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Octamethylferrocenylethynyl units as peripheral groups in rigid, π-conjugated molecular architectures

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Abstract

The synthesis and full characterization of octamethylethynylferrocene **2** is described. Additionally, the reaction of **2** with copper(II) acetate, 1,4-diiodobenzene and 1,3,5-triiodobenzene to give 1.4-bis(octamethylferrocenyl)butadiyne **3**, 1,4-bis(octamethylferrocenylethynyl)benzene **4** and 1,3,5-tris(octamethyferrocenyllethyny)benzene **5** is presented. As a result of electrochemical investigations of **2–5** only **3** shows two one-electron oxidations with a peak-separation of 150 mV. © 1997 Elsevier Science S.A.

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1. Introduction

Ferrocene-containing rigid molecular architectures can exhibit interesting electronic and structural properties such as optical nonlinearity [1,2], inter- and intramolecular electron transfer [3–6] and magnetism [7]. The incorporation of ferrocenes as end-capping groups into molecules with a precisely defined three-dimensional structure and an extensively conjugated π-system can be realized by a terminal alkyne moiety [8]. Although the chemistry of unsubstituted ethynylferrocene has been in the focus of many research groups, until now not much attention has been paid to polymethylated ferrocenes connected by rigid, π-conjugated spacers [9,10]. The electron-donating effects induced by the methyl groups increase the electron density (of the ferrocene-core) and lower the oxidation potential. Additionally the geometric shape of the ferrocene changes from a more compact, cylindrical molecule to a geometrical structure where two parallel discs surround the iron-center. Consequently the sandwich compound is better suited for the formation of donor–acceptor-stacks with planar, polycyanated organic acceptors (TCNE, TCNQ,...). Although these CT complexes have been extensively studied by Miller, Epstein and coworkers in connection with their magnetic properties [11], the non-covalent intermolecular forces that hold together and organize the solid-state structure so far have not been used as tools for the preparation of supramolecular assemblies.

In this paper we present the synthesis of octamethylethynylferrocene (**2**) and its coupling products 1,4-bis(octamethylferrocenyl)butadiyne (**3**), 1,4-bis(octamethylferrocenylethynyl)benzene (**4**) and 1,3,5-tris(octamethylferrocenylethynyl)benzene (**5**). Additionally we present some electrochemical data for the compounds **2–5**.

2. Results

2.1. Synthesis

Octamethylethynylferrocene **2** can be synthesized in a one-pot reaction starting from octamethylformylferrocene (**1**) via Wittig olefination and subsequent dehydrohalogenation in analogy to a procedure published for the parent compound [12].

In contrast to unsubstituted ethynylferrocene the reaction of the oligomethylated derivative proceeds much slower because of the increased steric hindrance at the reactive carbon center. The elimination of HCl from octamethyl-β-chlorovinylferrocene (mixture of E/Z

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isomers) using KO^{t}Bu as a base requires 10 d in refluxing THF (Scheme 1). After aqueous workup, purification using flash-chromatography and recrystallization from acetonitrile, **2** can be obtained as a yellow–brown crystalline solid in 68% overall yield.

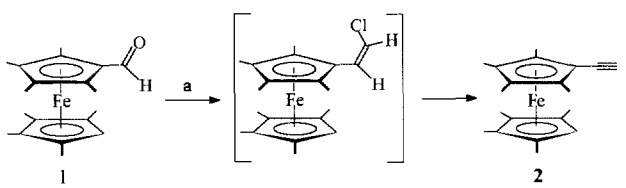
Copper(II)-mediated homocoupling of ethynylferrocene known as Glaser-coupling is the easiest way to obtain a biferrocene in which the iron centers are joined by a rigid π-conjugated organic spacer. Based on the procedure by Schlögl and Egger [13] used for the preparation of the parent compound, **3** can be synthesized in 42% yield. According to the experience of other groups [14], yields in the Glaser-coupling using alkynylferrocenes are generally quite low. One reason for this could be the fact that polymerization is an important side-reaction in a process involving alkynyl radicals [15].

To prepare multimetallic assemblies of defined architecture containing octamethylferrocene moieties as peripheral units the well-established palladium-catalyzed cross-coupling of terminal alkynes with aryl halides (reported by Dieck and Heck [16] and Sonogashira et al. [17]) is an attractive synthetic pathway. It tolerates a wide variety of functional groups and enables the coupling of several alkyne moieties around a multihalogenated core.

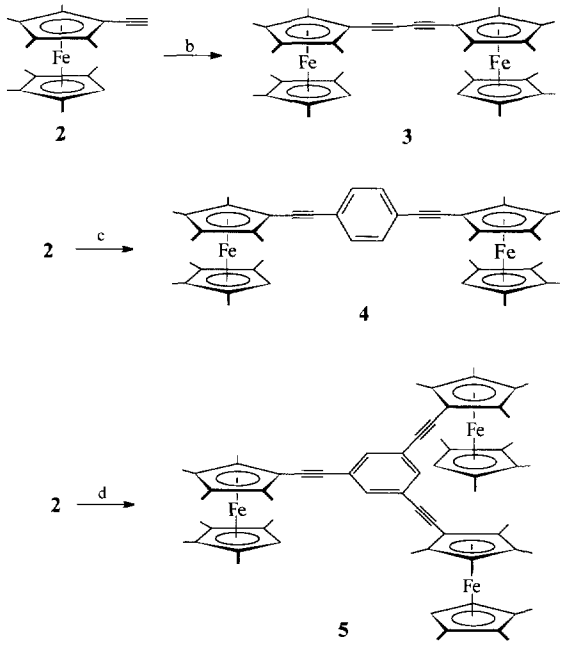
In this procedure aryl iodides are advantageous with respect to aryl bromides because they allow the coupling reaction to be performed at lower temperatures. The lifetime of the active catalytic species can be extended [18] and the yields increased.

Treatment of the terminal alkyne **2** with 1,4-diiodobenzene or 1,3,5-triiodobenzene in the presence of a palladium-catalyst and an amine solvent at elevated temperatures, leads to the orange–red two-fold coupling-product **4** in medium (50%) and to the yellow–orange threefold coupling product **5** in good yields (83%), respectively (Scheme 2). While **4** is almost insoluble at room temperature in all common solvents, **5** is easily soluble in polar organic solvents such as THF and $CHCl_3$.

The novel compounds **2–5** are characterized by NMR and MS data and by elemental analyses (see Section 3). They are stable in air and moisture and can be stored in pure form without limitations.



Scheme 1. (a) $Ph_3PCH_2Cl^+Cl^-$ / n-BuLi, THF; KO^{t}Bu, 10 d, reflux.



Scheme 2. (b) $Cu(OAc)_2$, methanol:ether:pyridine 1:2:1, 3 h reflux; (c) 1,4-diiodobenzene, $Pd(dba)_2$, CuI, PPh_3, $HNEt_2$, reflux 24 h; (d) 1,3,5-triiodobenzene, $Pd(dba)_2$, CuI, PPh_3, NEt_3, 60°C 24 h.

2.2. Electrochemistry

The cyclic voltammograms of **2–5** have been measured versus Ag/AgCl reference electrode in methylene chloride containing 0.1 m [nBu$_4$N][PF$_6$] as electrolyte. For the compounds **2**, **4**, and **5**, one peak representing a reversible one-, two- or threefold oxidation appears in the area of 160–180 mV (for details see Section 3). The simultaneous transfer of electrons observed in **4** and **5** indicates the independence of the two or three redox-centers, respectively. Complex **3** exhibits two reversible one-electron oxidations with half-wave potentials at 190 and 340 mV, respectively. The peak-separation of 150 mV is approximately 50 mV larger than in the parent compound [5]. This difference may be attributed to the increase in the electron density brought about by the electron donating effects induced by the methyl groups on the Cp ligands.

3. Preparation / experimental details

3.1. General

All reactions were carried out under a dry nitrogen atmosphere using Schlenk-techniques. THF was distilled under argon from potassium metal. Diethylamine, triethylamine and pyridine were distilled from calcium hydride under nitrogen. Methanol was dried over sodium metal. Starting materials, acetonitrile, hexane and

trichloromethane were used as purchased without any purification. $Pd(dba)_2$ [19] 1,3,5-triiodobenzene (in analogy to Ref. [20]) and octamethylformylferrocene [21] were synthesized according to literature procedures. Silica gel (60) for flash-chromatography and column chromatography was purchased from Merck.

The analytical equipment for spectroscopic characterization comprises: Bruker Avance DRX 500: ^{1}H NMR (500.1 MHz); ^{13}C{^{1}H} NMR (125.8 MHz). Chemical shifts for ^{1}H and ^{13}C{^{1}H} spectra were recorded in ppm downfield from TMS. The mass spectra were determined by using a VG AutoSpec instrument. Only characteristic fragments and isotopes of the highest abundance are listed. Melting points were determined using a Büchi 510 melting point apparatus and are uncorrected. Elemental analyses were carried out by Analytisches Labor der Fakultät für Chemie, Bielefeld. Cyclovoltammetry: EG&G VersaStat potentiostat (M250/270 software); three-electrode arrangement; Pt disc electrode; Ag/AgCl reference electrode; Pt support-electrode. All experiments were carried out in a dry 0.1 m $[nBu_4N][PF_6]/CH_2Cl_2$ solution.

3.2. One-pot synthesis of 1',2,2',3,3',4,4',5 octamethylethynylferrocene 2

To a suspension of 12.5 g (chloromethyl)triphenylphosphonium chloride (36.0 mmol) in 120 ml THF is slowly added one equivalent of *n*-BuLi (1.60 m solution in *n*-Hexane). After stirring for 20 minutes a solution of 10.6 g **1** (32.0 mmol) in 50 ml THF is slowly added through a septum. The reaction-mixture is further stirred for 3 hours, then 7.18 g KO^{t}Bu (64.0 mmol) is added and the reaction-mixture is refluxed for 10 d. The course of the reaction can be followed by TLC (hexane, heating of the plates is necessary to distinguish the spots). When the reaction is completed, 100 ml water and 150 ml hexane are added and the aqueous layer is washed eight times with 50 ml-portions of water. The organic phase is dried over Na_2SO_4. The solvent is removed and the product is separated from impurities by flash-chromatography (hexane). Recrystallization from acetonitrile yields **2** as a yellow–brown crystalline solid (7.00 g, 68%)

^{1}H NMR (500 MHz, $CDCl_3$): 1.67; 1.73; 1.75; 1.84 (4 × s, 4 × 6H, Cp–CH_3), 2.91(s, 1H, ≡C–*H*),), 3.29 (s, 1H, Cp–*H*); ^{1}H NMR (500 MHz, C_6D_6): 1.61; 1.66; 1.73; 1.89 (4 × s, 4 × 6H, Cp–CH_3), 2.75 (s, 1H, ≡C–*H*), 3.32 (s, 1H, Cp–*H*); ^{13}C NMR (125 MHz, C_6D_6): 8.9; 10.0; 10.7; 10.9; 64.5; 71.8; 77.1; 80.4; 80.7 (two C); 82.5; 82.7; MS (CI; $CDCl_3$) *m/z* 323 (100) [M$^+$]; Anal. Calcd. (found) $C_{20}H_{26}Fe$: C 74.53 (74.39); H 8.38 (8.13); IR (KBr): ν[cm^{-1}] = 3312 (m) 3291 (m) 2966 (m) 2944 (m) 2902 (s) 2858 (m) 2099 (s) 1376 (s) 1029 (s); mp: 151°C; CV: $E_{1/2}$ (vs. SCE at 50 mV/s): 160 mV.

3.3. Synthesis of 1.4-bis(octamethylferrocenyl)butadiyne 3

A suspension of 2.09 g (11.5 mmol) copper(II) acetate in 18 ml methanol is added to a solution of 1.09 g **2** (3.37 mmol) in 50 ml ether and 24 ml pyridine. The reaction mixture is heated to reflux for 3 h. During this time the colour changes from brown to green. The mixture is diluted with 40 ml ether and filtered. The filtrate is washed successively with ether. The solvent is removed in vacuo. The residue is treated with a mixture of 100 ml CH_2Cl_2 and 20 ml 1 n aq. HCl. The aqueous layer is extracted three times with 20 ml portions of CH_2Cl_2. The organic layer is dried over Na_2SO_4, filtered, and the solvent is evaporated in vacuo. After flash-chromatography (THF) **3** can be obtained as an orange solid in 42% yield (0.71 g, 1.10 mmol).

^{1}H NMR (500 Mhz, $CDCl_3$): 1.67; 1.71; 1.74; 1.85 (4 × s, 4 × 12H, Cp–CH_3); 3.36 (s, 2H, Cp–*H*); ^{13}C NMR (125 MHz, $CDCl_3$): 8.7; 10.0; 10.6; 10.7; 64.1; 71.8; 74.6; 78.6; 81.2; 81.3; 81.5; 83.21; MS (FAB +): 642 (99) [M$^+$], 464 (11) [M$^+$ − tCpFe], 400 (100) [M$^+$ − 2 tCp]; Anal. Calcd. (found) $C_{40}H_{50}Fe_2$: C 74.27 (74.23); H 7.84 (7.94); mp: > 260°C (decomp.); CV: $E_{1/2}$ (vs. SCE at 20 mV/s): 190 mV; 340 mV.

3.4. Synthesis of 1,4-bis(octamethylferrocenylethynyl)benzene 4

[1]

A flask connected with a reflux condenser is charged with 1.25 g (3.88 mmol) **2**, 0.64 g 1,4-diiodobenzene (1.94 mmol) and 50 ml diethylamine. The flask is evacuated under liquid nitrogen and back-filled with nitrogen three times, sealed and the catalyst-mixture is added (0.05 g $Pd(dba)_2$, 0.07 g CuI, 0.15 g PPh_3). After 24 h reflux the solvent is evaporated and the product is extracted with 50 ml THF using a soxhlet apparatus. The product separates while the solution is cooled to room temperature. After suction, the orange solid is washed with small amounts of THF and hexane and dried in vacuo. Yield: 0.69 g (50%).

MS (EI$^+$) [*m/z* (rel. int. %)]: 718 (100) [M$^+$], 359 (29) [M^{2+}]; Anal. Calcd. (found) $C_{46}H_{54}Fe_2$: C 76.88 (76.66); H 7.57 (7.85); mp: > 260°C (decomp.); CV: $E_{1/2}$ (vs. SCE at 50 mV/s): 160 mV.

3.5. Synthesis of 1,3,5-tris(octamethylferrocenylethynyl)benzene 5 [1]

A single-neck flask with a side arm is charged with 1.35 g **2** (4.21 mmol), 0.46 g triiodobenzene (1.39

[1] An X-ray crystal structure analysis of **5** confirms the proposed structure but the quality of the crystal did not allow a satisfactory refinement of the data set.

mmol) and 60 ml triethylamine. Then 0.07 g copper(I) iodide, 0.10 g PPh_3 and 0.09 g $Pd(dba)_2$ are added. The flask is evacuated under liquid nitrogen and back-filled with nitrogen three times, sealed and stirred at 60°C for 24 h. The stepwise substitution can be monitored by TLC ($CHCl_3$:hexane 1:4). After completion, the solvent is removed and the residue is solved in CH_2Cl_2. After flash-chromatography (CH_2Cl_2), the product is separated using column chromatography, eluting with $CHCl_3$:hexane 1:4. Evaporation of the solvent gives **5** as an orange solid (1.20 g; 83%).

^{1}H NMR (500 Mz, $CDCl_3$): 1.71, 1.76, 1.79, 1.92 (4 × s, 4 × 18H, Cp–CH_3); 3.34 (s, 3H, Cp–*H*); 7.50 (s, 3H, arom. *H*); ^{13}C NMR (125 MHz, $CDCl_3$): 8.89; 10.0; 10.6; 10.8; 64.4; 71.6; 80.8; 81.0; 81.1; 82.3; 88.0; 89.4; 125.3; 132.2; MS (FAB +)[*m/z* (rel. int. %)]:1038 (100) [M^+]; mp: 240°C (decomp.); CV: $E_{1/2}$ (vs. SCE at 100 mV/s): 180 mV.

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