ARTICLE IN PRESS

Journal of Organometallic Chemistry xxx (2016) 1–8

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Tetrakis(ferrocenylethynyl)ethene: Synthesis, (Spectro) electrochemical and quantum chemical characterisation

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ARTICLE INFO

Article history:
Received 11 February 2016
Received in revised form
6 April 2016
Accepted 12 April 2016
Available online xxx

Dedicated to Prof. Dr. Heinrich 'Henri' Lang, on the occasion of his 60th Birthday, and in celebration of his science, collaborations, and friendship.

Keywords:
Ferrocene
Quantum cellular automata
Spectroelectrochemistry
DFT

ABSTRACT

Tetrakis(ferrocenylethynyl)ethene (**1**) has been prepared in four steps from ethynyl ferrocene (**2**). In a dichloromethane solution containing 10^{-1} M $NBu_4[PF_6]$, only a single oxidation process is observed by cyclic voltammetry, corresponding to the independent oxidation of the four ferrocenyl moieties. However, in dichloromethane containing 10^{-1} M $NBu_4[BAr^F_4]$ electrolyte, where $[BAr^F_4]^-$ is the weakly associating anion $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$, four distinct oxidation processes are resolved, although further spectroelectrochemical investigation revealed essentially no through bond interaction between the individual ferrocenyl moieties. Quantum chemical treatment of **1** identified several energetic minima corresponding to different relative orientations of the ferrocenyl moieties and the plane of the all-carbon bridging fragment. Further computational investigation of the corresponding monocation $[\mathbf{1}]^+$ supported the notion of charge localisation with no evidence for significant through bond electronic interactions.

1. Introduction

Molecular compounds that feature multiple, identical redox sites related by some element of symmetry, and which localize charge upon changes to the oxidation states of the redox centres are of interest as data elements and logic systems through the Quantum-dot Cellular Automata (QCA) concept [1–6], charge storage and memory applications [7]. The well-behaved redox chemistry of ferrocene derivatives has led to interest in molecules containing more than two ferrocene units around a common core, such as 1,3,5-tris(ferrocenylethynyl)benzene [8], tetrakis(ferrocenyl)nickel dithiolene [9] and hexakis(ferrocenylethynyl)benzene [10,11], and the electronic structures of the mixed-valence compounds derived from them. For example, the mono- and dications derived by one- or two-electron oxidation of $[\{CpFe(\eta^5\text{-}C_5H_4)\}_4(\eta^4\text{-}C_4)CoCp]$ have been characterised as Class II and Class II–III mixed valence species based on the solvatochromic properties of the IVCT band, IR and Mössbauer spectroscopy [6]. The metal-free porphyrin-bridged complex 5,10,15,20-tetrakis(ferrocenyl)porphyrin (H_2TFcP) exhibits four independent one-electron oxidation waves in a 5×10^{-2} M $NBu_4[B(C_6F_5)_4]$ *ortho*-dichlorobenzene or CH_2Cl_2 solution, with comprehensive spectroscopic analysis leading to description of $[H_2TFcP]^{n+}$ ($n = 1, 2, 3$) as weakly coupled (Class II) mixed valence species, with coupling terms H_{ab} derived from the classical Hush expressions of the order of 550–1150 cm^{-1} [12]. Analogous transition metal porphyrin-bridged tetraferrocenyl complexes behave similarly [13].

In looking to extend such studies, the cross-conjugated 1,1,2,2-tetraethynylethene can be identified as a possible bridge structure capable of linking multiple redox-active sites to a common,

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http://dx.doi.org/10.1016/j.jorganchem.2016.04.018

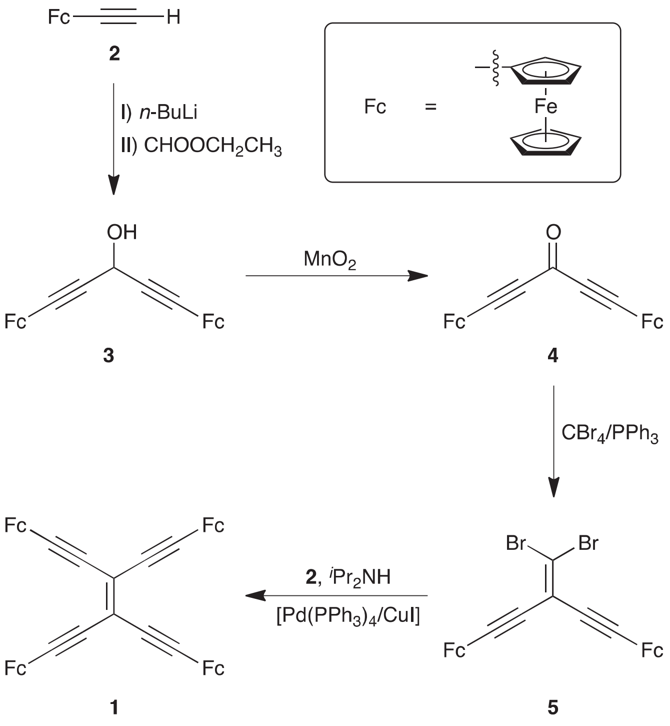
Please cite this article in press as: K.B. Vincent, et al., Journal of Organometallic Chemistry (2016), http://dx.doi.org/10.1016/j.jorganchem.2016.04.018

conjugated core. The synthetic chemistry of this carbon-rich motif has been well established [14,15] and hence tetrakis(ferrocenylethynyl)ethene (**1**) was envisioned as a potential target compound. This paper describes the synthesis of **1**, the electrochemical and spectroelectrochemical (IR, UV-vis-NIR) response of this unusually conjugated multi-ferrocenyl redox system, and a description of the electronic structure from quantum chemical (BLYP35-D3/def2-TZVP/COSMO(CH_2Cl_2)) calculations.

2. Results and discussion

2.1. Synthesis

Complex **1**, incorporating four ferrocenyl moieties around the 1,1,2,2-tetraethynylethene core, was synthesised according to Scheme 1. The intermediates in the synthesis of **1** were obtained according to literature procedures. First, the reaction of lithiated ethynyl ferrocene (**2**) with ethyl formate gave the diferrocenyl alcohol **3** [16] that was oxidised to ketone **4** [17] with activated manganese dioxide. Dibromo-olefination [16] of **4** allowed the preparation of **5**, containing the suitably functionalised ethenyl core, and subsequent Sonogashira-style [18–21] cross coupling of **5** with ethynyl ferrocene (**2**) afforded the desired tetrakis(ferrocenylethynyl)ethene (**1**) in 19% yield relative to **5**. Despite the high conversion observed in the preparation of **1** from **5** (crude **1** is obtained in approximately 75% yield and 80–90% purity, as assessed by ^{1}H NMR, directly from the reaction mixture) the pure compound could only be isolated in relatively low yield. Compound **1** proved to have limited stability under chromatographic conditions; however, no other method of removing the primarily ferrocene based contaminants proved successful. Thus chromatography was necessary in order to produce electrochemically and spectroscopically pure **1** despite the loss of overall yield this entailed. This instability is presumably related to the arrangement of four electron-donating ferrocene units around a highly conjugated organic core. Similarly, we have recently observed analogous instability in organic cross-conjugated systems based on an (*E*)-hexa-3-en-1,5-diyne-3,4-diyl fragment when the cross-conjugated core is substituted with four electron donating moieties [22].



Scheme 1. Synthesis of tetrakis(ferrocenylethynyl)ethane (**1**).

The synthesis of **5** largely followed the methods outlined in the work of Diederich [17] and Ren [16]. While the literature methods were found to be generally efficacious, several points are worth highlighting. In this work, the MnO_2 used in the synthesis of **4** was prepared according to a method described in the early literature [23]. Commercial MnO_2 was found to react inconsistently as the properties of this compound as an oxidant are highly dependent on the particle size/surface area of the material, and this appears to vary depending on the source. In addition we note that of the two previous reports on the series of compounds **3**–**5**, only one noted successful preparation of compound **5** [16], the earlier attempt using an ostensibly identical method having failed [17]. In our hands, the literature procedure for dibromo-olefination [16] functioned perfectly well *provided* that the carbon tetrabromide used was purified by vacuum sublimation before use. Sublimation was necessary regardless of the reagent origin or age and following purification it could be stored for several months under nitrogen without loss of efficacy in this reaction.

2.2. Cyclic voltammetry

In dichloromethane containing 10^{-1} M $NBu_4[PF_6]$ as supporting electrolyte, a single, reversible redox process was observed in the cyclic voltammogram of compound **1** (Fig. 2). This single wave has the shape of a one-electron process, indicating independent oxidation of all four ferrocenyl groups (Fig. 1, Table 1). However, when $NBu_4[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$ ($NBu_4[BAr^F{}_4]$) containing the weakly ion-pairing or associating anion $[BAr^F{}_4]^-$ was employed as an electrolyte, a significant separation of the individual redox events ensued, and four sequential, reversible, one-electron processes could be discerned (Fig. 1, Table 1). These individual events, better resolved by differential pulse voltammetry (DPV), can be attributed to the sequential oxidation of the four ferrocenyl termini in a similar manner to other multi-ferrocenyl compounds [9–11] as outlined above, and consistent with a significant 'through-space' interaction between the ferrocenyl moieties [9,24].

2.3. Spectroelectrochemistry

IR and UV-vis-NIR spectroelectrochemistry was carried out in $CH_2Cl_2/NBu_4[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$ in an attempt to spectroscopically observe each of the four redox products indicated by the resolved individual redox waves in the cyclic and differential pulse voltammograms of **1** in this electrolyte. From the electrochemical data, comproportionation constants $K_c = e^{\Delta EF/RT}$, and in turn the maximum purity of the intermediate mixed-valence oxidation products at equilibrium, can be estimated as: $[\mathbf{1}]^+$ $K_c = 70$ (80%); $[\mathbf{1}]^{2+}$ $K_c = 110$ (84%); $[\mathbf{1}]^{3+}$ $K_c = 190$ (87%). Thus, the electronic absorption and IR spectra of these oxidised species will most certainly contain features from the adjacent redox partners within the comproportionated mixture.

The IR spectrum of **1** (Fig. 2) exhibits a relatively low intensity, broad $\nu(C\equiv C)$ band envelope with an apparent maximum at 2191 cm^{-1} and an even weaker feature near 2219 cm^{-1}. During the early stages of oxidation (comproportionated mixtures of $[\mathbf{1}]^{n+}$, $n = 0, 1, 2$) the primary $\nu(C\equiv C)$ band envelope gains intensity appreciably, but shifts in energy only modestly to smaller wavenumbers (2171 cm^{-1}). The weaker feature remains unaffected by the oxidation. The vibrational band envelopes clearly contain multiple vibrational modes which may indicate the presence of multiple conformations in the relevant oxidation states ($n = 0, 1, 2$). The limited shift in the wavenumber of these $\nu(C\equiv C)$ bands,

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