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Reaction Between Ferrocene-carboxaldehyde and Dioxaphospholene: Characterization and Crystal Structures of an Unexpected Bisferrocenyldioxolane

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ABSTRACT

Reacting an 1:1 stoichiometric molar ratio of ferrocenecarboxaldehyde and 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene, neat, at room temperature for one week, leads to the diastereoselective formation of a bis-ferrocenyl 1,3-dioxolane complex 1-(4-methyl-2,5-diferrocenyl-1,3-dioxolan-4-yl)ethanone **(1)**, in 30% isolated yield. The compound has been fully characterized by FT-IR, mono- and two-dimensional ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and cyclic voltammetry. Complex **1** has also been characterized by single crystal X-ray analysis.

Keywords: ferrocene;1,3-dioxolane; bimetallic complex; heterocycle; X-ray structure

1. Introduction

Fifty years ago, Ramirez and co-workers [1-3] disclosed a powerful and simple organic methodology to synthetize in high yields, symmetrically 3-substituted 2,4-pentanediones $RCH(C(O)CH_3)_2$, by condensing the biacetyl-trimethyl phosphite 1:1 adduct [2] with aldehydes (RCHO), especially benzaldehyde and its derivatives [1,3,4], to form essentially one diastereomeric form of the 2,2,2-trimethoxy-4-methyl-4a-acetyl-5a-R-1,3,2-dioxapholane (Scheme 1, **A**), which upon methanolysis gave the desired 3-R-β-diketones, through an intramolecular rearrangement involving the 1,2 shift of an acetyl group during the loss of the trimethylphosphate [2]. Such 1,3-dicarbonyl compounds have been extensively used in organic synthesis where they serve as starting materials in the preparation of various heterocyclic molecules that exhibit a wide variety of biological and pharmacological activities [5,6]. In addition, β-diketones are also important building blocks for the construction of asymmetric tridentate Schiff base metalloligands upon mono-condensation with aliphatic or aromatic diamines [7-9], whereas their high complexing ability accounts for the design of new transition metal architectures [10].

A   **B**

C   **D**
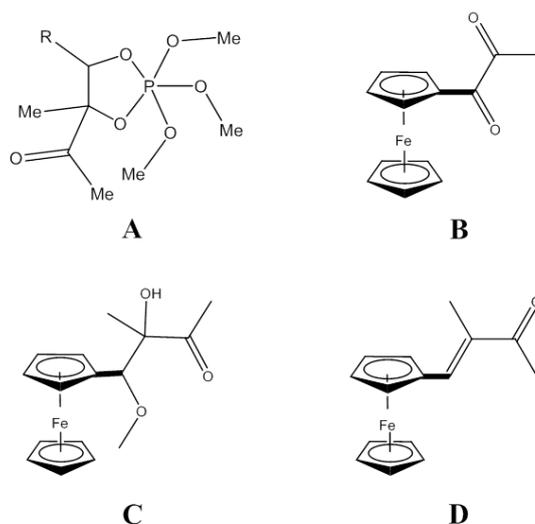
Scheme 1

Very recently, we have shown that in the reaction between ferrocenecarboxaldehyde with a slight excess (15%) of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxapholene, under Ramirez's conditions or slightly modified conditions, ferrocenecarboxaldehyde behaves very differently from aromatic aldehydes [11]. The expected symmetrical target compound 3-ferrocenyl-2,4-pentanedione is, indeed, never obtained. Instead, three new oxygenated C_3- and C_4-chain-containing ferrocenes, namely, 1-ferrocenyl-1,2-propanedione (**B**), 4-methoxy-4-

ferrocenyl-3-hydroxy-3-methyl-2-butanone (**C**) and the ferrocenyl enone, 4-ferrocenyl-3-methyl-3-buten-2-one (**D**) (Scheme 1), were isolated and fully characterized, including by single-crystal X-ray diffraction analysis. It was postulated that these three compounds arise from the same cyclic saturated oxyphosphorane intermediate, molecule **A** of scheme 1 (R = ferrocenyl). The difference of behavior could be due to the stabilization of a carbonium ion in α-position by ferrocene, through the fulvene mesomeric form [12] during the intramolecular rearrangement step. We, therefore, set out to trap the 1,3-dioxaphospholane system (Scheme 1, **A**, R = ferrocenyl) by reacting ferrocenecarboxaldehyde and the diacetyl trimethylphosphite adduct in a precise 1:1 stoichiometric ratio, in a solventless process. To our surprise, we isolated the new bimetallic analogue of intermediate **A**, 1-(4-methyl-2,5-diferrocenyl-1,3-dioxolan-4-yl)ethanone (**1**), in which the phosphite unit has been replaced by a ferrocenyl methylene fragment (see formula in Scheme 2). It is worth nothing that complex **1** is formed as a single diastereoisomer despite of the three assymetric carbons of the 1,3-dioxolane ring. Herein, we report on its isolation, full analytical and spectroscopic characterization and its crystal and molecular structure.

2. Experimental
2.1. General Experimental Methods

Reactions were performed under dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled under dinitrogen by standard methods prior to use. All chemicals were purchased from commercial sources and used without further purification. The pholpholene 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene was prepared using the literature method [2]. IR spectra were recorded on a Perkin Elmer model 1600 FT-IR spectrophotometer, in the range 4000-450 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Avance III 400 spectrometer at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to the residual deuterated solvent peaks (CDCl$_3$: ^{1}H $\delta = 7.26$ ppm, ^{13}C $\delta = 77.16$ ppm). Coupling constants (J) are expressed in Hertz (Hz). Microanalyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the CRMPO at the University of Rennes 1. Migration coefficients (Rf) were determined on silica gel TLC. Melting points were measured in evacuated capillaries on a Kofler Bristoline melting point apparatus and are uncorrected.

2.2. Synthesis of 1-(4-methyl-2,5-diferrocenyl-1,3-dioxolan-4-yl)ethanone (1)

To a Schlenk tube loaded with 300 mg (1.40 mmol) of ferrocenecarboxaldehyde were added dropwise by syringe, under dry dinitrogen, 0.30 mL (1.40 mmol) of freshly prepared 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene. The reaction mixture was stirred for one week at room temperature (rt). Then, 8 mL of CH_2Cl_2 were added and the organic phase was washed with water, and dried over $MgSO_4$. After evaporation of the solvents under reduced pressure, the crude oil was purified by column chromatography (3 x 24 cm) using silica gel (70-230 mesh) and a 4:1 mixture of hexane/ethyl acetate as eluent. Compound **1** was clearly observed as a yellow band on the column (Rf = 0.5). Removal of the solvents and drying under vacuum afforded 210 mg (0.47 mmol, 30.1%) of **1** as a yellow powder. Diffraction-quality single crystals of **1** were obtained as yellow rod-shaped crystals by slow evaporation of a saturated dichloromethane solution for 2 days at rt. M.p. 178 °C. Anal. Calcd for $C_{26}H_{26}O_3Fe_2$ (498.18 g mol^{-1}): C, 62.69; H, 5.26. Found: C, 62.34; H, 5.26%. IR (KBr, cm^{-1}): 3105(vw) ν(C-H arom); 2976 (w), 2926(w), 2855(w), ν(C-H aliph); 1718 (vs), 1632 (vs) ν(C=O) 1092 (vs) ν(O-C-O). ^{1}H NMR (400 MHz, CDCl$_3$): 1.46 (s, 3 H, CH$_3$), 1.97 (s, 3 H, COCH$_3$),4.14 and 4.29 (2 x m, 2 x 1 H, H$_{\alpha,\alpha'}$ C$_5$H$_4$-Fe2), 4.16 (m, 2 H, H$_{\beta,\beta'}$ C$_5$H$_4$-Fe2), 4.20 (s, 5 H, C$_5$H$_5$-Fe1), 4.28 (s, 5 H, C$_5$H$_5$-Fe2), 4.27 and 4.31 (2 x m, 2 x 1 H, H$_{\beta,\beta'}$ C$_5$H$_4$-Fe1), 4.49 and 4.60 (2 x q, $^3J_{H,H}$ = 2.4 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 x 1 H, H$_{\alpha,\alpha'}$ C$_5$H$_4$-Fe1), 4.74 (s, 1 H, CH), 6.03 (s, 1 H, O-CH-O). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): 21.18 (CH$_3$), 28.17 (COCH$_3$), 65.41 and 67.96 (C$_{\alpha,\alpha'}$ C$_5$H$_4$-Fe2), 67.08 and 68.02 (C$_{\alpha,\alpha'}$ C$_5$H$_4$-Fe1), 67.69 and 68.55 (C$_{\beta,\beta'}$ C$_5$H$_4$-Fe2), 68.68 and 68.86 (C$_{\beta,\beta'}$ C$_5$H$_4$-Fe1), 69.04 (C$_5$H$_5$), 82.48 (C$_{ipso}$ C$_5$H$_4$-Fe1), 82.75 (C$_{ipso}$ C$_5$H$_4$-Fe2), 86.40 (CH), 89.01 (*C*-CH$_3$), 102.46 (O-CH-O), 210.00 (C=O).

2.3. Crystal structure determination

X-ray data for a yellow rod-shaped crystal of **1**, obtained as described above, were collected at 150(2) K on a Bruker APEXII AXS diffractometer, equipped with a CCD detector, using Mo-Kα radiation (λ = 0.71073 Å). The crystal of approximate dimensions $0.35 \times 0.07 \times 0.05$ mm, was coated in Paratone-N oil and mounted on a Kaptan loop. The loop was transferred to the diffractometer, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. The structure was solved by direct methods using *SIR97 program* [13], and then refined with full-matrix least-square methods based on F^2 (*SHELXL-*

97) [14], with the aid of *WINGX* program [15]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were finally included in their calculated positions. The disorder observed for the carbon atoms of the free cyclopentadienyl ring of one ferrocenyl moiety (C(21) to C(25)) was modelled using two positions per carbon with a fixed 0.5 occupancy for each carbon. ORTEP and ball-and-stick views are generated using OLEX2 [16].

Crystal data: $C_{26}H_{26}Fe_2O_3$, M_r = 498.17, monoclinic, P2$_1$/c, a = 14.0199(8) Å, b = 7.4129(5) Å, c = 21.1930(14) Å, β = 97.388(2)°, V = 2184.3(2) Å^3, Z = 4, ρ_{calcd} = 1.515 g cm^{-3}, μ = 1.354mm^{-1}, $F(000)$ = 1032, 17559 reflections measured, 4983 unique (R_{int} = 0.0472), parameters refined: 270, R_1/wR_2 ($I > 2\sigma(I)$) = 0.0431/0.0998, R_1/wR_2 (all data) = 0.0752/0.1171, GOF = 0.888, $[\Delta\rho]_{min}/[\Delta\rho]_{max}$: -0.533/0.580 eÅ^{-3}. Additional crystallographic details are in the CIF file.

3. Results and Discussion

3.1. Isolation and characterization

Reactions of neat ferrocenecarboxaldehydes and freshly prepared 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene, in an exact 1:1 stoichiometric ratio for one week at room temperature, leads, upon extraction in dichloromethane, chromatographic purification and crystallization, to the formation of the bis-ferrocenyl 1,3-dioxolane derivative **1** (Scheme 2). It was isolated as a yellow solid in 30% yield [17], and is air and thermally stable, and moisture insensitive on storage under ordinary conditions. Compound **1** exhibits good solubility in common organic solvents such as dichloromethane, diethyl ether or acetone, but is insoluble in *n*-hexane or pentane. Its composition and identity was deduced from elemental analysis that is consistent with the proposed formula, FT-IR and multinuclear and 2D NMR spectroscopies (see Section 2.2 for details). Additionally, the crystal and molecular structure of complex **1** was determined by single crystal X-ray diffraction analysis (see below).
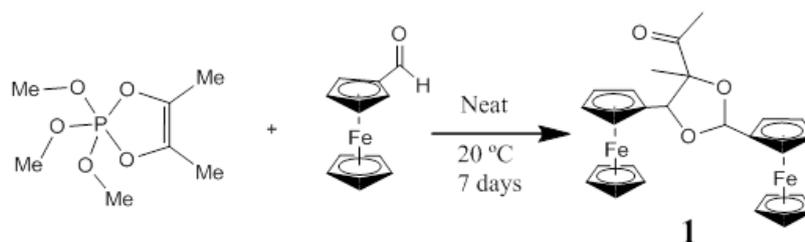
Scheme 2 Synthesis of 1-(4-methyl-2,5-diferrocenyl-1,3-dioxolan-4-yl)ethanone (**1**)

The solid-state FT-IR spectrum of **1** showed intense bands at 1718 and 1632 cm^{-1} attributed to the ν(C=O) stretching modes, and at 1092 cm^{-1} due to the ν(O-C-O) stretching vibration of the dioxolane skeleton.

From both its one- and two-dimensional NMR spectral data, compound **1** is characterized on the basis of chemical shift, coupling constants, multiplicity and proton-proton connectivity. The ^{1}H NMR spectral data clearly indicated that **1** is formed as a single diastereoisomer, displaying only a set of signals. The free cyclopentadienyl rings of the two ferrocenyl moieties appeared as two sharp singlets, integrating each for five protons, at 4.20 and 4.28 ppm, whereas the protons of the methyl and acetyl groups resonated as two singlets at 1.46 (3 H) and 1.97 (3 H) ppm, respectively. The protons of the two CH units, the acetalic one and that at the 5-position of the 1,3-dioxolane ring, showed up at 6.03 and 4.74 ppm, respectively. In addition, the eight multiplets observed in the range 4.14 - 4.60 ppm are due to the magnetically non-equivalent protons of the two substituted cyclopentadienyl rings.

The presence of only one diastereoisomer in solution is also attested by ^{13}C NMR spectroscopy, where the complete assignment of all the peaks was carried out with the help of two-dimensional ^{1}H-^{13}C HMQC and HMBC spectra. The spectrum exhibited a single sharp resonance for each chiral carbon atom of the 1,3-dioxolane core at 86.40 (C-5), 89.01 (C-4) and 102.46 (C-2) ppm, two signals at 82.48 and 82.75 ppm for the two C$_{ipso}$ carbon atom of the substituted C$_5$-ring, and one low field resonance at 210.00 ppm for the acetyl carbonyl carbon. Moreover, the number of lines for the CH$_3$, C$_5$H$_4$ and C$_5$H$_5$ groups, and their respective chemical shifts testified to structure **1**, that was further unambiguously confirmed by X-ray crystallographic analysis (see below). Such spectroscopic features are in accordance with chemical shifts previously reported for purely organic [18] and ferrocene-containing 1,3-dioxolane systems [19,20].

3.2. X-ray diffraction study

Yellow rod-shaped X-ray quality crystals of 1-(4-methyl-2,5-diferrocenyl-1,3-dioxolan-4-yl)ethanone (**1**) were obtained by slow evaporation of a saturated dichloromethane solution. Complex **1** crystallizes in the monoclinic centrosymmetric space group P21/c with a single molecule in the asymmetric unit. The molecular structure of **1** with the atom labeling scheme is presented in Fig. 1 with selected bond distances and angles given in Table 1. Complex **1** consists of a 1,3-dioxolane ring bearing ferrocenyl substituents in positions 2 and 5, and methyl and acetyl groups substituting the 4-position of the heterocycle; forming

monomeric units that are separated by normal van der Waals distances. Both ferrocenyl moieties, Fc1, Fc2a and Fc2b (the free C_5-ring occupies two positions in Fc2; Fc = [(η^5-C_5H_5)Fe(η^5-C_5H_4)] feature linear sandwich structures with typical [η^5-Fe-η^5] coordination mode. The two cyclopentadienyl rings are nearly eclipsed with twist angles of 3.54° for Fc1, 6.85 and 12.40° for Fc2a and Fc2b, respectively. The iron atom is coordinated to the free and substituted cyclopentadienyl rings at a ring centroid-iron distances of 1.646/1.641 Å for Fc1, 1.642/1.704 Å for Fc2a and 1.642/1.600 Å for Fc2b, with ring centroid-iron-ring centroid angle of 178.4° (Fc1), 171.4° (Fc2a) and 175.2° (Fc2b), respectively, indicating that there is a Fe(II) oxidation state in each metallocene [21].
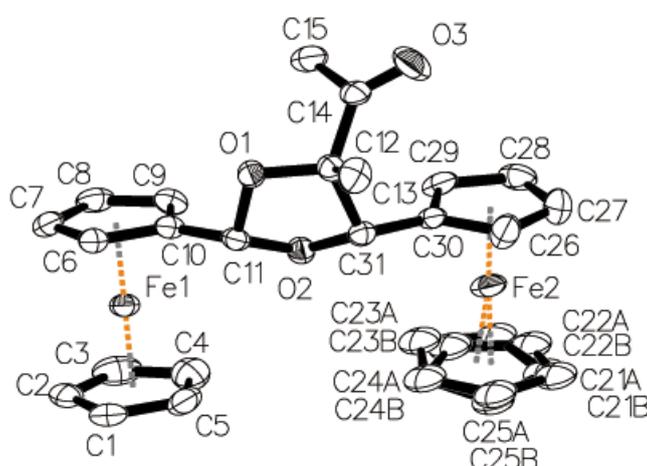

Fig. 1 Molecular structure of **1** with the atom numbering scheme. The thermal ellipsoids are drawn at the 40% probability level and the hydrogen atoms are omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) for compound **1**

Bond distances			
C(10)-C(11)	1.479(4)	C(30)-C(31)	1.489(4)
C(11)-O(1)	1.445(3)	C(31)-O(2)	1.422(3)
C(11)-O(2)	1.410(3)	C(12)-C(31)	1.562(4)
C(12)-O(1)	1.435(3)	C(12)-C(13)	1.520(4)
C(12)-C(14)	1.530(4)	C(14)-O(3)	1.208(3)
C(14)-C(15)	1.495(4)	Fe(1)-C_{Cp} (avg)	2.038
Fe(1)-$C_{Cp'}$ (avg)	2.038	Fe(2)-C_{Cp} (avg)	2.036
Angles			
C(10)-C(11)-O(1)	111.0(2)	C(10)-C(11)-O(2)	110.8(2)
O(1)-C(11)-O(2)	105.50(19)	C(11)-O(1)-C(12)	107.84(19)
C(11)-O(2)-C(31)	105.1(2)	O(1)-C(12)-C(31)	103.5(2)
O(2)-C(31)-C(12)	103.2(2)	C(30)-C(31)-O(2)	111.5(2)
C(12)-C(14)-O(3)	119.5(3)	C(15)-C(14)-O(3)	121.8(3)

Abbreviations: Cp = C_5H_5, Cp' = C_5H_4.

The dioxolane ring adopts an envelope conformation with the atoms C(11)-O(1)-C(12)-C(31) being almost co-planar, the deviation from the mean plane are of -0.012, 0.018, -0.017 and 0.011 Å, respectively, whereas the O(2) atom is out of this mean plane by 0.527 Å. As a result, the dihedral angle between the C(11)-O(1)-C(12)-C(31) and C(11)-O(2)-C(31) planes is 21.57°. In the monoferrocenyl-1,3-dioxolane complexes reported by Manoury *et al.* [19], it is the C-5 carbon atom of the ring that is out of the O-C-O-C mean plane. In compound **1**, the C-O-C-C mean plane is twisted with respect to the two attached Fc1 and Fc2 cyclopentadienyl rings by 67.33 and 74.75°, respectively. The lengths of the C-C and C-O bonds inside the dioxolane ring (see Table 1) are identical to those previously reported for such structurally characterized species [18,19]. On the other hand, the geometry and metrical parameters of the $[C(CH_3)C(=O)CH_3]$ fragment at C(12) are in accordance with those reported by Ramirez and co-workers for the five-membered cyclic acyl phosphate $[(CH_3O)(O=)P(O-C(=O)-C(CH_3)(COCH_3)-O)]$, [22]. The C-C and C-Fe bond distances in the ferrocene sandwiches as well as the C=O bond distance fall all within the range of standard values [23]. The bond angles at the chiral carbons C(11), C(12) and C(31) averaging for 105.4(2), 108.4(2) and 110.1(2)°, respectively, are idealized values for sp^3-hybridized atoms, whereas the acetyl O(3)-C(14)-C(15) angle of 121.8(3)° is similar to those measured for compounds **B** (123.79(19)°), **C** (122.13(14)°) and **D** (119.35(16)°) (Scheme 1) [11]. Lastly, within the crystal structure of **1**, intermolecular C-H···O hydrogen bonds (Table 2) generate a staircase-type structure (Fig. 2).
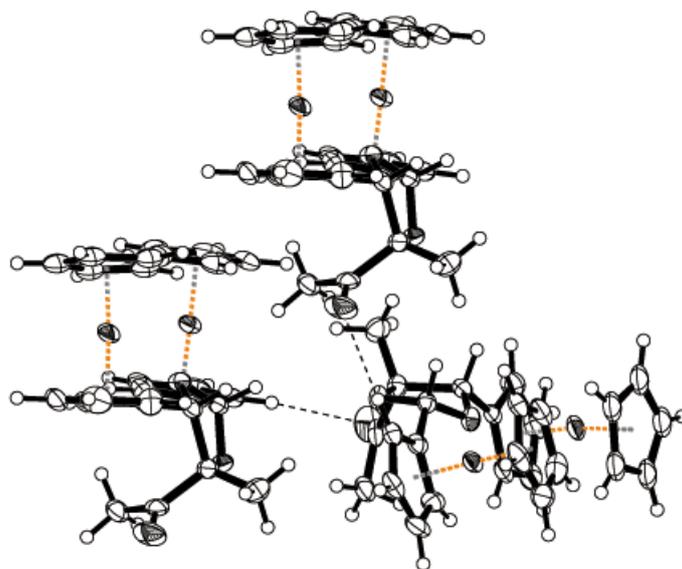

Fig. 2 Intermolecular hydrogen bond interactions forming a staircase-type structure.

Table 2 Hydrogen Bonding interaction parameters for **1**

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
C2—H2···O3[i]	0.95	2.49	3.205(4)	132
C6—H6···O3[ii]	0.95	2.40	3.336(4)	167

Symmetry Codes: (i) x,1/2-y,1/2+z; (ii) 2-x,-1/2+y,1/2-z

3.3. Cyclic voltammetry

The electrochemical features of compound **1** were investigated by cyclic voltammetry in dichloromethane solution containing 0.1 M [n-Bu$_4$N][BF$_4$] as supporting electrolyte. Measurements were carried out in 10^{-3} M solutions at room temperature in the potential range +1.5 to -1.0 V with scan rate 100 mV s^{-1}. The cyclovoltammogram of a solution containing **1** shows a chemically reversible oxidation process with current ratio i_{pa}/i_{pc} equal to unity, at $E_{1/2}$ = 0.070 V vs FcH/FcH$^+$ couple. As compound **1** lacks π-conjugated spacer between the two ferrocenyl moieties separated by four single bonds, it is reasonable to attribute this oxidation wave to a two-electron process [24]. One can also note that the $E_{1/2}$ value is positively shifted with respect to that of free ferrocene, thus featuring some electron withdrawing ability of the dioxolane system.

4. Conclusion

In summary, we have shown that ferrocenecarboxaldehyde behaves differently from benzaldehydes through a new reaction with equimolar amount of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxapholene in a solventless process, giving the unexpected 1-(4-methyl-2,5-diferrocenyl-1,3-dioxolan-4-yl)ethanone (**1**). The microcrystalline bis-ferrocenyl 1,3-dioxolane compound, formed as a single diastereoisomer, was fully characterized by analytical and spectroscopic methods, including its total assignment using the 2D NMR techniques, and by single crystal X-ray diffraction analysis. It is noteworthy that compound **1** is, to the best of our knowledge, the first structurally characterized 1,3-dioxolane-type intermediate In such condensation reactions of aliphatic 1,2-diketones with aldehydes. Development of new synthetic strategy to prepare our target symmetrical precursor 3-ferrocenyl-2,4-pentanedione and further study of monocondensation reactions with primary diamines in order to obtain new tridentate metalloligands are underway in our laboratories, and results will be reported in due course.

Acknowledgments

Appendix A. Supplementary material

CCDC 925532 (for **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.as.uk/data_request/cif.

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