ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2018, Vol. 44, No. 12, pp. 786–791. © Pleiades Publishing, Ltd., 2018.

Synthesis, Crystal Structure, and Studies on Mechanism of D-π-A Ferrocene Derivative[1]

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Received January 22, 2018

Abstract—Microwave-assisted solvent-free synthesis of new (D-π-A) chromogenes, 2-ferrocenyl-1,1-dicyanobuta-1,3-diene derivatives (**II**), have been accomplished through the condensation of 2-(1-ferrocenylethylidene)malononitrile (**I**) and aromatic aldehydes with sarcosine as the catalyst and identified by ^{1}H NMR, ^{13}C NMR and FT-IR. Compound **IId** was determined by X-ray crystallography (CIF file CCDC no. 1056735). The crystal belongs to monoclinic, space group $P2_1/c$. The possible reaction mechanism has been studied.

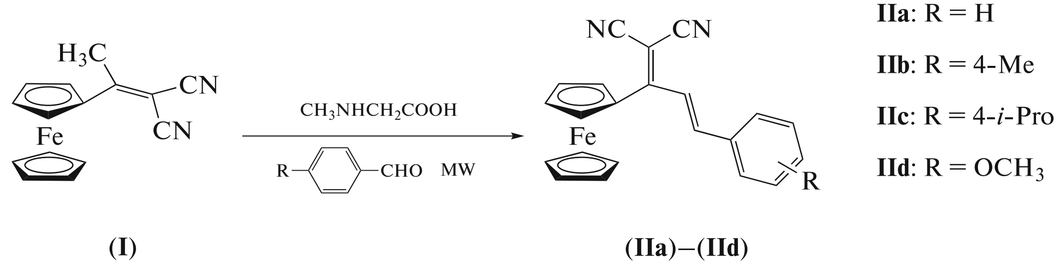
Keywords: ferrocene derivative, crystal structure, sarcosine-catalyst, microwave irradiation, reaction mechanism

DOI: 10.1134/S1070328418120114

INTRODUCTION

Ferrocenes play important roles in various fields, such as medicine [1, 2], asymmetric catalysts [3, 4], biosensors [5, 6], semiconductors [7, 8], and nonlinear optics (NLO), etc. [9]. A whole range of ferrocene derivatives are known to manifest NLO properties [10, 11], these reported ferrocenyl derivatives contain long conjugated systems. Microwave irradiation has been found to have a wide use in ferrocene synthesis because it has advantages (i.e. yield, reaction time) on the preparation of target molecules over conventional methods [12, 13]. In this paper, we describe the straightforward synthesis of new π-conjugated ferrocene derivatives (**II**).

We finished the reaction of 2-(1-ferrocenylethylidene)malononitrile (**I**) with sarcosine and aromatic aldehydes. The reactions were carried out under solvent-free and microwave irradiation conditions. Novel compounds, 2-ferrocenyl-1,1-dicyanobuta-1,3-diene derivatives (**II**), were isolated in 42–46% yield (Scheme 1). The crystal structure of **IId** was determined by single-crystal X-ray diffraction too.



Scheme 1.

EXPERIMENTAL

General procedure. Commercially available chemicals were used without further purification unless stated otherwise. Melting points were determined on an electrothermal digital melting point apparatus and uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 500 (500 MHz) spectrometer in $CDCl_3$ with TMS as the reference. IR

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spectra were obtained using KBr pellets on a Nicolet 179SX FT-IR spectrometer. Elemental analysis of the compound was performed on an Elementar Vario EL (Germany) instrument. Microwave reactions were carried out in a xianghu XH-100B Microwave synthesis instrument. TLC analysis was performed on 0.25 mm silica gel GF254 plates.

Synthesis of I was carried out by literature methods [14]. Melting point: 105–106°C (uncorrected); dark purple powder; ^{1}H NMR ($CDCl_3$; 500 MHz; δ, ppm): 5.07 (s., 2H, C_5H_4), 4.76 (s., 2H,C_5H_4) ,4.27 (s., 5H, C_5H_5), 2.51 (s., 3H, CH_3).

Synthesis of [(2*E*)-3-phenyl-1-ferrocenyl-2-propen-1-ylidene]malononitrile (IIa). A mixture of **I** (1 mmol), benzaldehyde (1 mmol) and sarcosine (1 mmol) were irradiated for 10 min at 120°C. After the completion of the reaction (the reaction was followed by TLC), the mixture was allowed to cool to room temperature. The crude product was chromatographed on silica gel (200–300 mesh) using a mixture of petroleumether–ethyl acetate as eluent to afford the pure product IIa. Dark purple powder; m.p. 168–170°C. The yield was 43%.

IR (KBr; ν, cm^{-1}): 2211, 1612, 1600, 1499, 1489, 1119, 1041, 999, 759, 705. ^{1}H NMR ($CDCl_3$; 500 MHz; δ, ppm): 7.43–7.58 (m., 6H, ArH, =CH), 7.21 (s., 1H, =CH), 5.02 (d., 2H, *J* = 2.0 Hz, C_5H_4), 4.76 (d., 2H, *J* = 1.5 Hz, C_5H_4), 4.33 (s., 5H, C_5H_4). ^{13}C NMR ($CDCl_3$; δ, ppm): 71.3, 71.7, 73.1,75.0, 114.9, 115.7, 124.3, 128.1, 129.2, 130.7, 134.8, 144.0, 172.3.

For $C_{22}H_{16}N_2Fe$

Anal. calcd., %	C, 72.55	H, 4.43	N, 7.69
Found, %	C, 72.50	H, 4.46	N, 7.73

Compounds [(2*E*)-3-(4-methylphenyl)-1-ferrocenyl-2-propen-1-ylidene]malononitrile (**IIb**), [(2*E*)-3-(4-isopropylphenyl)-1-ferrocenyl-2-propen-1-ylidene]malononitrile (**IIc**), and [(2*E*)-3-(4-methoxyphenyl)-1-ferrocenyl-2-propen-1-ylidene]malononitrile (**IId**) were prepared in similar manner to that for the preparation of **IIa**, staring with aromatic aldehydes, respectively.

IIb: dark purple powder; m.p. 150–151°C. The yield was 45%.

IR (KBr; ν, cm^{-1}): 2211, 1600, 1499, 1489, 1119, 1041, 999, 759, 705. ^{1}H NMR ($CDCl_3$; 500 MHz; δ, ppm): 7.58 (d., *J* = 16.0 Hz,, 1H, CH=), 7.46 (d., 2H, *J* = 8.0 Hz, ArH), 7.24–7.21 (m., 3H, ArH, =CH), 5.02 (d., 2H, *J* = 2.0 Hz, C_5H_4), 4.74 (d., 2H, *J* = 1.5 Hz, C_5H_4), 4.32 (s., 5H, C_5H_4), 2.40 (s., 3H, CH_3). ^{13}C NMR ($CDCl_3$; δ, ppm): 21.6, 71.3, 71.8, 72.9, 74.9, 115.1, 115.9, 123.4, 128.1, 129.9, 132.0, 141.5, 144.4, 172.4.

For $C_{23}H_{18}N_2Fe$

Anal. calcd., %	C, 73.03	H, 4.80	N, 7.41
Found, %	C, 72.96	H, 4.83	N, 7.45

IIc: dark purple powder; m.p. 136–138°C. The yield was 42%.

IR (KBr; ν, cm^{-1}): 2126, 1637, 1566, 1414, 1155, 1080, 999, 810. ^{1}H NMR ($CDCl_3$; 500 MHz; δ, ppm): 7.59 (d., *J* = 16.0 Hz, 1H, CH=), 7.52 (d., *J* = 8.0 Hz, 2H, ArH), 7.30 (d., 2H, *J* = 8.0 Hz, ArH), 7.19 (d., *J* = 16.0 Hz, 1H, CH=), 5.00 (t., 2H, *J* = 2.0 Hz, C_5H_4), 4.74 (d., 2H, *J* = 1.5 Hz, C_5H_4), 4.32 (s., 5H, C_5H_4), 2.95(m., 1H, $CH(CH_3)_2$), 1.28 (d., 6H, *J* = 5.6 Hz, CH_3). ^{13}C NMR ($CDCl_3$; δ, ppm): 23.7, 34.2. 71.2, 71.8, 72.9, 74.8, 115.1, 115.9, 123.5, 127.3, 128.2, 132.4, 141.5, 144.4, 152.4, 172.4.

For $C_{25}H_{22}N_2Fe$

Anal. calcd., %	C, 73.90	H, 5.46	N, 6.89
Found, %	C, 73.86	H, 5.51	N, 6.93

IId: dark purple powder; m.p. 152–154°C. The yield was 43%.

IR (KBr; ν, cm^{-1}): 2211, 1600, 1499, 1489, 1119, 1041, 999, 810. ^{1}H NMR ($CDCl_3$; 500 MHz; δ, ppm): 7.58 (d., *J* = 16.0 Hz, 1H, CH=), 7.54 (d., *J* = 8.5 Hz, 2H, ArH), 7.15 (d., *J* = 16.0 Hz, 1H, CH=), 6.95 (d., 2H, *J* = 8.5 Hz, ArH), 4.99 (t., 2H, *J* = 2.0 Hz, C_5H_4), 4.73 (t., 2H, *J* = 1.5 Hz, C_5H_4), 4.32 (s., 5H, C_5H_4), 3.87(s., 3H, OCH_3). ^{13}C NMR ($CDCl_3$; δ, ppm): 55.5, 71.2, 71.8, 72.7, 74.4, 114.7, 115.2, 116.0, 122.1, 127.5, 129.5, 144.3, 161.9, 172.3.

For $C_{23}H_{18}N_2OFe$

Anal. calcd., %	C, 70.07	H, 4.60	N, 7.11
Found, %	C, 70.38	H, 4.58	N, 7.08

X-ray structure determination. Crystals suitable for X-ray structure determination were obtained from the filtration by slow evaporation of the solvent. The crystallographic data collections for compound IId were carried out on a BRUKER SMART 1000 CCD diffractometer equipped with a graphite-monochromatic MoK_α radiation (λ = 0.71073 Å) at 298(2) K. The structure was solved by direct methods using SHELXL-97 program and refined by full-matrix least-squares on F^2 [15, 16]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added according to theoretical modes. Crystallographic data and structure refinement redults for compound IId were given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Table 1. Crystallographic data and structure refinement results for **IId**

Parameter	Value
Formula weight	394.24
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a, Å	9.1662(8)
b, Å	10.0600(9)
c, Å	19.8516(17)
Volume, Å^3	1830.5(3)
Z	4
Crystal size	0.43 × 0.40 × 0.21
$\rho_{\rm calcd}$, Mg/m^{-3}	1.431
Absorption coefficient, mm^{-1}	0.839
F(000)	816
Limiting indices	$-10 \le h \le 10$ $-11 \le k \le 7$ $-22 \le l \le 23$
Reflections collected/unique ($R_{\rm int}$)	8829/3218 (0.0374)
Completeness to θ = 25.02, %	99.9
Data/restraints/parameters	3218/0/245
Goodness of fit on F^2	1.040
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0341$, $wR_2 = 0.0735$
R indices (all data)	$R_1 = 0.0570$, $wR_2 = 0.0869$
Largest diff. peak and hole, e Å^{-3}	0.284 and –0.232

$w = 1/[s^2(F_o^2) + (0.0307P)^2 + 0.8989P]$, where $P = (F_o^2 + 2F_c^2)/3)$.

Table 2. Selected bond lengths (Å) and angles (deg) for **IId**

Bond	d, Å	Bond	d, Å	Angle	ω, deg
Fe(1)–C(3)	2.040(3)	C(11)–C(12)	1.446(3)	C(5)C(1)C(11)C(12)	146.9(3)
Fe(1)–C(4)	2.029(3)	C(12)–C(13)	1.336(4)	C(21)C(11)C(12)C(13)	174.3(3)
Fe(1)–C(6)	2.045(3)	C(13)–C(14)	1.454(3)	C(11)C(12)C(13)C(14)	–178.4(2)
Fe(1)–C(7)	2.041(3)	C(20)–C(21)	1.438(4)	C(12)C(13)C(14)C(19)	0.7(4)
Fe(1)–C(2)	2.045(3)	C(21)–C(22)	1.436(4)	C(12)C(13)C(14)C(15)	179.1(3)
Fe(1)–C(5)	2.030(3)	C(1)–C(11)	1.467(3)	C(23)O(1)C(17)C(18)	1.2(4)
Fe(1)–C(1)	2.060(3)	O(1)–C(17)	1.364(3)	C(15)C(16)C(17)O(1)	–179.8(2)
Fe(1)–C(8)	2.038(3)	O(1)–C(23)	1.420(3)	C(12)C(11)C(21)C(22)	–0.8(4)
Fe(1)–C(10)	2.040(3)	C(1)–C(5)	1.436(4)	C(12)C(11)C(21)C(20)	176.3(2)
Fe(1)–C(9)	2.037(3)	C(3)–C(4)	1.397(4)	N(1)C(20)C(21)C(22)	–1(6)
N(1)–C(20)	1.136(3)	C(2)–C(3)	1.409(4)	N(1)C(20)C(21)C(11)	–179(100)
N(1)–C(22)	1.135(3)	C(16)–C(17)	1.383(4)	C(11)C(21)C(22)N(2)	124(11)
C(11)–C(21)	1.375(3)	C(17)–C(18)	1.381(4)	C(20)C(21)C(22)N(2)	–53(11)

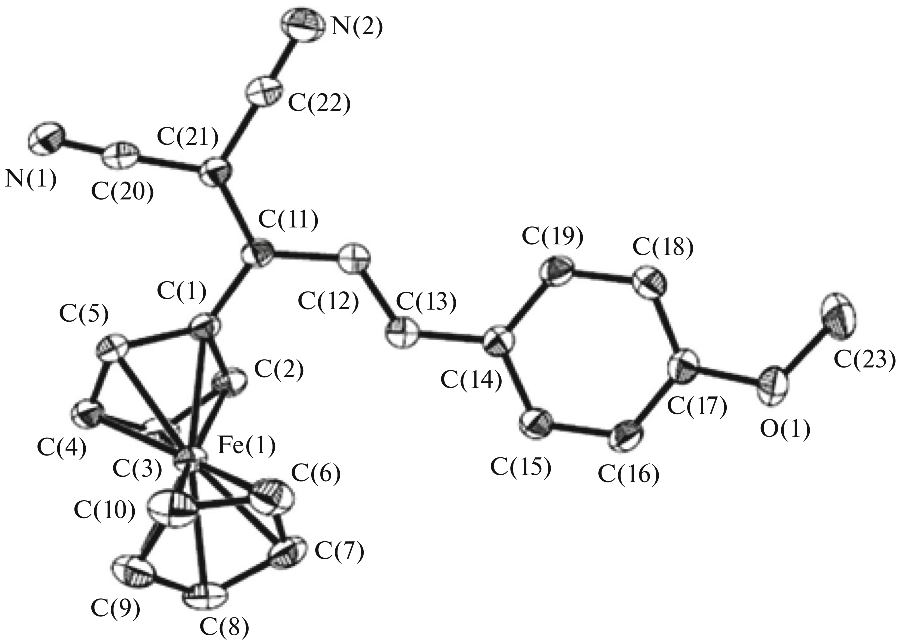


Fig. 1. ORTEP drawing of the structure of **IId**. Thermal ellipsoids are drawn at 30% probability level.

Full crystallographic details have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1056735; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

By analyzing the structures, we found that there was no sarcosine observed in the final products. Following the same reaction conditions, we tried to obtain the product **II** without sarcosine following the same reaction conditions, but it failed. It indicated that the sarcosine may play an important catalyzing role in that reaction. Compounds **II** were obtained exclusively as the *E*-isomer, as evidenced by their ^{1}H NMR spectrum, which exhibited two doublets at ~7.18 and 7.58 ppm attributed to the olefin protons with a coupling constant $J = 16.0$ Hz.

To extend the reaction to a library system, various kinds of aromatic aldehydes were reacted with 2-(1-ferrocenylethylidene) malononitrile (**I**) to give the corresponding 2-ferrocenyl-1,1-dicyanobuta-1,3-diene (**II**). All of aromatic aldehydes which bearing electron-donating groups (alkyl group) gave the desired products in moderate yields, under the same reaction conditions. However, we have not yet gotten the corresponding products with aromatic aldehydes which bearing electron-with drawing groups, such as halide, nitro as reactants.

In addition, we extended our investigation to the synthesis of **II** in toluene or DMF under classical heating conditions. After refluxing for 8 h, we were not able to detect the product. It should be noted that the interesting finding attributed to a specific non-thermal microwave effect. Until recently, X.-S. Wang et al. [17] and F. Diederich et al. [18] reported the synthesis

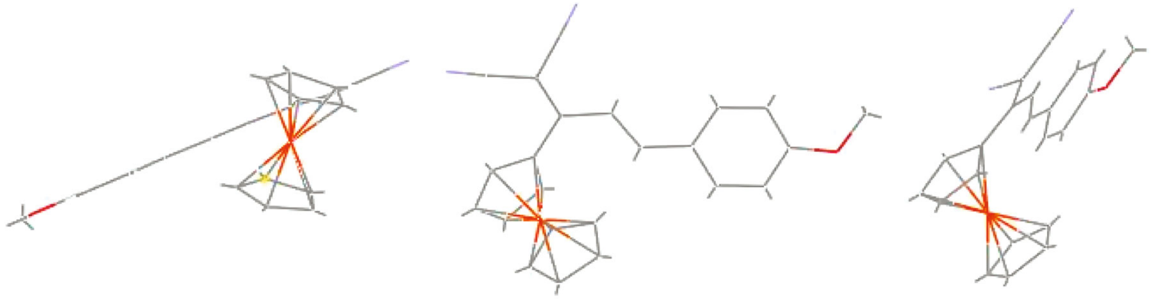


Fig. 2. View the conformations of compound **IId**.

of 1,1-dicyanobuta-1,3-diene derivatives but as far as we know, no condensation reactions with sarcosine or proline as catalyst have been reported.

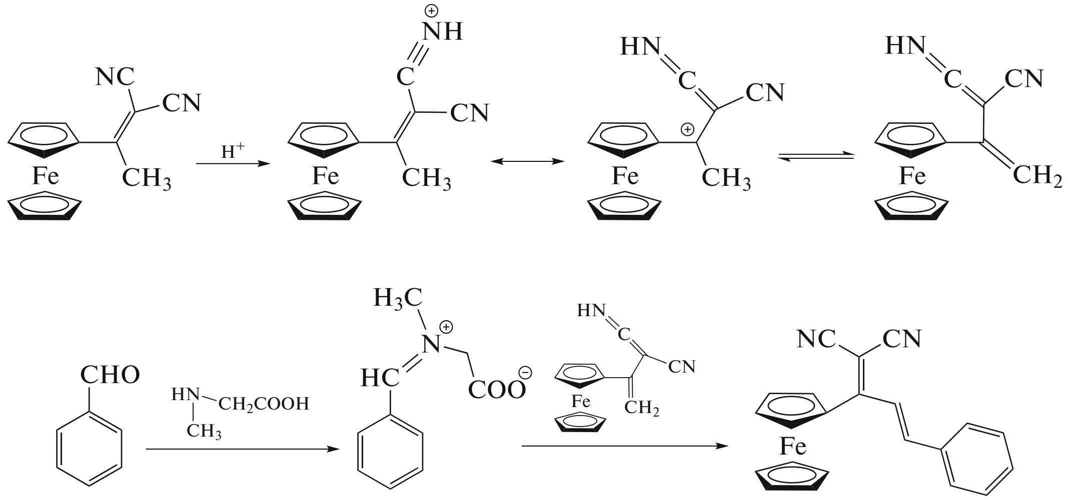
It can be seen from Fig. 1 that the molecular structure of new ferrocene derivative **IId** bearing the dicyanomethylene group and π-conjugated systems, exclusively as the *E*-isomer.

It can be seen from Fig. 2, phenyl ring and 1,1-dicyanobuta-1,3-diene almost in the same plane, as evidenced by the interplanar angles of 4.7° between the phenyl ring and conjugated double bond. There is no conjugate between the 1,1-dicyanobuta-1,3-diene and the ferrocene ring, as evidenced by the interplanar angles of 40.3° between the $\eta^5(C_5H_4)$ ringand the conjugated double bond.

As shown in Table 1, the cyclopentadienyl C–C bond-lengths are 1.397(4)–1.438(4) and 1.406(4)–1.412(4) Å for the $\eta^5(C_5H_4)$ and $\eta^5(C_5H_5)$ rings. The Fe atoms are almost at the center of the two cyclopentadienyl rings with the Fe(1)–*Cg*(1) distances are 1.647 and 1.651 Å, where *Cg*(1) and *Cg*(2) are the centroids of the $\eta^5(C_5H_4)$ and $\eta^5(C_5H_5)$ rings. Interestingly the two cyclopentadienyl rings are not parallel.

Three bond lengths (C(1)–C(11), C(11)–C(12), and C(13)–C(14) 1.467(3), 1.446(3), and 1.454(3) Å) were significantly shorter than normal C–C bond length (1.54 Å). The average bond length of benzene ring (1.38(4) Å) is shorter than the normal length of benzene ring. The results show that there is a good electronic delocalization in the molecule.

Although the detailed mechanism of the reaction has not been clarified yet, the formation of **II** can be tentatively explained by the pathway presented in Scheme 2.



Scheme 2.

The simplest approach to an azomethineylide is the reaction of a secondary amine, such as sarcosine or proline with an aldehyde (Scheme 2). In the acidic conditions, reaction of the resulting yield with the protonated 2-(1-ferrocenylethylidene)malononitrile **I** results in the formation of the corresponding 2-ferrocenyl-1,1-dicyanobuta-1,3-diene derivatives (**II**).

Thus, we have described a convenient method for the synthesis of new (D-π-A) chromogenes 2-ferrocenyl-1,1-dicyanobuta-1,3-diene (**II**). The reactions were carried out under microwave irradiation conditions. For the first time, we are reporting that sarcosine is used as a catalyst for such condensations reaction, a possible mechanism of the reaction has been proposed. Meanwhile, compound **IId** was confirmed by X-ray crystallography.

ACKNOWLEDGMENTS

This work was supported by Natural Science Foundation of Hebei Province (no. B2014208094).

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