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Note

The synthesis and electrochemical behavior of 1,4-di-(2,5-dimethylazaferrocenyl)-1,3-butadiyne

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Abstract

Rigid-rod ferrocene capped alkynes have attracted a lot of attention recently. In this note we report an efficient synthesis of the 1,4-di-(2,5-dimethylazaferrocenyl)-1,3-butadiyne which is the first known azaferrocene capped diacetylene derivative. The cyclic voltammetry measurements at different scan rates and temperatures indicate good electronic communication between two iron centers. Better shaped reduction peaks at higher scan rates in 22 °C and −40 °C can point to increased stability of the monocation.

Keywords: Azaferrocene; Metallocenyl-acetylide compounds; Cyclic voltammetry; Electronic communication

1. Introduction

Rigid-rod hetero and homo binuclear ferrocene capped systems are well suited to play a role in the field of molecular wires. By structural changing of the bridging group along with metal–metal distance modifications a metal–metal electronic interaction in such molecules can be tuned. Ethynylferrocene (**1**) (Fig. 1.) has been recognized as a stable, versatile redox active capping group. For example, **1** has been used as a terminal group in hetero nuclear Ru containing complexes [1,2], homo binuclear complexes with aromatic spacer groups [3], optically active polymers [4] and mononuclear oligo(phenylethynyl) molecular wires [5].

Extensive efforts have also been devoted to synthesize diferrocenylacetylenes [6–10]. Its coordinated complexes of triosmium and dicobalt carbonyls have been detailed structurally and electrochemically investigated [11–14].

From the diferrocenylacetylenes class of compounds, originates 1,4-diferrocenyl-1,3-butadiyne (**2**) (Fig. 1). The first synthesis of **2** was reported by Schlögl and Egger [7]. More recently, **2** has been obtained with in high 89% yield by dimerization of ethynylferrocene **1** under oxidative homocoupling reaction conditions [10]. Cyclic and differential pulse voltammetric measurements of **2** have been reported [11,13,14] and allowed to classify monocation $\mathbf{2}^{+}$ as class II of mixed valence compounds [15] according to the categories defined by Day [16].

We have been engaged in a program aimed at the synthesis, structural and biochemical characterization of various azaferrocene derivatives [17–21]. In the course of our study, recently, we synthesized and characterized 1′-ethynyl-2,5-dimethylazaferrocene (**3**) (Fig. 1) [22]. In this note we present application of **3** in the synthesis of the title compound **4** (Fig. 1) which is the nearest heteroanalog of 1,4-diferrocenyl-1,3-butadiyne (**2**). Synthesis of azaferrocene compound **4** was justified by searching for new metallocene complexes with possible metal–metal interactions. It is worth underlining that the electrochemistry of azaferrocene derivatives has long lagged behind that of ferrocene but has begun to be more established over last few years [22–24]. Cyclic voltammetric studies of **4** performed at various temperatures and potential sweep rates are reported here.

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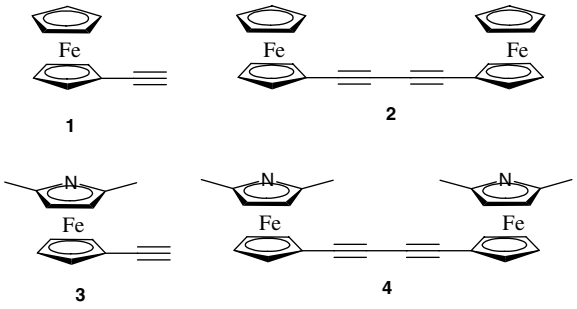


Fig. 1. The structures of compounds **1**, **2**, **3**, and **4**.

2. Results and discussion

2.1. Synthesis of 4

In our first attempt (method A) to synthesize 1,4-di-(2,5-dimethylazaferrocenyl)-1,3-butadiyne (**4**), 1′-ethynyl-2,5-dimethylazaferrocene (**3**) was dimerized in the presence of CuI/TMEDA and a continuous flow of O_2 in CH_2Cl_2 as a solvent at room temperature. Based on the literature data under similar copper catalyzed oxidative coupling conditions, a wide variety of acetylene compounds have been dimerized [25]. After workup, product **4** was isolated by column chromatography as an red solid in 17% yield.

In a second attempt (method B) 1′-ethynyl-2,5-dimethylazaferrocene (**3**) was dimerized in the presence of $CuI/PdCl_2(PPh_3)_2$ in Et_3N as a solvent for 14 h at 50 °C. After simple workup and purification by column chromatography product **4** was isolated in 84% yield. That yield was similar to those achieved in the synthesis of 1,4-diferrocenyl-1,3-butadiyne (**2**) [10]. The higher yield of method B presumably results from greater stability of the products in the reaction medium compared to the highly oxidative conditions of method A.

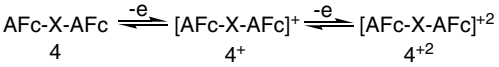
The ^{1}H NMR spectrum of **4** shows a four-proton singlet (4.45 ppm) for β-pyrrolyl protons, two four-proton triplets (4.44 and 4.27 ppm) from the substituted cyclopentadienyl ligand and a twelve-proton singlet (2.28 ppm) from the four α-pyrrolyl methyl groups. The ^{13}C NMR spectrum of **4** shows diagnostic signals of diacetylene carbon atoms at 77.6 (C_5H_4–*C*≡C–) and 72.3 (C_5H_4–C≡*C*–). In the high resolution mass spectrum (HRMS, EI, 70 eV) of **4** one can see a peak at *m/e* 476.0626 with the calculated value for $C_{26}H_{24}N_2Fe_2$ being 476.0638.

The 1,4-di-(2,5-dimethylazaferrocenyl)-1,3-butadiyne (**4**) is stable in solid state and can be stored for months protected against light at low temperatures.

2.2. Cyclic voltammetry study of 4

The neutral **4** undergoes two successive one-electron oxidations to yield the mono- $\mathbf{4}^+$ and dication $\mathbf{4}^{+2}$ (Scheme 1):

In the cyclic voltammograms of **4** (Fig. 2) at lower scan rates (0.1 V/s) in 22 °C, two oxidation peaks are observed at 0.457 V and 0.847 V. In −40 °C at this same scan rate, the first oxidation peak remains unchanged (0.457 V),



Scheme 1. The oxidation of compound **4**, AFc represents an 2,5-dimethylazaferrocenyl and X bridging acetylene fragment.

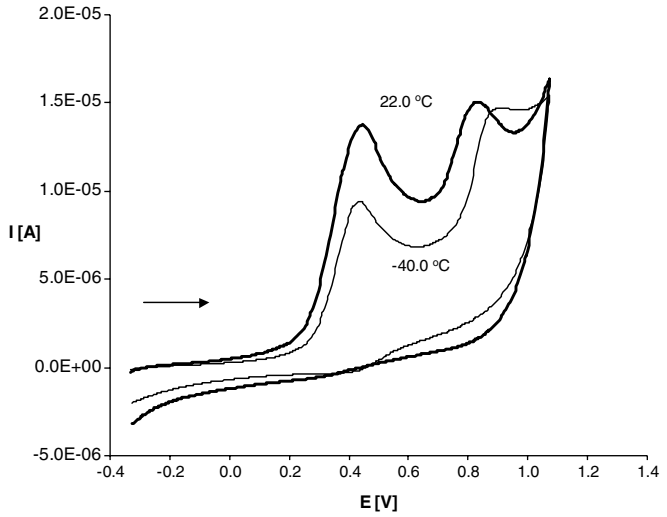


Fig. 2. Cyclic voltammograms of **4** (10^{-3} M) in CH_2Cl_2 with 0.1 M Bu_4NClO_4 at Pt-disk electrode, $\phi = 1.5$ mm, scan rate 0.1 V s^{-1} vs. Fc^+/Fc in temp. 22 °C and −40 °C.

whilst the second one is shifted to 0.878 V. The waves are chemically irreversible. The reduction peaks are not seen at lower scan rates (0.1 V/s). Only at −40 °C can one reduction process be seen as a poorly shaped peak at 0.404 V (Fig. 2). At higher scan rates (2.0 V/s) at 22 °C, a better shaped reduction peak at 0.404 V appears and the oxidation peaks are shifted to 0.546 V and 1.021 V, respectively (Fig. 3). On decreasing the temperature to −40 °C and 2 V/s scan rate we were able to record an even better

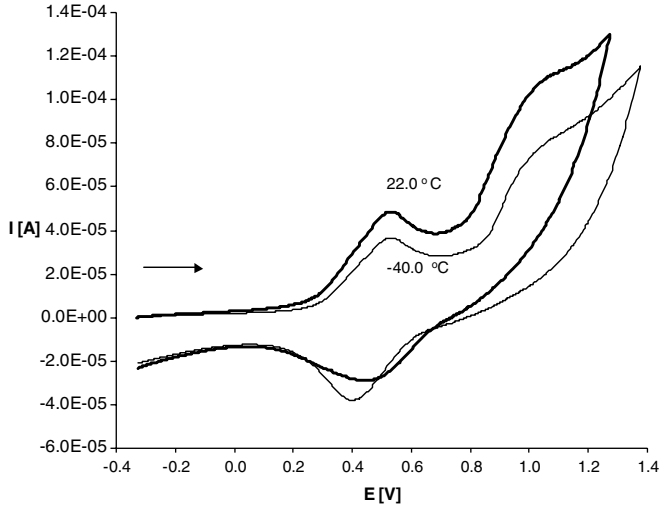


Fig. 3. Cyclic voltammograms of **4** (10^{-3} M) in CH_2Cl_2 with 0.1 M Bu_4NClO_4 at Pt-disk electrode, $\phi = 1.5$ mm, scan rate 2.0 V s^{-1} vs. Fc^+/Fc in temp. 22 °C and −40 °C, first scan.

Table 1
Electrochemical data on **4**

Scan rate (V/s)	Temp. (°C)	$E_{ox}(1)$ (V)	$E_{ox}(2)$ (V)	ΔE_{ox} (V)	$E_{red}(1)$ (V)
0.1	22. 0	0.457	0.847	0.390	–
0.1	−40. 0	0.457	0.878	0.421	0.404
2.0	22. 0	0.546	1.021	0.475	0.404
2.0	−40. 0	0.546	1.021	0.475	0.404

$\Delta E_{ox} = E_{ox}(2) - E_{ox}(1)$.

shaped reduction peak at 0.404 V. Thus, above results indicate that decreasing the temperature substantially affected kinetic parameters of the electrode reaction. One can assume that decreasing the temperature directly increases stability of the monocation $\mathbf{4}^+$. After the first scan the electrode surface is covered with a thin pale yellow film. Such behaviour has been observed previously in azaferrocene derivatives [22,23]. Based only on the ΔE_{ox} values (Table 1) we can partially estimate electronic communication between the two iron centers in **4** as 0.475 V (for 2 V/s scan rate). Comparison of this value to analogous one reported for 1,4-differrocenyl-1,3-butadiyne (**2**) ($E_{1/2}(1) = 0.58$ V and $E_{1/2}(2) = 0.68$ V; $\Delta E = 0.10$ V, [15]) suggests greater electronic communication between two iron centers in **4** than in **2**.

3. Conclusion

1,4-Di-(2,5-dimethylazaferrocenyl)-1,3-butadiyne (**4**), the first azaferrocene capped rigid-rod diacetylene derivative has been prepared and characterized. Two methods of its synthesis have been tested: CuI catalyzed coupling in the presence of molecular oxygen and $CuI/PdCl_2(PPh_3)_2$ catalyzed dimerization reaction. The latter method gave higher product yield. 1,4-Di-(2,5-dimethylazaferrocenyl)-1,3-butadiyne (**4**) is red solid moderately stable in solution and stable in solid state. The cyclic voltammetry measurements at different scan rates and temperatures indicate good electronic communication between the two iron centers. Better shaped reduction peaks at higher scan rates at 22 °C and −40 °C can point to increased stability of the monocation $\mathbf{4}^+$.

4. Experimental

4.1. General remarks

All preparations were carried out using standard Schlenk techniques. All solvents were distilled over standard drying agents under nitrogen directly before use.

NMR spectra were recorded using a Bruker AV500 spectrometer. Chemical shifts are reported in δ (ppm) using $CDCl_3$ (^1H δ 7.26 ppm) as the reference solvents. Mass spectra were recorded using EI methods on a micromass Autospec Q spectrometer. Microanalyses were carried out by Mr. S Boyer at SACS (Scientific Analysis and Consultancy Services) at the University of North London. 1′-Ethynyl-2,5-dimethylazaferrocene was prepared according to the literature method [22]. All other chemicals were purchased from the Aldrich Chemical Co.

The cyclic voltammetry measurements of **4** were carried out in dichloromethane solutions (10^{-3} M) with 0.1 M Bu_4NClO_4 under an Ar atmosphere on AUTOLAB (Eco Chemie BV) on a standard three-electrode system (platinum working electrode ($\phi = 1.5$ mm), saturated calomel electrode as a reference and cylindrical platinum gauze counter electrode). All potentials were recalculated and given vs. $FeCp_2^+/FeCp_2$ redox couple. The voltammograms were made within scan rate range 0.1–2 V/s in two temperatures: −40 °C and 22 °C.

4.2. Synthesis of 4

4.2.1. Method A

Through the stirred mixture containing DCM (15 ml), 1′-ethynyl-2,5-dimethylazaferrocene (**3**) (86 mg, 0.36 mmol), TMEDA (44 μl, 0.29 mmol) and CuI (40 mg, 0.21 mmol) gaseous O_2 was purged for 1.5 h at room temperature. During this time the colour of the reacting mixture was changed from orange to dark green-brown. The reaction was quenched by the addition of water and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$, and solvent evaporated. The resulting residue was purified by chromatography ($CHCl_3$:MeOH; 50:2) to give the product as a red solid (15 mg, 17%).

4.2.2. Method B

$PdCl_2(PPh_3)_2$ (21 mg, 0.03 mmol) and CuI (6 mg, 0.03 mmol) were placed into Schlenk tube and stirred dry under vacuum at room temperature for 30 min. Then the Schlenk tube was purged with nitrogen and 1′-ethynyl-2,5-dimethylazaferrocene (**3**) (73 mg, 0.3 mmol) in Et_3N (6 ml) was added. The reaction mixture was stirred for 14 h at 50 °C. During this time the colour of the reacting mixture slowly changed from orange to red. On the bottom of the Schlenk tube a dark solid precipitate appeared. Then the solvent was decanted, and the residue was washed with small volume of Et_3N. After drying the dark residue was purified by chromatography ($CHCl_3$:MeOH; 50:2) to give a product as a red solid (60 mg, 84%).

^1H NMR δ ($CDCl_3$) 500 MHz: 4.45 (s, 4H, β-pyrrolyl), 4.44 (t, $J = 2$ Hz, 4H, C_5H_4), 4.27 (t, $J = 2$ Hz, 4H, C_5H_4), 2.28 (s, 12H, α-CH_3 pyrrolyl). $^{13}C\{^1H\}$NMR δ ($CDCl_3$) 125 MHz: 103.2 (α-pyrrolyl), 77.6 (C_5H_4–*C*≡C–), 73.1 (C_5H_4), 72.4 (β-pyrrolyl), 72.3 (C_5H_4–C≡*C*–), 71.6 (C_5H_4), 65.3 (*ipso*-C_5H_4), 14.9 (CH_3 groups). MS (EI, 70 eV) $m/e = 476$ [M^+], 382 [M^+-C_6H_8N], 238 [M^+-$C_{13}H_{12}NFe$], 94 [C_6H_8N]. HRMS: $m/e = 476.0626$ (Calc. for $C_{26}H_{24}N_2Fe_2$: 476.0638). Anal. Calc. for $C_{26}H_{24}N_2Fe_2$: C, 65.58; H, 5.08; N, 5.88. Found C, 65.57; H, 5.15; N, 5.94%.

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