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1,6-Bis(ferrocenyl)-1,3,5-hexatriyne: Novel Preparation and Structural Study

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Summary: 1,6-Bis(ferrocenyl)-1,3,5-hexatriyne ($Fc(C{\equiv}C)_3Fc$) *was prepared from the reaction between 3-(dibromomethylidene)-1,5-bis(ferrocenyl)penta-1,4-diyne and BuLi via an alkynyl migration in a vinylidene carbenoid mechanism. Both the title compound and its precusors were thoroughly characterized, and the electronic couplings between two ferrocenyl units were assessed with voltammetric techniques.*

Ferrocene is undoubtedly the most celebrated organometallic compound,[1] and its value goes far beyond sentimental. With its robust (+1/0) couple, ferrocene is one of the most utilized redox probes for biomolecules[2] and has been incorporated into both redox-active main chain polymers[3] and redox-active dendrimers as either the foci or peripheral pendants.[4] As a prochiral building block, ferrocene has also played a key role in the development of asymmetric catalysts during the last 10 years.[5] Of particular interest to us is its unique role in probing charge transfer efficieny across molecular fragments (X) on the basis of the mixed-valent nature of $[Fc{-}X{-}Fc]^+$,[6] where, in the cases of efficient bridging (strong coupling), two Fc's are oxidized stepwise and the potential difference between two oxidations ($\Delta E_{1/2}$) can be used as a convenient gauge of coupling strength.[6] Recent years have seen intense efforts in the estimation of hole transfer efficiency of metal complexes by placing a pair of $FcC{\equiv}C$ groups in trans deposition in mononuclear[7] and polynuclear compounds.[8] Other noteworthy studies of the [Fc−X−Fc] type systems include the demonstration of visible light modulated electron transfer[9] and revelation of an unusually large $\Delta E_{1/2}$ manifested by a quadruple hydrogen-bonding motif.[10]

Among the family of α,ω-bis(ferrocenyl) polyynes ($Fc(C{\equiv}C)_mFc$), $FcC{\equiv}CFc$ and $Fc(C{\equiv}C)_2Fc$ were prepared respectively from the cross coupling (Cadiot−Chodkiewicz type) between $FcC{\equiv}CH$ and FcI and oxidative coupling (Glaser type) of $FcC{\equiv}CH$ in the 1960s.[11,12] Subsequent study by Cowan revealed $\Delta E_{1/2}$ values of 130 mV ($m = 1$) and 100 mV ($m = 2$) and a class II Robin−Day designation for the mixed-valent ions of both compounds.[13] Two extended members, namely those of $m =$ 4[14] and 6,[15] were reported in recent years, and both were readily prepared from the oxidative coupling reaction of FcC_mH. The synthesis of an α,ω-bis(ferrocenyl) polyyne of *odd m*, on the other hand, is more challenging. In addition to $FcC{\equiv}CFc$, the title compound was previously synthesized from two routes: (i) Schlögl and Steyrer obtained the compound in the form of a mixture from the oxidative coupling of $FcC{\equiv}CH$ and $Fc(C{\equiv}C)_2H$, but failed to isolate it,[16] and (ii) Wakatsuki et al. prepared the compound in a nearly quantitative yield from the reductive-(elimination)-coupling of $(\eta^5\text{-}C_5H_4TMS)_2Ti(\sigma\text{-}C{\equiv}CFc)(\sigma\text{-}(C{\equiv}C)_2Fc)$ and reported NMR and combustion analysis data.[17] Reported in this communication is the preparation of $Fc(C{\equiv}C)_3Fc$ using a method that is distinctively different from all prior syntheses of $Fc(C{\equiv}C)_mFc$[11,12,14−17] and characterization of this compound and its precursors.

As depicted in Scheme 1, our approach has been inspired by the successful preparation of polyynes from alkynyl migration in vinylidene carbenoids.[18] Preparations of compounds **1** and **2** were slightly modified from the early literature:[19] the reaction between FcC_2Li and 0.5 equiv of ethylformate resulted in compound **1** (1,5-bis(ferrocenyl)penta-1,4-diyn-3-ol), and subsequent oxidation of compound **1** with pyridinium chlorochromate led to compound **2** (1,5-bis(ferrocenyl)penta-1,4-diyn-3-one). Both compounds gave spectroscopic data consistent with the previously reported values, and compound **2** was further characterized by single-crystal X-ray diffraction.[20] As shown in Figure 1, the middle fragment (C1−C2−C3(=O)−C4−C5) of molecule **2** is planar and the metric parameters are consistent

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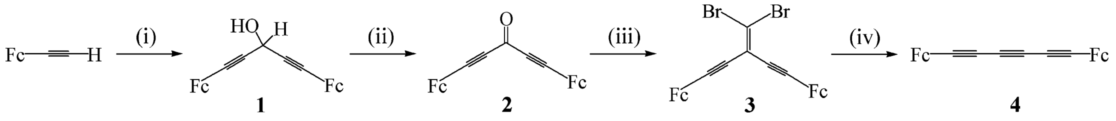
10.1021/om0607550 CCC: $33.50

Scheme 1. Synthetic Route for FcC_6Fc^a



[a] Conditions: (i) ^{n}BuLi (1.04 equiv), ethylformate (0.52 equiv), THF, 0 °C; yield of **1**: 71%; (ii) pyridinium chlorochromate (1.5 equiv), Celite/molecular sieves, CH_2Cl_2, 12 h; yield of **2**: 72%; (iii) CBr_4 (2.0 equiv), PPh_3 (4.0 equiv), benzene, 12 h; yield of **3**: 71%; (iv) ^{n}BuLi (1.25 equiv), dry benzene, −15 °C, 1 h; yield of **4**: 82%.

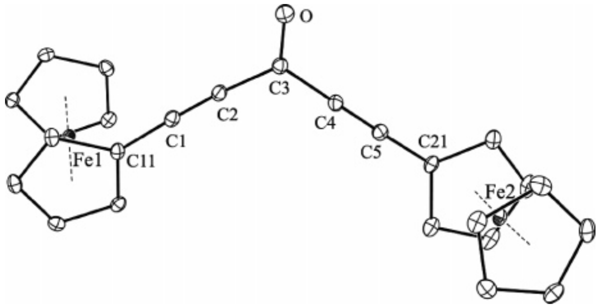


Figure 1. ORTEP plot of molecule **2** at the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2, 1.200(2); C2−C3, 1.442(2); C3−O, 1.220(2); C3−C4, 1.446(2); C4−C5, 1.205(2); O−C3−C2, 123.7(2); O−C3−C4, 122.6(2); C2−C3−C4, 113.7(1).

with a localized penta-1,4-diyn-3-one designation. The unique axes of two ferrocenyl groups, i.e., the vector defined by linking the centroid of the Cp rings and Fe center (shown as a dash in Figure 1), are roughly orthogonal to the penta-1,4-diyn-3-one plane and pointed in opposite directions. The Fe···Fe and edge(Fc)−edge(Fc) distances are 9.72 and 6.69 Å, respectively. The topological features of **2** are significant since there is no structural characterization of compounds containing a penta-1,4-diyn-3-one fragment despite their significant role in the synthesis of carbon-rich compounds.[19,21]

Compound **2** was further converted to 3-(dibromomethylidene)-1,5-bis(ferrocenyl)penta-1,4-diyne (**3**) in satisfactory yield via the reaction with CBr_4 in the presence of PPh_3 (Corey−Fuchs dibromoolefination reaction).[22,23] It is surprising that a prior attempt under nearly identical conditions did not produce **3** at all.[19] In addition to ^{1}H and ^{13}C NMR spectroscopic identification, compound **3** was also characterized by X-ray crystallography,[20] and its structural plot is shown in Figure 2. Molecule **3** contains a crystallographic 2-fold axis defined by C3 and C4 centers, and the 3-(dibromomethylidene)penta-1,4-diyne fragment is planar. Interestingly, the unique axes of both ferrocenyl groups are roughly coplanar with the 3-(dibromomethylidene)penta-1,4-diyne plane, and the Fe···Fe′ and edge−edge distances are about 10.55 and 6.62 Å, respectively. There is only one literature precedent related to **3**, namely, 3-(dibromomethylidene)-1,5-diphenylpenta-1,4-diyne by Diederich,[24] which displays metric parameters for the 3-(dibromomethylidene)penta-1,4-diyne fragment nearly identical to those of **3**.

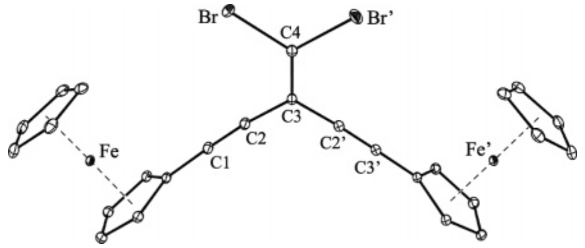


Figure 2. ORTEP plot of molecule **3** at the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2, 1.207(2); C2−C3, 1.427(2); C3−C4, 1.352(2); C4−Br, 1.871(1); C2−C3−C4, 121.66(7); C2−C3-C2′, 116.7(1); C3−C4−Br, 122.57(4); Br−C4−Br′, 114.87(9).

Tykwinski and co-workers demonstrated recently that 1,5-substituted 3-(dibromomethylidene)penta-1,4-diynes with either silyl or aryl substituents could be converted to 1,6-substituted 1,3,5-hexatriynes via the reaction with BuLi in rigorously anhydrous hydrocarbons.[18] Hence, the reaction between compound **3** and BuLi in slight excess at −15 °C afforded compound **4** (1,6-bis(ferrocenyl)-1,3,5-hexatriyne) in excellent yield.[25] Compound **4** has been characterized by all necessary techniques including X-ray crystallography,[20] and its structural plot is shown in Figure 3. There is a crystallographic inversion center bisecting the C3−C3′ bond, and the bond lengths and angles of the hexatriyne chain conform to the formalism of alternating carbon−carbon single and triple bonds.[26] The unique axes of the two Fc units are parallel but pointed in opposite directions, as imposed by the inversion center, and the Fe···Fe′ and edge−edge distances are respectively 12.02 and 9.20 Å.

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(20) X-ray diffraction data for crystals **2**−**4** were collected on a Bruker SMART APEX2 CCD diffractometer using Mo Kα at 100 K. *Crystal data for* **2**: $C_{25}H_{18}Fe_2O$, $M = 446.09$, monoclinic, $P2_1/c$, $a = 14.0726(8)$ Å, $b = 10.7833(7)$, $c = 13.0568(9)$ Å, $\beta = 110.112(4)°$ Å, $V = 1860.5(2)$ Å^3, $Z = 4$, $\rho = 1.593$ g cm^{-3}. Least-squares refinement based on 6533 reflections with $I = 2\sigma(I)$ and 325 parameters led to convergence with final $R1 = 0.034$ and $wR2 = 0.075$. *Crystal data for* **3**: $C_{26}H_{18}Br_2Fe_2$, $M = 601.92$, monoclinic, $C2/c$, $a = 20.8530(8)$ Å, $b = 7.4096(2)$ Å, $c = 14.3157(5)$ Å, $\beta = 103.641(3)°$, $V = 2149.6(1)$ Å^3, $Z = 4$, $\rho = 1.860$ g cm^{-3}. Least-squares refinement based on 4247 reflections with $I = 2\sigma(I)$ and 173 parameters led to convergence with final $R1 = 0.022$ and $wR2 = 0.056$. *Crystal data for* **4**: $C_{26}H_{18}Fe_2$, $M = 442.10$, monoclinic, $P2_1/c$, $a = 7.6034(2)$ Å, $b = 10.9464(3)$ Å, $c = 11.6264(3)$ Å, $\beta = 101.823(1)°$, $V = 947.13(4)$ Å^3, $Z = 2$, $\rho = 1.550$ g cm^{-3}. Least-squares refinement based on 2892 reflections with $I = 2\sigma(I)$ and 163 parameters led to convergence with final $R1 = 0.020$ and $wR2 = 0.056$.

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(23) *Preparation of* **3**. To a 45 mL benzene solution containing **2** (0.100 g, 0.22 mmol) were added CBr_4 (0.146 g, 0.44 mmol) and PPh_3 (0.231 g, 0.88 mmol) at room temperature. The reaction mixture was stirred for 12 h. Upon solvent removal, the residue was redissolved in hexane/CH_2Cl_2 (2/1, v/v) and filtered. The solvent was removed from the filtrate to yield a yellow solid, which was purified on column chromatography with dichloromethane and hexanes (1/5, v/v) to yield pure compound **3** (0.095 g, 71%). Data for **3**: R_f 0.41 (hexane/CH_2Cl_2, 2.5/1, v/v); ^{1}H NMR ($CDCl_3$) 4.52 (s, 4 H); 4.26 (s, 14 H); ^{13}C NMR ($CDCl_3$) 115.4; 104.9; 96.4; 83.3; 72.6; 71.2; 70.4; 64.7; MS-ESI (*m/e*) 602 ([**3**]$^+$).

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(25) *Preparation of* **4**. To a 50 mL benzene solution containing **3** (0.130 g, 0.2 mmol) was added 0.1 mL of *n*-BuLi (2.5 M in hexanes) at −15 °C under N_2. The reaction mixture was allowed to warm to about −10 °C over a period of 1 h and then quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with CH_2Cl_2, and the organic phase was collected and dried with Na_2SO_4. Upon solvent removal, the residue was purified on column chromatography with dichloromethane and hexanes (1/5, v/v) to give pure compound **4** (0.080 g, 82%). Data for **4**: R_f 0.41 (hexane/CH_2Cl_2, 3/1, v/v); ^{1}H NMR ($CDCl_3$) 4.52 (s, 4 H); 4.24 (s, 14 H); ^{13}C NMR ($CDCl_3$) 79.4; 73.5; 72.1; 71.2; 70.6; 65.8; 63.2; MS-MALDI (*m/e*) 442 (**4**$^+$).

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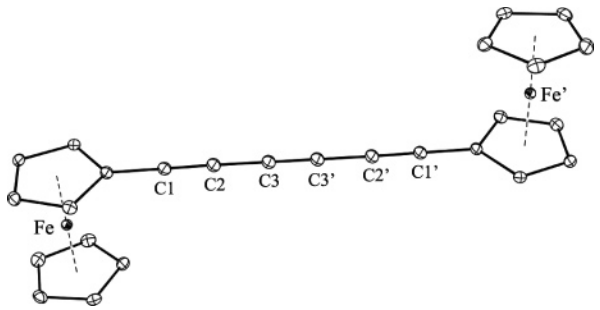

Figure 3. ORTEP plot of molecule **4** at the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2, 1.211(1), C2−C3, 1.362(1), C3−C3′, 1.215(2), C1−C2−C3, 178.9(1), C2−C3−C3′, 179.7(2).

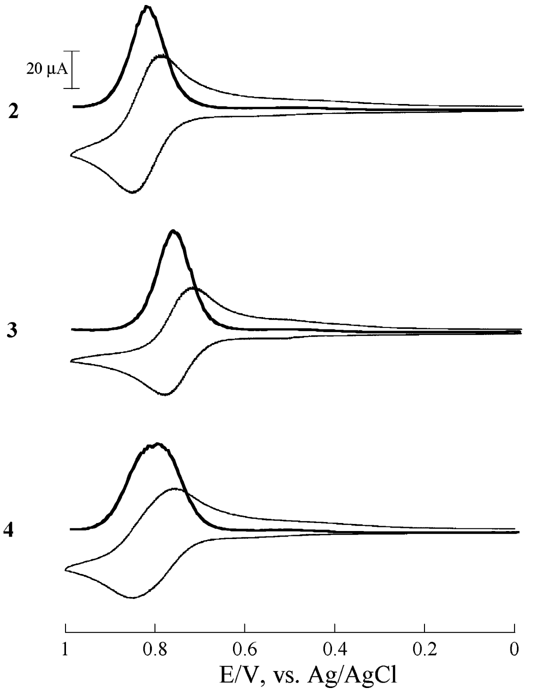

Figure 4. CVs (thin line) and DPVs of compounds **2**−**4** recorded in 0.20 M $^{n}Bu_4NPF_6$ THF solution at 21 ± 1 °C. The scan rate for CV measurements was 100 mV/s; the step increment and pulse width for DPV measurements were 4 mV and 0.05 s, respectively.

The availability of compounds **2**−**4** and their structural information provides an excellent opportunity for expanding the electronic coupling structure−property relationship in the α,*ω*-bis(ferrocenyl) polyyne series. Both the cyclic and differential pulse voltammograms (CV and DPV) recorded for compounds **2**−**4** in the anodic region are shown in Figure 4, and the oxidation of two Fc units appears as a pseudo-two-electron wave in all three cases on the basis of both the current comparison with a ferrocene internal standard and the shape of the voltammograms.[27] Prior studies of $FcC\equiv CFc$ and $Fc(C\equiv C)_2Fc$ revealed the stepwise one-electron oxidations that are indicative of effective electronic couplings between two Fc centers,[13] and that of $Fc(C\equiv C)_6Fc$ revealed a true two-electron oxidation and thus the absence of electronic coupling.[15] Clearly, compounds **2**−**4** are the intermediate of two extremes, as one might anticipate from the length of the spacers. Although a direct determination of $\Delta E_{1/2}$ is impossible due to the pseudo-two-electron nature of oxidation, the $\Delta E_{1/2}$ values (lower limit) for compounds **2**−**4** can be estimated using the Taube−Richardson model[27] as 35, 30, and 60 mV,[28] respectively. It is interesting that the electronic coupling in **4** is the strongest of three despite the longest Fe···Fe′ (edge−edge) distance. A plausible rationale is that although the C3 center in both **2** and **3** is sp^2 hybridized, the p_π orbital is polarized toward the more electronegative oxygen/dibromomethylene group and contributes little toward the superexchange pathway between the two Fc units.

Four decades after the synthesis of the first α,*ω*-bis(ferrocenyl) polyyne of odd *m* ($FcC\equiv CFc$) by Rosenblum,[11] we succeeded in preparing $Fc(C\equiv C)_3Fc$ via a novel alkynyl migration in vinylidene carbenoid route. The same methodology may be employed in the synthesis of both the next member of odd *m* ($Fc(C\equiv C)_5Fc$) and polyynes of other metal-capping groups such as diruthenium complexes, the latter of which have been the hallmark of our recent research.[29]

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Note Added after ASAP Publication. In the version of this paper published on the Web Sept 20, 2006, the volume number and page number of the last citation in ref 1 were transposed. The version that now appears is correct.

Supporting Information Available: Detailed synthesis and characterization of compounds **1**−**4** and X-ray crystallographic files in CIF format for the structure determination of compounds **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) A $\Delta E_{1/2}$ of 60 mV was reported for **4**, but the details of measurement were not given in: McAdam, C. J.; Brunton, J. J.; Robinson, B. H.; Simpson, J. *Dalton Trans.* **1999**, 2487. Some $\Delta E_{1/2}$ values for the α,*ω*-bis(ferrocenyl) polyyne series were summarized in: Low, P. J.; Roberts, R. L.; Cordiner, R. L.; Hartl, F. *J. Solid State Electrochem.* **2005**, *9*, 717.

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