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1-Cyano-1′-ethynyl-ferrocene: Synthesis and reaction chemistry

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Several consecutive synthetic methodologies for the preparation of $Fe(\eta^5\text{-}C_5H_4C{\equiv}N)(\eta^5\text{-}C_5H_4C{\equiv}CH)$ (**3**) are described. Ferrocene $Fe(\eta^5\text{-}C_5H_4C{\equiv}N)(\eta^5\text{-}C_5H_4C(O)Me)$ (**1**) reacts under typical Vilsmeier conditions to give as the main product $Fe(\eta^5\text{-}C_5H_4C{\equiv}N)(\eta^5\text{-}C_5H_4CCl{=}CH_2)$ (**2**) and in minor yield $Fe(\eta^5\text{-}C_5H_4C{\equiv}N)(\eta^5\text{-}C_5H_4CCl{=}CHC(O)H)$ (**4**). Compound **2** could be directly converted to **3** by addition of KO^tBu. The title compound is also accessible by the gradual reaction of **4** with NaOH to give $Fe(\eta^5\text{-}C_5H_4C(O)NH_2)(\eta^5\text{-}C_5H_4C{\equiv}CH)$ (**5**), which upon treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and $P(O)Cl(OEt)_2$ produced **3**. Organometallic **3** could be homo-coupled to $[Fe(\eta^5\text{-}C_5H_4C{\equiv}N)(\eta^5\text{-}C_5H_4C{\equiv}C)]_2$ (**7**) in an Eglinton coupling upon addition of $[Cu(OAc)_2]$. With [CuI] and NEt_2H in dichloromethane, compound $Fe(\eta^5\text{-}C_5H_4C{\equiv}N)(\eta^5\text{-}C_5H_4C{\equiv}CCH_2NEt_2)$ (**6**) was produced by copper-catalyzed three-component coupling. The structures of **3**–**5** in the solid state were determined by single crystal X-ray structure analysis. While the X-ray structures of **3** and **4** show no peculiarities, the structure of **5** possesses a network structure due to hydrogen bridge bond formation. The electrochemical behavior of **3**, **6** and **7** was studied by cyclic voltammetry. It could be shown that **3** possesses a reversible redox event at 550 mV ($\Delta E = 65$ mV), while in homo-coupled **7** two consecutive redox processes at 524 and 680 mV were found indicating that the ferrocenyl units in **7** can be oxidized in a stepwise manner to $\mathbf{7}^+$ and $\mathbf{7}^{2+}$, respectively. The redox separation ΔE with 156 mV implies a possible electron transfer in the mixed-valent species $\mathbf{7}^+$, which was confirmed by spectroelectrochemical studies. From these studies, **7** could be classified as a weakly coupled class II system according to Robin and Day.

Introduction

There is considerable interest in the synthesis of transition metal compounds in which the metals are bridged by π-conjugated organic units, because such species allow to studying electron transfer processes in their mixed-valent state [1–8]. These molecules can be considered as model compounds for molecular wires with possible application in, for example, the down-scaling of electronic devices [9–17]. In this respect, ethynyl linkers were recently be introduced as connectivities between redox-active terminal organometallic groups, including ferrocenes and half-sandwich iron, ruthenium and osmium moieties [1–4,17–27]. It was found that compounds incorporating diverse organic units between the ethynyl building blocks such as heterocycles and transition metal-containing fragments show only weak electronic interactions between the redox-active terminal groups [7,28–39].

Alkynides are isoelectronic to nitriles, which are, as compared to alkynyl ligands, good two-electron σ donors and also have been recently used as bridging units in homo- and hetero-bimetallic transition metal chemistry to study electron transfer in the appropriate mixed-valent species [40–42]. In 2011, Astruc and coworkers reported about the synthesis and electronic communication between iron atoms bridged by phenylene bis- and tris-nitrile units [43]. It was found that the respective nitrile entities efficiently quench the electronic interaction between the metal centers. In contrast, Taube, Henry and Lewis found that in heteronuclear mixed ion-containing ruthenium and ferrocenyl metal-organic and organometallic complexes inter-valence charge transfer processes took place between the appropriate metal centers [44,45]. Within these molecules, the ferrocenecarbonitrile fragment was directly bonded to the ruthenium ion. In addition, Vahrenkamp *et al.* reported on the weak electron delocalization between cyanide bridged transition metal units [46].

This prompted us to introduce both, the ethynyl and the nitrile unit in a redox-active species, which opens the possibility to directly compare the influence of these groups on the electronic

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interaction in mixed-valent transition metal complexes. We herein report on the synthesis of Fe(η^5-$C_5H_4C{\equiv}N$)(η^5-$C_5H_4C{\equiv}CH$) and its reaction chemistry. The electrochemical and spectroelectrochemical properties of [Fe(η^5-$C_5H_4C{\equiv}N$)(η^5-$C_5H_4C{\equiv}C$)]$_2$ and Fe(η^5-$C_5H_4C{\equiv}N$)(η^5-$C_5H_4C{\equiv}CCH_2NEt_2$) are discussed as well.

Materials and methods

General procedure

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were purified as follows: *N*,*N*-dimethylformamide by distillation from P_4O_{10}; tetrahydrofuran by distillation from sodium/benzophenone ketyl; pyridine by distillation from CaH_2. Dichloromethane and hexane were dried using a MBraun MB SPS-800 system (double column solvent filtration, working pressure 0.5 bar).

Reagents

1,8-Diazabicyclo[5.4.0]undec-7-ene, diethyl chlorophosphate, copper(I) iodide, copper(II) acetate and ^{n}butyllithium were purchased from commercial suppliers and were used as received. 1′-Acetyl-1-cyano ferrocene (**1**) was synthesized according to a published procedure [47].

Instruments

Infrared spectra were recorded with a Thermo Nicolet 200 FT-IR spectrometer using the KBr press technique for sample preparation. NMR spectra were recorded using a Bruker Avance III 500 FT NMR spectrometer (^{1}H NMR at 500.303 MHz, ^{13}C{^{1}H} NMR at 125.813 MHz) at ambient temperature, unless otherwise noted. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane using the solvent as internal reference ($CDCl_3$: ^{1}H NMR δ 7.26 ppm; ^{13}C{^{1}H} NMR δ 77.16 ppm) [48]. Coupling constants (*J*) are reported in Hertz (Hz) and integrations are reported in numbers of protons. The following abbreviations were used to describe peak patterns: s = singlet, d = doublet, pt = pseudo-triplet, pq pseudo-quintet. The melting points (sealed off in argon-flushed capillaries) were determined using a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed with a Thermo FLASHEA 1112 Series instrument. High-resolution mass spectra were recorded with a Bruker micrOTOF QII with an Apollo II ESI source.

Electrochemistry

Electrochemical measurements were conducted in 1.0 mmol L^{-1} solutions in dichloromethane containing 0.1 mol L^{-1} of [^{n}Bu$_4$N][B(C_6F_5)$_4$] as supporting electrolyte under an argon atmosphere at 25 °C utilizing a Voltalab PGZ 100 radiometer electrochemical workstation interfaced with a personal computer. A three electrode cell, which utilized a Pt auxiliary electrode, a glassy carbon working electrode, and an Ag/AgCl (0.01 mol L^{-1} [$AgNO_3$]) reference electrode, mounted on a Luggin capillary was used. The working electrode was pretreated by polishing on a Buehler microcloth first with a 1 μm and then with a 0.25 μm diamond paste. The reference electrode was constructed from a silver wire inserted into a solution of 0.01 mol L^{-1} of [$AgNO_3$] and 0.1 mol L^{-1} of [^{n}Bu$_4$N][B(C_6F_5)$_4$] in acetonitrile, in a Luggin capillary with a porous Vycor tip. This Luggin capillary was inserted into a second Luggin capillary with porous Vycor tip filled with a 0.1 mol L^{-1} of a [^{n}Bu$_4$N][B(C_6F_5)$_4$] solution in dichloromethane. Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within 5 mV. Experimental potentials were referenced against an Ag/AgCl reference electrode but results are presented referenced against ferrocene or decamethylferrocene (Fc*) as an internal standard, as required by IUPAC [49]. To achieve this, since the ferrocene couple FcH/FcH$^+$ (Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)) interferes with the ferrocenyl potentials, each experiment was first performed in the absence of any internal standard and then repeated in the presence of 1 mmol L^{-1} of ferrocene. Data were then manipulated on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH$^+$ couple to 0.0 V. Under our conditions the Fc*/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/AgCl, $\Delta E_p = 61$ mV [50].

Single crystal X-ray diffraction analysis

Diffraction data for **3**–**5** were collected with an Oxford Gemini S diffractometer, with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using oil-coated shock-cooled crystals. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 [51,52]. Graphics of the molecular structures have been created by using SHELXTL [52] and ORTEP [53].

Crystal data of **3**: $C_{13}H_9FeN$, $M = 235.06$ g mol^{-1}, orange prism, 0.4 × 0.25 × 0.15 mm, space group $P2_1/c$, monoclinic, $a = 8.0003(4)$ Å, $b = 9.6596(5)$ Å, $c = 13.5278(6)$ Å, $\beta = 105.859(4)°$, $V = 1005.63(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.553$ g cm^{-3}, $T = 100$ K, θ range 3.38–25.25°, 3807 reflections collected, 1803 independent reflections, $R_{int} = 0.0732$, $R1 = 0.0572$, $wR2 = 0.1361$ ($I > 2\sigma(I)$).

Crystal data of **4**: $C_{14}H_{10}ClFeNO$, $M = 299.53$ g mol^{-1}, orange prism, 0.4 × 0.2 × 0.2 mm, space group $P\bar{4}2_1c$, tetragonal, $a = b = 16.8903(3)$ Å, $c = 8.4110(3)$ Å, $V = 2399.51(10)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.658$ g cm^{-3}, $T = 110.00(10)$ K, θ range 3.41–25.99°, 5486 reflections collected, 2236 independent reflections, $R_{int} = 0.0293$, $R1 = 0.0258$, $wR2 = 0.0518$ ($I > 2\sigma(I)$), absolute structure parameter [54] 0.172(19).

Crystal data of **5**: $C_{13}H_{11}FeNO$, $M = 253.08$ g mol^{-1}, orange prism, 0.4 × 0.3 × 0.2 mm, space group Cc, monoclinic, $a = 22.2883(6)$ Å, $b = 11.0335(3)$ Å, $c = 13.1325(4)$ Å, $\beta = 99.751(3)°$, $V = 3182.86(16)$ Å^3, $Z = 12$, $\rho_{calcd} = 1.584$ g cm^{-3}, $T = 100$ K, θ range 3.34–26.00°, 11,669 reflections collected, 4701 independent reflections, $R_{int} = 0.0386$, $R1 = 0.0309$, $wR2 = 0.0668$ ($I > 2\sigma(I)$), absolute structure parameter [54] 0.007(14).

Synthesis

Synthesis of **2** and **4**

1-Cyano-1′-acetyl-ferrocene (**1**) (5.24 g, 20.7 mmol) was dissolved in 10 mL of DMF under an argon atmosphere in a three-necked flask, equipped with a dropping funnel and a gas in- and outlet. The mixture was cooled to 0 °C. In a second Schlenk flask 6 mL (10.1 g, 65.7 mmol) of $POCl_3$ were added carefully to 6 mL (5.7 g, 80.0 mmol) of DMF under ice bath cooling. The resulting mixture was transferred to the dropping funnel and added dropwise to the solution of **1** and DMF within 30 min. The reaction mixture was stirred for 2 h at 0 °C. The dropping funnel was replaced by a reflux condenser and 15 mL of diethyl ether were carefully added and stirred for 10 min. With continuous ice cooling, 23 g (0.17 mol) sodium acetate trihydrate were added for neutralization followed by 2 mL of water. The solution was stirred for additional 4 h at ambient temperature, whereby further 2 mL of diethyl ether were added after the first hour. The mixture was transferred to a separation funnel together with 50 mL of water and diethyl ether each. The aqueous phase was extracted several times with 20 mL portions of diethyl ether. The combined organic layers