

The synthesis, spectroscopic, electrochemical and X-ray diffraction characterization of novel bridged ferrocene precursors for use in self-assembled monolayers

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Abstract

The synthesis of 1,6-diferrocenylhexane-1,6-dione (**I**), 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene (**II**) and 1,6-diferrocenylhexane (**III**) is reported. All three compounds were characterized by ¹H NMR, ¹³C NMR, and infra-red spectroscopy, mass spectrometry, cyclic voltammetry and chronoamperometry. Compounds **I** and **III** each exhibit a single two electron transfer, while compound (**II**) exhibits two single electron transfers. Compounds (**I**) and (**II**) were further studied by single crystal X-ray diffraction. In compound (**I**), both carbonyl groups are in plane with the adjacent ferrocenyl Cp ring. For compound (**II**) one of the ferrocenyl Cp rings is coplanar with the carbonyl group, the other with the double bond of the cyclopentene ring, but the C=O moiety and the double bond are basically perpendicular to each other.

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1. Introduction

Since its first discovery in 1951 [1], ferrocene has been the focus of extensive studies due to its unique structural, spectroscopic and electrochemical properties. Ferrocene containing compounds and polymers, and especially compounds exhibiting multiple ferrocene groups with the opportunity for producing mixed-valent states, have been extensively explored for their potential use in chemical and biochemical sensors [2], as redox active catalysts [3], because of their use for molecular magnets [4] and for use in self-assembled monolayers [5]. Such monolayers, when being made from molecules with multiple covalently connected ferrocene groups, can be prepared in mixed-valent, fully oxidized or fully reduced states. Thus, the chemical properties of the monolayer can be readily controlled via application of the appropriate

voltage, increasing their potential for the above applications. The electron transfer of ferrocenes is generally chemically and electrochemically reversible and happens via an outer-sphere redox mechanism, thus making ferrocene derivatives not only perfect candidates to be incorporated into technological devices, but also ideal molecules for the study of interfacial electron and charge transfer.

During our investigations on the synthesis of such self-assembled monolayers we have been able to synthesize, isolate and characterize several novel bridged diferrocene compounds, including a unique aldol condensation product (Compound **II**) with a cyclopentene ring bridging two ferrocene moieties. In this paper, we will report on the synthesis, spectroscopic and electrochemical properties of 1,6-diferrocenylhexane-1,6-dione (**I**), 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene (**II**) and 1,6-diferrocenylhexane (**III**). The solid state structural properties of compounds (**I**) and (**II**) will also be reported.

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2. Experimental

2.1. Chemicals

Methylene chloride (Certified ACS, 99.9%) and acetonitrile (HPLC Grade) were distilled over CaH₂ under nitrogen and used immediately. Tetra-*n*-butylammonium perchlorate (98%) was recrystallized three times from ethanol and dried under vacuum. All other chemicals were purchased from commercial vendors in purities higher than 98% and were used as received. For reactions in which an inert atmosphere was required, pre-purified argon was delivered via a Schlenk line. Where appropriate, glassware was oven dried overnight at 110 °C and cooled under flowing argon. An overhead mechanical stirrer was used for reactions in which vigorous stirring was required.

2.2. Instrumentation

2.2.1. Spectroscopy

¹H and ¹³C NMR spectra were recorded on a Varian-Gemini 2000 400 MHz NMR spectrometer; chemical shifts are reported in ppm downfield from TMS. IR spectra were obtained using an FT/IR 410 JASCO spectrometer, with the sample prepared as a KBr pellet. Direct probe mass spectrometry was performed using a Finnigan Model GCQ ion-trap spectrometer utilizing electron ionization.

2.2.2. X-ray diffraction

All crystals were grown via kinetically controlled solvent evaporation. Both 1,6-diferrocenylnhexane-1,6-dione and 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene crystals formed from a 75%/25% hexane/ethyl acetate solution.

The X-ray diffraction data for 1,6-diferrocenylnhexane-1,6-dione (**I**) were collected at 153(2) K on a Siemens P4 Single Crystal Diffractometer equipped with a serial detector utilizing molybdenum radiation (Mo K α , λ = 0.71073 Å). The Siemens (Bruker) XSCANS operating program [6] was used for unit cell determination and data collection, and the data were absorption corrected via empirical psi scan methods.

Diffraction data for 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene (**II**) were collected using a Bruker AXS SMART APEX CCD diffractometer at 100(2) K using monochromatic Mo K α radiation with the omega scan technique. The unit cell was determined using SMART [7] and SAINT+ [8], and the data were empirically absorption corrected using SADABS [8]. The structure of **I** was solved by direct methods, that of **II** by Patterson methods. Both were refined by full matrix least squares against F^2 with all reflections using SHELXTL [9]. Non-hydrogen atoms were refined anisotropically while hydrogen atoms were added in calculated positions and were refined with an isotropic thermal displacement parameter 1.2 times that of the adjacent carbon atom. Crystal data and experimental details are listed in Table 1.

2.2.3. Electrochemistry

Electrochemical measurements were performed in a single compartment cell with a BioAnalytical Systems 100B potentiostat at room temperature. Analyte and supporting electrolyte concentrations were 1.0 mM and 0.10 M in acetonitrile, respectively. All potentials were referenced to a non-aqueous Ag/Ag⁺ reference electrode (1.0 M and 1.0 mM in TBAP and AgNO₃, respectively, in acetonitrile). Platinum disk (1.6 mm diameter) working electrodes, platinum wire counter electrodes and non-aqueous Ag/Ag⁺ reference electrodes were obtained from BioAnalytical Systems. The number of electrons transferred for each oxidation wave was confirmed by chronoamperometry using ferrocene as a standard.

2.3. Synthesis

2.3.1. Synthesis of 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene (**II**), and 1,6-diferrocenylnhexane-1,6-dione (**I**)

A modified version of the Friedel–Crafts acylation as described by Chidsey [5] was used to prepare 1,6-diferrocenylnhexane-1,6-dione (**I**) and 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene (**II**). Ferrocene (61.23 g, 0.329 mol) was dissolved in 700 mL of dry methylene chloride and cooled in an ice bath for 15 min. Adipoyl chloride (24 mL, 0.165 mol) and anhydrous aluminum chloride (43.64 g, 0.327 mol) were added to the dissolved ferrocene. The ice bath was removed after 15 min of stirring. After 1.5 h of additional stirring at room temperature, 250 mL of de-ionized water were added dropwise via an addition funnel. The reaction began to reflux slowly. After an additional hour of vigorous stirring, the organic phase was extracted with de-ionized water until the aqueous layer was colorless, followed by three extractions with brine solution. The product was dried overnight over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified via column chromatography using silica gel as the stationary phase and 75%/25% hexane/ethyl acetate as the eluent. Upon purification, two products were isolated. The first product (R_f = 0.7, 56% yield) was 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene (**II**), while the second (R_f = 0.5, 28% yield) was 1,6-diferrocenylnhexane-1,6-dione (**I**). Spectroscopic data for (**I**): ¹H NMR (400 MHz, CDCl₃, ppm) 1.799 (broad m, 4H, COCH₂CH₂), 2.774 (t, 4H, COCH₂), 4.201 (s, 10H, C₅H₅), 4.499 (broad m, 4H, C₅H₄), 4.798 (broad m, 4H, C₅H₄). ¹³C NMR (100 MHz, CDCl₃, ppm) 25.715 (COCH₂CH₂), 40.850 (COCH₂), 70.492 (Cp), 70.939 (Cp), 73.352 (Cp), 80.159 (Cp), 205.191 (CO). IR (ν_{\max} /cm⁻¹) 3000–2950 (ν CH₂), 1658 (ν C=O), 1453 (δ CH₂), 1069 (δ_{oop} = C–H), 827 (δ_{oop} = C–H). MS: Calc. for C₂₆H₂₆Fe₂O₂: 482 m/z . Parent ion peak observed at 482 m/z . Spectroscopic data for (**II**): ¹H NMR (400 MHz, CDCl₃, ppm) 1.256 (m, 2H, CH₂), 2.076 (m, 2H, CH₂), 2.888 (m, 2H, CH₂), 4.072 (s, 5H, C₅H₅), 4.105 (broad m, 2H, C₅H₄), 4.162 (s, 5H, C₅H₅), 4.194 (broad m, 2H, C₅H₄), 4.418 (broad m, 2H, C₅H₄),

Table 1
Crystal data and structure refinement of (I) and (II)

Empirical formula	C ₂₆ H ₂₆ Fe ₂ O ₂	C ₂₆ H ₂₄ Fe ₂ O ₁
Formula weight	482.17	464.15
Solvent	EtOAc/hexane	EtOAc/hexane
Crystal habit, color	Block, purple	Block, red
Temperature (K)	153(2)	100(2)
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	5.7654(5)	8.2877(4)
<i>b</i> (Å)	22.7856(2)	10.1649(5)
<i>c</i> (Å)	8.2065(5)	12.0575(6)
α (°)		94.074(1)
β (°)	101.778(6)	100.692(1)
γ (°)		97.667(1)
Volume	1055.4(1)	984.41(8)
<i>Z</i>	2	2
Radiation source, Mo K α (Å)	$\lambda = 0.71073$	$\lambda = 0.71073$
Absorption coefficient (mm ⁻¹)	1.395	1.488
Crystal size (mm ³)	0.42 × 0.18 × 0.05	0.41 × 0.37 × 0.20
θ Range for data collection	1.79–29.99°	1.73–28.28°
Index ranges	–8 ≤ <i>h</i> ≤ 8, –32 ≤ <i>k</i> ≤ 32, –11 ≤ <i>l</i> ≤ 11	–11 ≤ <i>h</i> ≤ 11, –13 ≤ <i>k</i> ≤ 13, –16 ≤ <i>l</i> ≤ 16
Reflections collected	6669	10242
Independent reflections	3072	4866
Absorption correction	Empirical	Multi-scan
Maximum to minimum transmission	0.933 and 0.758	0.74 and 0.601
Data/restraints/parameters	3072/0/137	4866/0/262
Goodness-of-fit on <i>F</i> ²	1.047	1.030
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0480, <i>wR</i> ₂ = 0.1057	<i>R</i> ₁ = 0.0280, <i>wR</i> ₂ = 0.0716
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1079, <i>wR</i> ₂ = 0.1395	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0733
Extinction coefficient	0.0033(14)	Not refined
Largest difference in peak and hole (e Å ⁻³)	0.645 and –0.989	0.523 and –0.330

4.668 (broad m, 2H, C₅H₄). ¹³C NMR (100 MHz, CDCl₃, ppm) 24.349 (CH₂), 38.765 (CH₂), 39.189 (CH₂), 69.567 (Cp), 69.977 (Cp), 70.250 (Cp), 70.933 (Cp), 71.570 (Cp), 73.255 (Cp), 80.181 (Cp), 81.312 (Cp), 136.984 (alkene), 142.143 (alkene), 203.248 (CO). IR ($\nu_{\max}/\text{cm}^{-1}$) 3000–2950 (ν CH₂), 1631 (ν C=O), 1444 (δ CH₂), 1103 ($\delta_{\text{oop}} = \text{C-H}$), 823 ($\delta_{\text{oop}} = \text{C-H}$). MS Calc. for C₂₆H₂₄Fe₂O: 464 *m/z*. Parent ion peak observed at 464 *m/z*.

2.3.2. Synthesis of 1,6-diferrocenylhexane (III)

1,6-Diferrocenylhexane was prepared via Clemmensen reduction based on the method of Rowe [5]. 1,6-Diferrocenylhexane-1,6-dione (8.49 g, 0.018 mol) was dissolved in 100 mL of toluene and transferred to a three neck round bottom flask. A zinc/mercury amalgam was prepared by dissolving mercuric chloride (1.20 g, 0.00442 mol) in 30 mL of de-ionized water, followed by addition of zinc dust (17.59 g, 0.269 mol). De-ionized water (30 mL) and concentrated hydrochloric acid (12 M, 47 mL, 1.54 mol) were added to the solution and the mixture was heated to reflux under static argon for 6 h. An overhead mechanical stirrer was used to ensure the biphasic mixture was in proper contact with the amalgam at all times throughout

the reaction. Additional portions of HCl (12 M, 12 mL, 0.394 mol) were added after 2.5 and 5 h. The reaction was allowed to stir for another hour. Once the mixture had cooled to room temperature, the organic portion was extracted three times with de-ionized water, followed by three extractions with brine solution. The resulting crude product was then dried over anhydrous sodium sulfate overnight and the solvent was removed under reduced pressure. The product was purified using column chromatography with silica gel as the stationary phase and 75%/25% hexane/ethyl acetate as the mobile phase. The first band to elute off the column was determined to be 1,6-diferrocenylhexane (*R*_f = 0.6, 76% yield). ¹H NMR (400 MHz, CDCl₃, ppm) 1.337 (broad m, 4H, C₅H₄CH₂CH₂CH₂), 1.500 (broad m, 4H, C₅H₄CH₂CH₂), 2.308 (t, 4H, C₅H₄CH₂), 4.054 (m, 4H, C₅H₄), 4.071 (m, 4H, C₅H₄), 4.106 (s, 10H, C₅H₅). ¹³C NMR (100 MHz, CDCl₃, ppm) 22.799 (C₅H₄CH₂CH₂CH₂), 29.620 (C₅H₄CH₂CH₂), 31.175 (C₅H₄CH₂), 67.114 (Cp), 68.169 (Cp), 68.594 (Cp), 89.617 (Cp). IR ($\nu_{\max}/\text{cm}^{-1}$) 2917 cm^{-1} –2847 cm^{-1} (ν CH₂), 1020 cm^{-1} ($\delta_{\text{oop}} = \text{C-H}$ stretching), 815 cm^{-1} ($\delta_{\text{oop}} = \text{C-H}$ stretching). MS Calc for C₂₆H₃₀Fe₂: 454 *m/z*. Parent ion peak observed at 454 *m/z*.

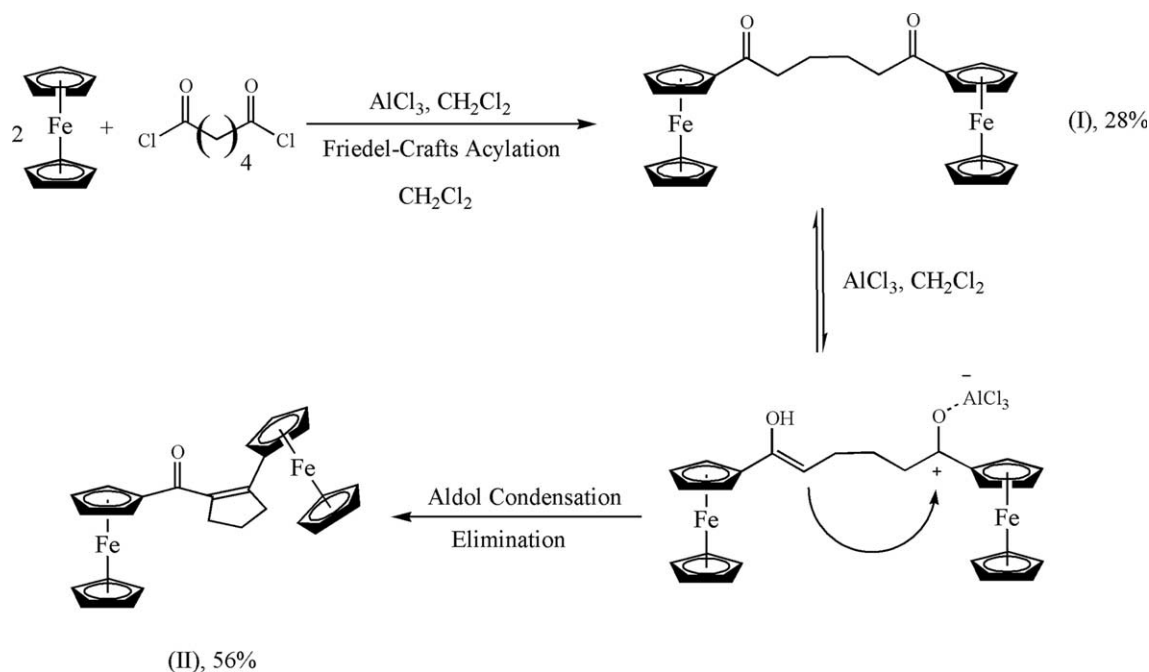
3. Results and discussion

3.1. Synthesis and spectroscopic characterization

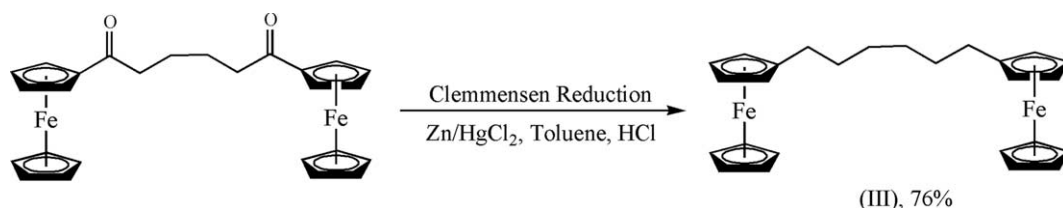
The title compounds were synthesized as outlined in Schemes 1 and 2. All compounds have been characterized by ^1H NMR, ^{13}C NMR and IR spectroscopy as well as mass spectrometry. The reaction of ferrocene with adipoyl chloride under Friedel–Crafts conditions with aluminum chloride as the catalyst yielded two products (**I**) and (**II**). 1,6-Diferrocenylhexane-1,6-dione (**I**), the intended product of a double Friedel–Crafts acylation of the dichloride with two molecules of ferrocene, was isolated in only 28% yield. The major reaction product (56%) was identified as 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene (**II**), the product of an internal aldol condensation of (**I**), followed by elimination of water to form the cyclopentene double bond. Both the Friedel–Crafts acylation as well as the aldol condensation can be Lewis acid catalyzed, and under the conditions used here they seem to proceed at a similar rate with ca. 2/3 of the dione (**I**) being converted into the cyclopentene derivative (**II**) during the reaction period, and the remaining third being not yet transformed [10]. It is of

interest to note that the reaction of ferrocene with 1,7-heptanedioyl dichloride under identical conditions did not yield the cyclized product, even though the six-membered ring should be thermodynamically more stable than the five membered ring. The sole product obtained in this reaction was 1,7-diferrocenylheptane-1,7-dione [11]. Bis-ferrocenyl compounds similar to the aldol product observed here have been previously produced by Jong et al. [12] via a samarium diiodide cyclodimerization of 1-ferrocenyl-2-propene-1-one derivatives as mixtures of several isomers (Scheme 3). With SmI_2 as the catalyst the reaction sequence stopped at the aldol product and no elimination of water was observed.

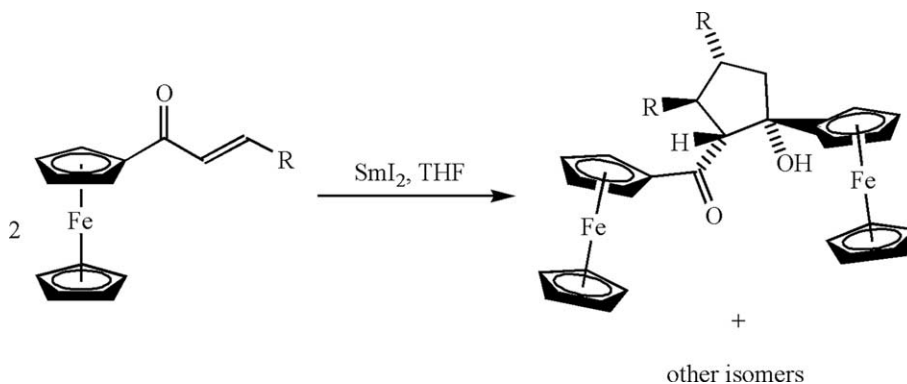
The third compound discussed here, 1,6-diferrocenylhexane, was synthesized from the dione (**I**). It has been produced in 76% yield using a Clemmensen type reduction reaction with zinc/mercury amalgam under acidic conditions (Scheme 2). The compound was thoroughly characterized via ^1H , ^{13}C and infra-red spectroscopy, in addition to mass spectrometry. In addition, we have prepared and characterized via single crystal X-ray diffraction 1,12-diferrocenyl dodecane, which was prepared under conditions identical to those described above [13].



Scheme 1. Synthesis of compounds (**I**) and (**II**).



Scheme 2. Synthesis of compound (**III**).



Scheme 3. Synthesis of aldol products using SmI_2 as a catalyst for 1-ferrocenyl-3-phenyl-2-propene-1-one [12].

3.2. X-ray crystallography

For both the compounds (**I**) and (**II**), single crystals suitable for X-ray diffraction could be obtained by slow evaporation from ethyl acetate/hexane solutions. Crystal structure and refinement data for both compounds are presented in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3.

Compound (**I**) crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell (Fig. 1). An inversion center is located at the center of each molecule. The chain of four saturated CH_2 groups does not form a

straight all-*trans* zig-zag chain, but the carbon atoms form an s-shaped structure and the bonds C12–C13 (and C12i–C13i) are showing a *syn*-conformation in the solid state; the bond C13–C13i displays anti conformation. As a result, the space between the ferrocene units is nearly close packed and the ferrocene moieties are closer to each other in the solid state (10.233(1) Å) than they would be on average in solution. The ferrocene groups themselves are in the eclipsed conformation and the bond lengths and angles

Table 3
Bond lengths (Å) and angles (°) for (**II**)

C10–C11	1.467(2)	C9–C10–C6	125.4(1)
C11–O3	1.222(2)	C6–C10–C11	126.6(1)
C11–C12	1.499(2)	O3–C11–C10	122.1(1)
C12–C13	1.344(2)	O3–C11–C12	119.8(1)
C12–C16	1.513(2)	C10–C11–C12	118.1(1)
C13–C17	1.463(2)	C13–C12–C11	126.8(1)
C13–C14	1.514(2)	C13–C12–C16	112.3(1)
		C11–C12–C16	120.9(1)
		C12–C13–C17	128.6(1)
		C17–C13–C14	120.8(1)
		C21–C17–C13	124.3(1)
		C18–C17–C13	128.8(1)

Table 2
Bond lengths (Å) and angles (°) for (**I**), symmetry operation $i: -x + 1, -y, -z$

C12–C11	1.506(5)	C11–C12–C13	115.0(3)
C12–C13	1.506(5)	C6–C10–C11	124.8(3)
O1–C11	1.221(4)	C9–C10–C11	128.0(3)
C10–C11	1.460(4)	O1–C11–C10	119.7(3)
C13–C13 ⁱ	1.515(7)	O1–C11–C12	121.0(3)
		C10–C11–C12	119.3(3)
		C12–C13–C13 ⁱ	113.2(3)

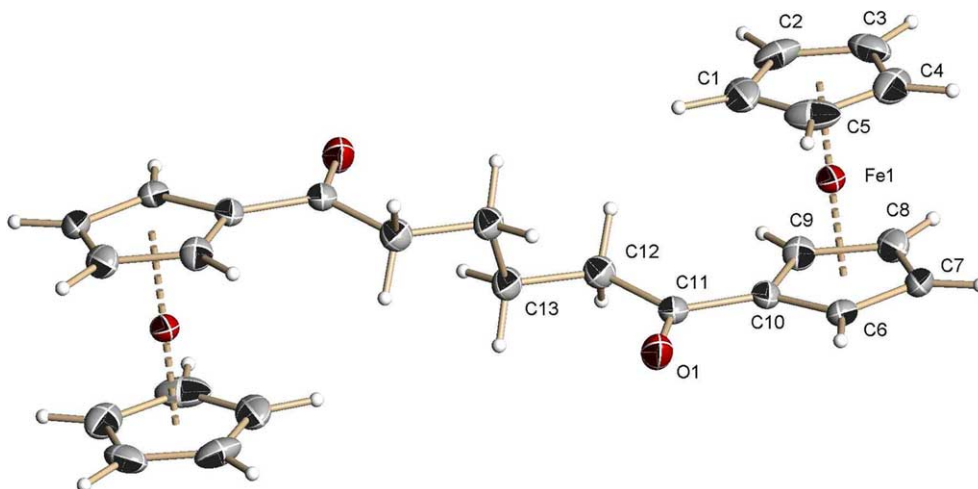


Fig. 1. Solid state structure of 1,6-diferrocenylhexane-1,6-dione (**I**) at 50% thermal ellipsoids.

associated with the ferrocene groups are as expected. The carbonyl substituents are close to coplanar with the plane of the adjacent Cp rings (Cp vs. C=O dihedral angle: $9.7(2)^\circ$), thus maximizing the π -orbital overlap and electronic interactions between the two groups.

Compound (**II**) crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell (Fig. 2). The cyclopentadienyl rings are in the eclipsed conformation and display no unusual bond lengths or angles. As in compound (**I**), the carbonyl substituent is rotated into the plane of the Cp ring with a dihedral angle of only $5.6(1)^\circ$. The carbon–carbon double bond exhibits a bond length of $1.344(2)$ Å and bond angles typical for sp^2 hybridized carbon atoms under the strain of a five membered ring ($110.6(1)^\circ$ for C12–C13–C14 to $128.6(1)^\circ$ for C12–C13–C17). Similar to the observations for the keto group, the C=C bond is close to coplanar with the adjacent Cp ring with a dihedral angle of $14.00(8)^\circ$ between the planes of the Cp ring and the double bond (C11–C14, C16, C17). The keto group and the double bond in (**II**) can, due to steric overcrowding caused by the inflexible cyclopentene ring, not assume the electronically preferred coplanar conformation, but they are forced to be close to perpendicular to each other with a dihedral angle of $88.92(4)^\circ$ between the planes of the alkene and C=O moieties (C6–C10 vs. C10–C12, O3).

3.3. Electrochemistry

Cyclic voltammetry experiments on 1,6-diferrocenylhexane-1,6-dione (**I**) and 1,6-diferrocenylhexane (**III**) each display a single two-electron transfer centered at 272 and

-11 mV, respectively. This is in agreement with the usual shift of the redox potential towards more anodic values in the presence of electron withdrawing substituents and vice-versa for electron donating substituents [5]. The observation of a single redox wave for both compounds indicates that there is no direct or indirect electronic communication between the two ferrocene groups of each molecule, i.e., an electronic interaction via (saturated) covalent bonds does not happen and the ferrocene centers are spatially (by average) too far apart from each other for a significant coulombic interaction to occur. In (**I**) and (**III**) both ferrocene centers are chemically equivalent. This is not the case for the asymmetric bisferrocene derivative (**II**). Its voltammograms (Fig. 3) display two single-electron transfers centered at 87 and 344 mV for the cyclopentene and carbonyl substituted ferrocenes, respectively. It is interesting to note that the voltammetric waves for compound (**II**) have both been shifted to more anodic potentials with respect to compounds (**I**) and (**III**). The anodic shift associated with the cyclopentene substituted ferrocene is likely due to the double bond being less electron donating than an alkyl substituent. The shift to more anodic potentials for the carbonyl substituted ferrocene is most likely due to coulombic shielding of the second ferrocene group in the monocation, and the proximity of the cyclopentene substituted ferricenium cation to the other ferrocene group results in a higher oxidation potential for the keto substituted ferrocene unit. A direct electronic interaction between the two ferrocene centers via the unsaturated carbon backbone, on the other side, will be largely prevented by the large dihedral angle between the carbonyl and the alkene moieties of the molecule, and it has to be assumed

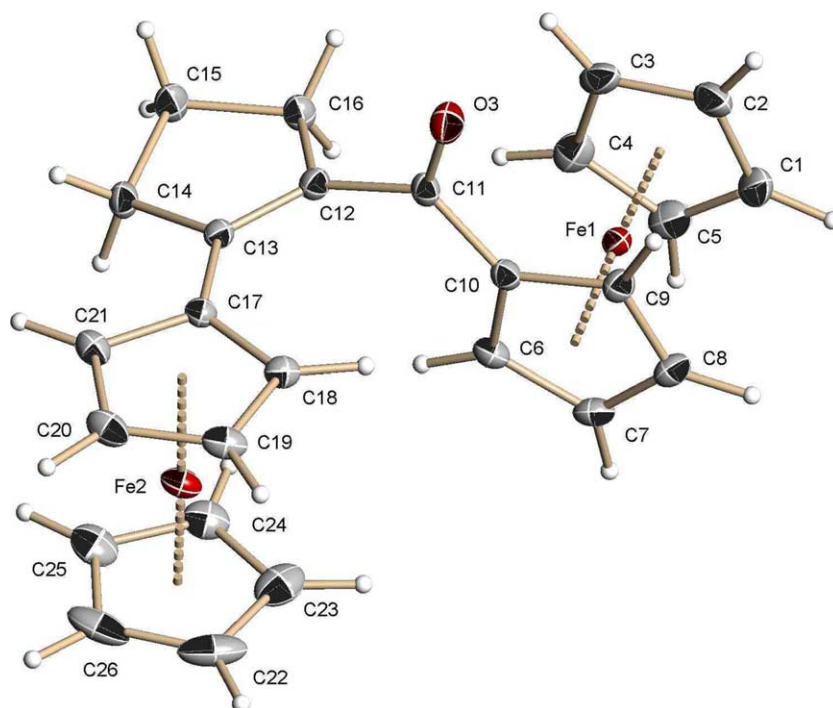


Fig. 2. Solid state structure of 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene (**II**) at 50% thermal ellipsoids.

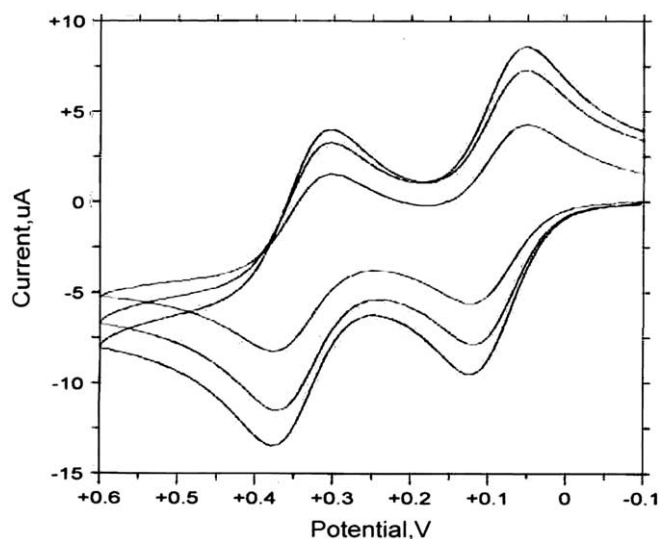


Fig. 3. Cyclic voltammograms of 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene (II) at scan rates of 50, 100 and 150 mV/s. (Potentials referenced to non-aqueous Ag/Ag⁺).

that the positive charge in the monocation is localized basically totally at the alkene substituted ferrocene group. Analysis of the voltammetric data revealed that in all cases the electron transfers were diffusion controlled and both chemically and electrochemically reversible. The number of electrons transferred for each oxidation wave was confirmed via chronoamperometry using ferrocene as the standard.

3.4. Summary and outlook

The spectral, electrochemical and X-ray diffraction characteristics of several novel bridged ferrocene dimers have been reported. The main product of a Friedel–Crafts acylation between ferrocene and adipoyl chloride turned out to be an aldol condensation product (1-ferrocenylcarbonyl-2-ferrocenylcyclopentene), rather than the primary acylation product 1,6-diferrocenylhexan-1,6-dione. Electrochemical data shows that the bisferrocene derivatives have the expected shift in formal potentials and that the ferrocene groups are not in direct electronic communication.

The primary reason for the synthesis of these novel bisferrocene derivatives is for use in self-assembled monolayer chemistry. Other compounds containing different chain lengths between the two ferrocene groups have been synthesized in order to study the influence of the bridging chain length on the oxidation potential, electrochemical accessibility and extent of electronic communication of the two ferrocene moieties. Further applications of these types of compounds will be in the area of ferrocene-containing polymers in which the ferrocene groups are present in the back-bone of the polymer chain. These polymers could possibly be formed through conventional elimination polymerizations. It is hoped that the bridging alkane chains will impart greater solubility to the polymer and thus

higher molecular weights and better visco-elastic properties. Such polymers may prove to be useful in chemical and biochemical sensing applications, catalysis and the study of molecular magnetism.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre: CCDC No. 279027 and 279028 for compound (I) and (II), respectively. Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk. or <http://www.ccd.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2005.10.009.

References

- [1] T.J. Kealy, P.L. Pauson, *Nature* 168 (1951) 1039.
- [2] (a) A.E. Navarro, F. Fages, C. Moustrou, H. Brisset, N. Spinelli, C. Chaix, B. Mandrand, *Tetrahedron* 61 (16) (2005) 3497; (b) K.L. Brown, J.S. Pinter, K.L. Ewing, T.R. Ruch, R. Travis, M. Ambrose, I. Hesslesweet, *Anal. Lett.* 38 (5) (2005) 169; (c) M. Okochi, T. Hiroko, T. Tanaka, T. Matsunaga, *Biotech. Bioeng.* 90 (1) (2005) 14; (d) J.J. Hickman, D. Ofer, P.E. Laibinis, G.M. Whitesides, M.S. Wrighton, *Science* 252 (1991) 688.
- [3] (a) A. Togni, T. Hayashi (Eds.), *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*, VCH, Weinheim, 1995; (b) M. Sawamura, Y. Ito, *Chem. Rev.* 93 (1992) 857; (c) G. Nicolosi, R. Patti, R. Morrone, M. Piatelli, *Tetrahedron: Asymmetry* 5 (1994) 1639.
- [4] J.S. Miller, A.J. Epstein, W.M. Reiff, *Chem. Rev.* 88 (1996) 201.
- [5] (a) C.E.D. Chidsey, C.R. Bertozzi, T.M. Putvinski, A.M. Muijsce, *J. Am. Chem. Soc.* 112 (1990) 4301; (b) S.E. Creager, G.K. Rowe, *J. Electroanal. Chem.* 140 (1997) 291.
- [6] XSCANS Version 2.2, Siemens Energy & Automation Inc., Madison, WI, USA, 1993–1996.
- [7] Bruker, Advanced X-ray Solutions SMART for WNT/2000 (Version 5.628), Bruker AXS Inc., Madison, WI, USA, 1997–2002.
- [8] Bruker, Advanced X-ray Solutions SAINT (Version 6.45), Bruker AXS Inc., Madison, WI, USA, 1997–2003.
- [9] Bruker, Advanced X-ray Solutions SHELXTL (Version 6.10), Bruker AXS Inc., Madison, WI, USA, 2000.
- [10] No attempts have been made here to optimize the yield of either of the two compounds.
- [11] L.S. Curtin, R.E. Hoff, P.J. Miner unpublished results.
- [12] S.J. Jong, C.T. Chen, J.M. Fang, Y.H. Liu, G.H. Lee, Y. Wang, *Acad. Sci. Paris, Chimie* 4 (2001) 487.
- [13] D.M. Bequeath, R.L. Porter, M.W. Lufaso, T.R. Wagner, R.L. Kusnic, M. Zeller, L.S. Curtin, *Acta Cryst.* E61 (2005) 1.