



Di(biferrocenyl)ethyne and -butadiyne: Synthesis, properties and electron transfer studies

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ARTICLE INFO

Article history:

Received 19 September 2013

Received in revised form

22 November 2013

Accepted 25 November 2013

Keywords:

Biferrocene

Electron transfer

(Spectro)electrochemistry

Alkyne

Inter-valence charge transfer

ABSTRACT

Di(biferrocenyl)ethyne (**3**) and -butadiyne (**4**) have been prepared by Negishi, Eglinton and Sonogashira C,C cross-coupling reactions using *bfc*-I (**1**) and *bfc*-C≡CH (**2**) (*bfc* = 1:1'-biferrocenyl) as starting materials. Compound **4** was structurally analyzed by single crystal X-ray diffraction studies. The individual ferrocenyl units are all coplanar and anti-parallel oriented. Electrochemical measurements showed that all four ferrocenyl units can reversibly be oxidized. The electrochemical characteristics of these molecules represent a combination of the properties of biferrocene and the appropriate ferrocenyl analogs diferrocenyl ethyne and diferrocenyl butadiyne, respectively. While the dicationic oxidation state of both compounds showed characteristics of a charge transfer within the biferrocenium units, the tricationic form allows electron transfer through the $(-C\equiv C-)_n$ ($n = 1, 2$) functionalities. The observed inter-valence charge transfer (IVCT) interaction of **3** and **4** in any mixed-valent oxidation state allowed the characterization of these species as class II systems according to Robin and Day. *In situ* IR spectroscopy of **3** and **4** showed that within 3^{n+} and 4^{n+} ($n = 0, 2, 4$) no $\nu_{C\equiv C}$ band is present, while 3^+ and 3^{3+} showed two $\nu_{C\equiv C}$ stretching vibrations due to Fermi resonance. Compound 4^{3+} exhibits only one sharp $\nu_{C\equiv C}$ frequency.

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1. Introduction

Within the field of electronics one major priority is to develop techniques to minimize the gate distance for transistors in order to maximize the number of logical units per area [1,2]. These developments ultimately lead to the question if single molecules can act as functional units within a logical electronic device. Especially carbon-rich building blocks such as -yneyl $-C\equiv C-$ and polyynediyl $(-C\equiv C)_n-$ have shown to be promising candidates for the development of nanoscaled wires [3–5]. For example, di(ferrocenyl) ethyne and -butadiyne have been recognized as good model systems for the investigation of electro- and spectroelectrochemical properties via the $(-C\equiv C-)_n$ ($n = 1, 2$) bridging unit, revealing electron transfer interactions between the ferrocenyl/ferrocenium termini within the mixed-valent oxidation state [6–8]. Furthermore, the use of the biferrocenyl moiety as redox-active terminus is advantageous, since it is very stable in both the mono- and dicationic oxidation state [9,10]. The relationship between the structure of substituted biferrocenes and their

electrochemical (redox potentials, electronic conductivity), spectroscopic and magnetic properties has been studied on some examples [11]. In dependence of the structure, mixed-valent biferrocenes can be considered as class II or even as class III systems according to Robin and Day [9,12]. Especially the connection of two or more biferrocenyl units by π -conjugated organic building blocks forming multinuclear metal complexes are of great interest, since the mixed-valent forms of these compounds offer electronic coupling of the individual metal centers through different inter-connection paths. In this respect, we herein present the introduction of biferrocenyl terminal groups to carbon-rich backbone moieties as represented in di(biferrocenyl)ethyne and -butadiyne. The electrochemical and spectroelectrochemical characterization of these compounds is discussed.

2. Materials and methods

2.1. General data

All reactions were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were distilled prior to use. Tetrahydrofuran, diethyl ether and *n*-hexane were purified by distillation from sodium/benzophenone ketyl; dichloromethane, *N,N*-dimethylformamide and *N,N*-diisopropyl

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ylamine were purified by distillation from calcium hydride; pyridine was purified by distillation from KOH. For column chromatography silica was used with a particle size of 40–60 μm (230–400 mesh (ASTM), Fa. Macherey–Nagel) or alumina with a particle size of 90 μm (standard, Merck KGaA).

2.2. Instruments

NMR spectra were recorded with a Bruker Avance III 500 spectrometer (500.3 MHz for ^1H and 125.7 MHz for $^{13}\text{C}\{^1\text{H}\}$). Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane ($\delta = 0.0$) with the solvent as reference (^1H NMR: CHCl_3 , $\delta = 7.26$; $^{13}\text{C}\{^1\text{H}\}$ NMR: CDCl_3 , $\delta = 77.16$). The melting points were determined using a Gallenkamp MFB 595 010 M melting point apparatus. High-resolution mass spectra were recorded with a Bruker Daltonik micrOTOF-QII spectrometer. Infrared spectra were recorded with a Nicolet IR 200 spectrometer (Fa. Thermo).

2.3. Electrochemistry

Electrochemical measurements of 1.0 mmol L^{-1} solutions of compounds **3** and **4** in dichloromethane were performed in a dried, argon purged cell at 20 $^\circ\text{C}$ with a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer. $[\text{N}^n\text{Bu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.1 mol L^{-1}) in dichloromethane was used as supporting electrolyte. For the measurements a three electrode cell containing a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm^2) and an Ag/Ag^+ (0.01 mmol L^{-1} [AgNO_3]) reference electrode fixed on a Luggin capillary was used. The working electrode was pretreated by polishing on a Buehler microcloth first with a 1 micron and then with a 0.25 micron diamond paste. The reference electrode was constructed from a silver wire inserted in a 0.01 mmol L^{-1} [AgNO_3] and 0.1 mol L^{-1} [N^nBu_4] [$\text{B}(\text{C}_6\text{F}_5)_4$] acetonitrile solution in a Luggin capillary with a Vycor tip. This Luggin capillary was inserted in a second Luggin capillary containing a 0.1 mol L^{-1} [N^nBu_4] [$\text{B}(\text{C}_6\text{F}_5)_4$] dichloromethane solution and a Vycor tip. Experiments under the same conditions showed that all reduction and oxidation potentials were reproducible within 5 mV. Experimental potentials were referenced against an Ag/Ag^+ reference electrode. The presented results are referenced against ferrocene as an internal standard as recommended by IUPAC [13]. To achieve this, each experiment was repeated in the presence of 1 mmol L^{-1} decamethylferrocene (Fc^*). Data were processed on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH^+ couple ($\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)$) to 0.0 V. Under our conditions the $\text{Fc}^*/\text{Fc}^{*+}$ couple was at -614 mV vs FcH/FcH^+ , $\Delta E_p = 60$ mV, while the FcH/FcH^+ couple itself was at 220 mV vs Ag/Ag^+ , $\Delta E_p = 61$ mV [14].

2.4. Spectroelectrochemistry

Spectroelectrochemical UV–vis/NIR and IR measurements of 2.0 mmol L^{-1} (UV–vis/NIR) or 10 mmol L^{-1} (IR) solutions of **3** and **4** in dry dichloromethane containing 0.1 mol L^{-1} of [N^nBu_4] [$\text{B}(\text{C}_6\text{F}_5)_4$] as the supporting electrolyte were performed in an OTTE (=Optically Transparent Thin-Layer Electrochemistry, quartz windows for UV–vis/NIR; CaF_2 windows for IR) [15] cell with a Varian Cary 5000 spectrophotometer (UV–vis/NIR) or a Thermo Nicolet IR 100 spectrometer (IR) at 20 $^\circ\text{C}$. The values obtained by deconvolution could be reproduced within $\varepsilon_{\text{max}} = 100$ $\text{L mol}^{-1} \text{cm}^{-1}$, $\nu_{\text{max}} = 50$ cm^{-1} , and $\Delta\nu_{1/2} = 50$ cm^{-1} . Between the spectroscopic measurements the applied potentials have been increased stepwisely using step heights of 100, 50, 25 or 20 mV. At the end of the measurements the analyte was reduced at -500 mV for 10 min

and an additional spectrum was recorded to prove the reversibility of the oxidations.

2.5. Single crystal X-ray diffraction analysis

Suitable single crystals of **4** for X-ray diffraction analysis were obtained by slow evaporation of a saturated dichloromethane/chloroform solution (v/v , 1/5) of **4** at ambient temperature. Data were collected with an Oxford Gemini S diffractometer at 110 K with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ \AA). The structure was solved by direct methods and refined by full-matrix least-square procedures on F^2 [16]. All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the treatment of the hydrogen atom positions.

$\text{C}_{181.2}\text{H}_{146.4}\text{Cl}_{10.4}\text{Fe}_{16}$, $M = 3586.06$ g/mol, monoclinic, $C2/c$, $a = 38.251(3)$ \AA , $b = 7.5604(6)$ \AA , $c = 12.4781(7)$ \AA , $\beta = 94.063(7)^\circ$, $V = 3599.5(4)$ \AA^3 , $Z = 1$, $\rho_{\text{calcd}} = 1.654$ mg m^{-3} , $\mu = 1.808$ mm^{-1} , $T = 110(2)$ K, θ range = $3.13\text{--}25.00^\circ$, reflections collected: 8097, independent: 3115 ($R_{\text{int}} = 0.0538$), $R_1 = 0.1241$, $wR_2 = 0.2790$ [$I > 2\sigma(I)$].

2.6. Reagents

All starting materials were obtained from commercial suppliers and used without further purification. Bromoferrocene [17] and 1,1'-diiodoferrocene [17] have been prepared according to literature methods. 1'-Ethynyl-1''-biferrocene [18a] was synthesized by an alternative synthetic methodology as described below.

2.7. Synthesis

2.7.1. Synthesis of 1'-iodo-1''-biferrocene (**1**)

To 5.0 g (18.9 mmol) of bromoferrocene dissolved in 50 mL of tetrahydrofuran, 7.6 mL (18.9 mmol) of a 2.5 M solution of *n*-butyllithium in *n*-hexane was added at -80 $^\circ\text{C}$. After 1 h of stirring at this temperature, 5.3 g (18.9 mmol) of dry $[\text{ZnCl}_2 \cdot 2 \text{thf}]$ were added in a single portion. The reaction was kept for 10 min at -80 $^\circ\text{C}$ and was then allowed to warm to 0 $^\circ\text{C}$ during an additional hour. Afterward, 6 mg (0.09 mmol/0.5 mol%) of $[\text{P}(\text{C}_4\text{H}_9)_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{Pd}(\mu\text{-Cl})_2]$ and 9.1 g (20.8 mmol, 1.1 eq) of diiodoferrocene were added to the reaction solution and the resulting mixture was stirred for 16 h at 70 $^\circ\text{C}$. After evaporation of all volatiles, the crude product was dissolved in 200 mL of dichloromethane and was washed three times with 100 mL portions of water. The organic phase was dried over MgSO_4 and the solvent was removed with a rotary evaporator. The remaining orange solid was purified by column chromatography (column dimension: 30 \times 2 cm) on silica gel using *n*-hexane as eluent. All volatiles were removed under reduced pressure. Compound **1** was obtained as an orange solid material. Yield: 4.2 g ((8.5 mmol) 45% based on bromoferrocene). $\text{C}_{20}\text{H}_{17}\text{Fe}_2\text{I}$ (495.9434 g/mol). Mp.: 130. IR (KBr, cm^{-1}): 809 (s), 1047 (m, $\nu_{\text{C-I}}$), 2854 (m), 2924 (m), 3082 (w). ^1H NMR (CDCl_3 , δ): 3.98 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 3.99 (s, 5H, C_5H_5), 4.16 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 4.20 (pt, $J_{\text{HH}} = 1.8$ Hz, 4H, C_5H_4), 4.21 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 4.30 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4), 4.41 (pt, $J_{\text{HH}} = 1.8$ Hz, 2H, C_5H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ) 40.81 ($\text{Cl}/\text{C}_5\text{H}_4$), 66.74 ($\text{CH}/\text{C}_5\text{H}_4$), 68.02 ($\text{CH}/\text{C}_5\text{H}_4$), 69.37 ($\text{CH}/\text{C}_5\text{H}_5$), 69.48 ($\text{CH}/\text{C}_5\text{H}_4$), 70.23 ($\text{CH}/\text{C}_5\text{H}_4$), 70.92 ($\text{CH}/\text{C}_5\text{H}_4$), 75.89 ($\text{CH}/\text{C}_5\text{H}_4$), 82.57 ($\text{C}'/\text{C}_5\text{H}_4$), 85.22 ($\text{C}'/\text{C}_5\text{H}_4$). HRMS (ESI-TOF, m/z): calcd. for $\text{C}_{44}\text{H}_{34}\text{Fe}_4$ 495.9069, found 495.9052 [M^+].

2.7.2. Synthesis of 1'-ethynyl-1''-biferrocene (**2**)

Deviating from Refs. [9a,18a] compound **2** was prepared as follows: To a suspension of 1.0 g (2.0 mmol) of **1** in 20 mL of degassed *N,N*-diisopropylamine, trimethylsilylthyne (0.56 mL, 4.0 mmol)

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