL

3.1. General remarks

All chemicals were commercially available and used as received, except that the solvents were purified by distillation. Compound **1** was synthesized by a known procedure (Damljanović et al., 2011). Electrolyses were carried out in an undivided cell using an Autolab potentiostat and a Uniwatt, Beha Labor-Netzgerät (NG 394). A glass vessel equipped with a spiral Zr-anode ($\phi = 15$ mm, made from a $\phi = 2$ mm wire) and a spiral Pt-cathode ($\phi = 8$ mm, made from a $\phi = 1$ mm wire) was used as the electrolytic cell. Chromatographic separations were carried out using silica gel 60 (Merck, 230–400 mesh ASTM), whereas silica gel 60 on Al plates, layer thickness 0.2 mm (Merck) was used for TLC. Melting points were determined on a Mel-Temp capillary melting points apparatus, model 1001 and are uncorrected. IR measurements were carried out with a Perkin-Elmer FTIR 31725-X spectrophotometer. NMR spectra were recorded on a Bruker Avance III (400 MHz) spectrometer and a Varian Gemini (200 MHz) spectrometer, using $(CD_3)_2SO$ and $CDCl_3$ as the solvents and TMS as the internal standard. Chemical shifts are expressed in δ (ppm). Ultrasonic cleaner Elmasonic S 10, 30W, was used for the ultrasonically supported syntheses.

3.2. General synthetic procedure

The electrolytic cell was filled with 20 mL of the corresponding electrolyte solution (see Tables 1 and 2), 240 mg (1 mmol) of enone **1** and the corresponding amount of compounds **2a-c** (1, 2 or 0.5 mmol; see Table 1) or sodium cyanide (one experiment was performed without sodium cyanide and one by the addition of this salt after the completion of the electrolysis; see Table 2). The cell was placed in an ultrasound bath (at a frequency of 37 kHz, with an effective ultrasonic power of 30 W and a peak of 240 W) and constant current electrolysis (20 mA) was run for 32 min (0.4 F·mol^{-1}) at room temperature. After the electrolysis was finished, the reaction mixture was left 30 min in the same bath or stirred overnight (see Tables 1 and 2) and, afterwards, the solvent evaporated. The residue was diluted with 20 mL of water, the obtained mixture extracted with three 20 mL portions of diethyl ether and the pooled organic layers dried overnight (anhydrous sodium sulfate). After the evaporation of the solvent, the crude reaction product was separated by column chromatography [SiO_2/hexane-ethyl acetate, 8:2 (reaction mixtures obtained from **2a-c**) or 7:3 (reaction mixtures obtained from sodium cyanide), v/v] to give the pure products. The obtained results are given in Tables 1 and 2.

The spectral data of compounds **3a-c**, **5** and **6** were in complete agreement with those published elsewhere (Pejović et al., 2013), whereas the data of **4a** follow.

Diethyl 2,2-bis(3-ferrocenyl-3-oxopropyl)malonate (4a). M.p. 113 °C. IR (KBr, ν, cm^{-1}) 2978, 2012, 1752, 1724, 1658, 1449, 1375, 1245, 1185, 1167, 1072, 1002, 825, 815. ^{1}H NMR (200 MHz, CDCl$_3$) δ 4.80 (pseudo t, $J = 1.9$ Hz, 4H, $2 \times C_5H_4$), 4.50 (pseudo t, $J = 1.9$ Hz, 4H, $2 \times C_5H_4$), 4.26 (q, $J = 7.1$ Hz, 4H, $2 \times OCH_2CH_3$), 4.21 (s, 10H, $2 \times C_5H_5$), 2.85 – 2.72 (m, 4H, $2 \times COCH_2CH_2$), 2.42 – 2.29 (m, 4H, $2 \times COCH_2CH_2$), 1.31 (t, $J = 7.1$ Hz, 6H, $2 \times OCH_2CH_3$). ^{13}C NMR (50 MHz, CDCl$_3$) δ 203.0, 171.2, 78.7, 72.30, 69.8, 69.3, 61.5, 56.5, 34.7, 27.9, 14.2.

3.3. X-ray crystal structure analysis of 4a

The diffraction data for a selected single crystal of compound **4a** were collected at room temperature with an Oxford Diffraction Xcalibur Gemini S four-circle diffractometer equipped with a Sapphire CCD detector, using Mo Kα radiation (λ = 0.71073 Å). Data integration and scaling of the reflections were performed with the CRYSALIS software (CrysAlisPro, 2012a). Empirical absorption corrections of the diffracted intensities were performed by SCALE3 ABSPACK (CrysAlisPro, 2012b) scaling algorithm implemented in the CRYSALIS suite.

The crystal structure was solved by direct methods using SIR2002 (Burla et al., 2012) as implemented in WINGX (Farrugia, 1999) program package. Structural refinements were done by full-matrix least-squares method based on F^2 using SHELXL program (Sheldrick, 2008). Hydrogen atoms attached to carbon atoms were placed at geometrically idealized positions with C–H distances fixed to 0.96, 0.97 and 0.93 Å from methyl, methylene and cyclopentadiene C atoms, respectively. The isotropic displacement parameters of the hydrogen atoms were equal to 1.2 U_{eq} of the parent methylene and cyclopentadiene C atoms and 1.5 U_{eq} of the methyl C atoms. The crystallographic data are listed in Table 1. The PARST (Nardelli, 1983) program was used to perform geometrical calculation and the program ORTEP (Farrugia, 1997) was employed for the preparation of molecular graphics.

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ELEKTROHEMIJSKO GENERISANJE KATALIZATORA ZA MAJKLOVU ADICIJU DIKARBONILNIH JEDINJENJA I CIJANIDA NA AKRILOILFEROCEN

Opisana je Majklova adicija dietil-malonata, etil-acetoacetata, acetilacetona i cijanidnog anjona na akriloilferocen pomoću katalizatora generisanog in situ *sa rastvorne anode od cirkonijuma. Većina dobijenih jedinjenja je identifikovana poređenjem njihovih fizičkih i spektroskopskih podataka sa literaturnim, a jedino novo jedinjenje je potpuno opisano spektroskopskim (IR, ^{1}H- i ^{13}C-NMR) i fizičkim podacima, kao i podacima iz kristalografske analize X-zracima.*

Ključne reči: *elektroliza, cirkonijum, rastvorna anoda, Majklova adicija, akriloilferocen, dikarbonili, cijanidi*