Ethynylferrocene Compounds of 1,3,5-Tribromobenzene

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The new compounds 1,3-dibromo-5-(ferrocenylethynyl)benzene **(1)**, 1-bromo-3,5-bis(ferrocenylethynyl)benzene **(2)**, and 1,3,5-tris(ferrocenylethynyl)benzene **(3)** have been synthesized by palladium-catalyzed cross-coupling reactions and characterized, and the crystal structures of **1** and **3** have been determined; electrochemical studies show chemically reversible oxidations with single-step one-electron, two-electron, and three-electron processes per molecule, respectively, indicating that in **2** and **3** the iron(II) centers do not electronically communicate with each other.

Introduction

Carbon-rich organometallics containing rigid π-conjugated chains are of increasing interest due to their uses in the syntheses of unsaturated organic species,[1] organometallic polymers,[2] and π-conjugated bi- or multimetallic systems.[3] These organometallic assemblies are key design targets for the study of electron-transfer processes,[4] the fabrication of nanostructured materials,[5] the formation of liquid crystalline organometallic polymers,[6] the construction of molecular devices,[7] and the creation of dendrimers containing inorganic or organometallic fragments.[8]

With their importance in the field of materials science,[9] there is currently great interest in the chemistry of ferrocenyl and ferrocenylene oligomers and polymers and their precursors. Here we report the utilization of palladium-mediated cross-coupling methodology to the reaction of ethynylferrocene with a 1,3,5-trisubstituted aromatic species to give, *via* a simple single-step synthetic procedure, a series of novel precursors for the production of interesting and potentially exciting cross-linked metal−aromatic polyyne networks.

Results and Discussion

The compounds 1,3-dibromo-5-(ferrocenylethynyl)benzene **(1)**, 1-bromo-3,5-bis(ferrocenylethynyl)benzene **(2)**, and 1,3,5-tris(ferrocenylethynyl)benzene **(3)** (along

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Scheme 1. Syntheses of 1−3

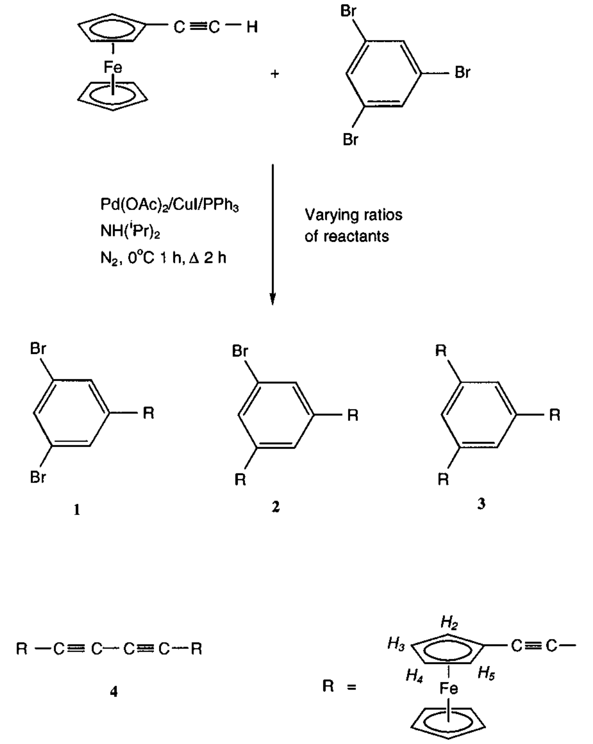

Table 1. Experimental Data for the Ratio of Reactants and Yield of Products

ratio of reagents (mol)		yields of products (%)			
FcC≡CH	$C_6H_3Br_3$	**1**	**2**	**3**	**4**
1	1	46	14		
2	1	36	36	12	
3	1			60	33

with the coupled dimer of ethynylferrocene, 1,4-diferrocenylbutadiyne (**4**)) were formed by the simple cross-coupling ("Heck-Cassar-Sonogashira-Hagihara") reaction[10] of ethynylferrocene[11] and 1,3,5-tribromobenzene (Scheme 1). This versatile single-step reaction was performed with different ratios of reagents, and depending on this ratio, the yields of the substitution products could be controlled (Table 1). The reactions were monitored by infrared spectroscopy, which showed that the ν(C≡C) stretching frequencies of the compounds are shifted by *ca.* 100 cm^{-1} to higher wavenumber, indicating a strengthening of the C≡C bond. After purification by column chromatography, the compounds were isolated as orange or orange-red air- and moisture-stable, microcrystalline solids. The solubility of **1**−**3** in chlorocarbon solvents decreases with increasing molecular weight. Eventually, orange crystals were obtained by slow evaporation of saturated solutions of **1** in *n*-hexane and **3** in benzene. The shape and geometry of these species are crucial to their utilization as precursors for building multidimensional metal−carbon networks.

The X-ray structural analysis of **1** shows (Figure 1) the ferrocenyl unit to have a characteristic eclipsed conformation and to be bonded linearly (C−C≡C−C angles of 178(1) and 179(1)°) to the dibromophenyl ring, which adopts a coplanar orientation with respect to the substituted cyclopentadienyl ring. There is distinct bond ordering within the C−C≡C−C linkage with single-bond lengths of 1.45(1) and 1.43(1) Å and a C≡C distance of 1.16(1) Å. The molecules pack within the crystal to form stacks that extend in the 110 plane, the dibromophenyl ring of one molecule being π-stacked with the unsubstituted cyclopentadienyl ring of a lattice-translated molecule (interplanar separation 3.47 Å, centroid···centroid distance 3.52 Å). The opposite face of the dibromophenyl ring is approached edge-on by the ferrocenyl group of another molecule, the Fe···centroid distance being 4.78 Å.

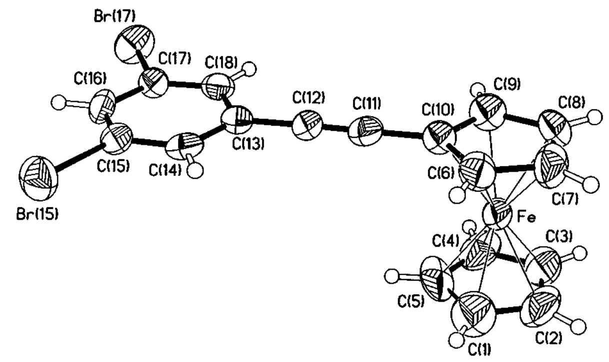

Figure 1. Solid state structure of **1**.

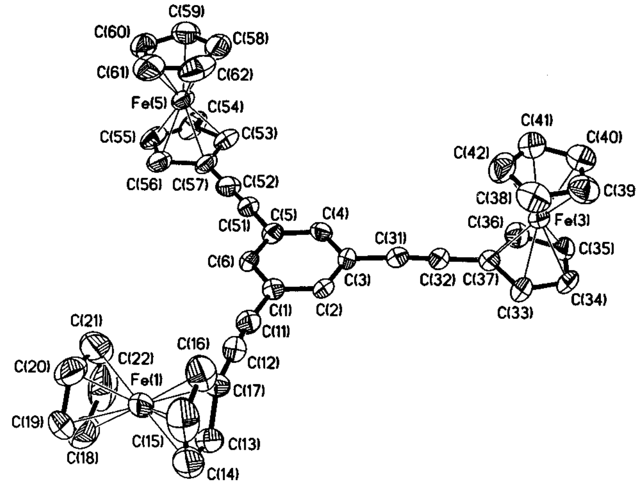

Figure 2. Solid state structure of **3**.

The X-ray analysis of **3** confirms the tris(ferrocenylacetylide) structure of the complex (Figure 2). Two of the substituted cyclopentadienyl rings are essentially coplanar with the 1,3,5-trisubstituted benzenoid nucleus (twist angles of between 1 and 2°), while the third (that associated with Fe(1)) is oriented orthogonally (twist angle *ca.* 86°). This geometry is in contrast to the almost all-planar, up−up−down arrangement observed in the related chromium tricarbonyl aryl complex.[8j] Interestingly, in **3** the pair of "in-plane" ferrocenyl moieties (associated with Fe(3) and Fe(5)) have normal eclipsed conformations for their C_5 rings, while in the orthogonally aligned unit, the rings are almost perfectly staggered. The geometries of the C−C≡C−C linkages are, in two instances, essentially linear with angles within the C(3)- - -C(37) and C(5)- - -C(57) chains in the range 175.0(9)−178.5(10)° and C≡C distances of 1.187(11) and 1.182(11) Å, respectively. For the third linkage, to the orthogonally oriented ferrocenyl unit,

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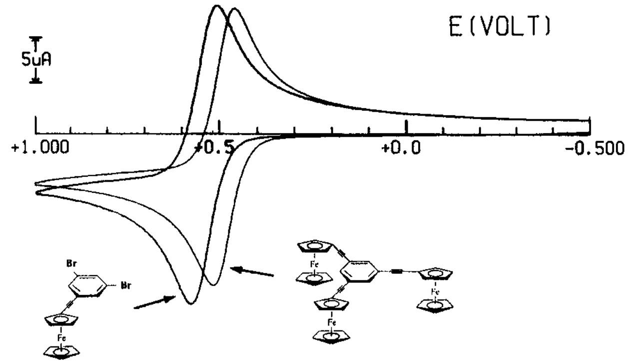

Figure 3. Cyclic voltammetric responses recorded at a platinum electrode on CH_2Cl_2 solutions containing **1** (1.1 × 10^{-3} mol dm^{-3}) and **3** (0.4 × 10^{-3} mol dm^{-3}), respectively ([NBu_4][PF_6] (0.2 mol dm^{-3}) supporting electrolyte; scan rate 0.1 V s^{-1}).

there is a noticeable bending at C(11) (170.4(10)°), the angle at C(12) remaining linear (179.1(11)°). The C(11)−C(12) bond exhibits a slight shortening at 1.145(11) Å. Adjacent "trimers" pack back-to-back with one of the C_5H_4 rings of one molecule aligned essentially parallel to and overlapping the benzenoid nucleus of the other and *vice versa* (mean interplanar separation 3.51 Å, centroid···centroid separation 3.71 Å). These back-to-back pairs form a stepped-stack arrangement with their neighbors in the crystal such that the iron atoms of the in-plane ferrocenyl moieties of one molecule lie almost in the plane of the benzenoid nucleus of the next.

In view of the interest in assessing the existence of electronic interactions among linked ferrocene subunits in oligoferrocene molecules,[12] we have examined the electrochemical behavior of **1**−**3**. Despite the fact that **2** and **3** contain multiple ferrocenyl subunits, cyclic voltammetry on their dichloromethane solutions displays only a single anodic process with features of chemical reversibility, as is seen for **1**. Figure 3 gives a comparative picture of the cyclic voltammetric responses exhibited by **1** and **3**. Controlled-potential coulometric tests show the consumption of one, two, and three electrons per molecule for **1**−**3**, respectively. As confirmation of the stability of the cations [**1**]$^+$, [**2**]$^{2+}$, and [**3**]$^{3+}$, cyclic voltammograms recorded on the olive green solutions resulting from the exhaustive oxidation of the relevant neutral yellow-orange species display voltammetric profiles complementary to the original ones. Analysis[13] of the cyclic voltammetric responses exhibited by **1** with scan rate increasing from 0.02 to 1.00 V s^{-1} is diagnostic of a simple, electrochemically reversible, one-electron oxidation ($i_{p,c}/i_{p,a}$ is constantly equal to 1, $i_{p,a}v^{1/2}$ is constant and ΔE_p departs slightly from the theoretical value of 59 mV, as in the oxidation process of ferrocene).

Table 2 gives the electrochemical and the associated spectroscopic parameters of the complexes studied here. If the unsaturation of the ethynyl substituent can account for the fact that the electron removal from either ethynylferrocene[14−16] or **1** is more difficult than from unsubstituted ferrocene (as is the case for FcC≡CPh[17]), then the explanation of the slightly negative shift which occurs upon progressive insertion of ethynylferrocenyl units around the central benzene is less obvious. The resulting decrease in overall electronic unsaturation could stem either from the removal of the electron-withdrawing bromide substituents or from the electron delocalization within the central bis- or tris(ethynyl)benzene fragments. The fact that **2** and **3** exhibit single-step oxidation processes is of relevance, as this implies that the central benzenoid nucleus does not allow the relevant peripheral ferrocenyl subunits to communicate electronically with each other. This conclusion is further supported by the fact that all the complexes reported in Table 2 display roughly similar peak-to-peak separations (bearing in mind that they are likely to be affected by the presence of uncompensated solution resistances, as is evident from the oxidation step of ferrocene). For molecules with multiple, noninteracting sites a peak-to-peak separation matching that of a one-electron step is consistent with theory.[18] As expected, IVET transitions are not observed in the partially oxidized species, due to the presence of single-step multielectron processes.

Table 2. Formal Electrode Potentials (in V), Peak-to-Peak Separations (in mV), and Maximum Wavelengths of the Oxidized Species (in nm) Exhibited by the Present Ethynylferrocenes[a]

complex	$E^{\circ}_{0/+}$	ΔE_p[b]	$E^{\circ\prime}_{0/2+}$	ΔE_p[b]	$E^{\circ\prime}_{0/3+}$	ΔE_p[b]	λ_{max}
FcC≡CH	+0.53	97					698
1	+0.54	81					760
2			+0.51	88			762
3					+0.49	74	772
FcH	+0.39	95					628

[a] In dichloromethane solutions containing [NBu_4][PF_6] as supporting electrolyte (0.2 mol dm^{-3}). Fc = (C_5H_5)Fe(C_5H_4). [b] Measured at 0.2 V s^{-1}.

As far as bis(ferrocenyl) complexes related to **2** are concerned, 1,4-bis(β-ferrocenylvinyl)benzene also undergoes a single-step two-electron oxidation,[19] whereas 1,4-diferrocenylbutadiyne **(4)**, which lacks the benzene bridge between the two ferrocenylethynes, exhibits two separated (by about 100 mV) one-electron oxidations.[15] In the field of tris(ferrocene) molecules, it is worth noting that the closely related triferrocenylbenzene behaves similarly to **3** ($E^{\circ\prime}_{0/3+}$ = +0.1 V, vs Fc/Fc$^+$, in

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CH_2Cl_2 solution ($[NBu_4][BF_4]$ 0.1 mol dm^{-3})),[20] as do tris(ferrocene) molecules in which the ferrocene units are appended to triaza crown ether[21] or borazine[22] rings. In contrast, tris(ferrocenes) having ferrocenyl units either appended to cyclopropene[23] or linked to open-chain frames[24] display separated one-electron-oxidation steps. The lack of communication between the ferrocene units in similar systems has been noted previously[25] and the nature of the chain length and the element type between the units proven to be crucial.

Experimental Section

All preparations were carried out using standard Schlenk techniques.[26] All solvents were distilled over standard drying agents under nitrogen directly before use, and all reactions were carried out under an atmosphere of nitrogen. Alumina gel (neutral-grade II) was used for chromatographic separations.

All NMR spectra were recorded on Bruker instruments, operating at 250.1 MHz. Chemical shifts are reported in δ using $CDCl_3$ (^1H, δ 7.25 ppm) as reference. Infrared spectra were recorded using NaCl solution cells (CH_2Cl_2) using a Perkin-Elmer 1710 Fourier transform IR spectrometer. Mass spectra were recorded using positive FAB methods, on a Kratos MS60 spectrometer. Microanalyses were carried out in the Department of Chemistry, Imperial College of Science, Technology and Medicine. Materials and apparatus for electrochemical measurements have been described elsewhere.[27] All the potential values are referred to the saturated calomel electrode (SCE).

Representative Reaction To Synthesize 1−3. The following procedure is representative for all the reactions performed to synthesize compounds **1**−**3**, and only the ratio of the reagents or the scale of the reaction was changed, not the procedure itself. Catalytic amounts of CuI (0.010 g), $Pd(OAc)_2$ (0.011 g), and PPh_3 (0.030 g) in diisopropylamine (50 mL) were stirred at 0 °C for 10 min. The mixture was then treated with ethynylferrocene (0.100 g, 0.47 mmol) and 1,3,5-tribromobenzene (0.074 g, 0.23 mmol) and stirring continued at 0 °C for 1 h before warming to room temperature and then heating under reflux for 2 h. After filtration and evaporation to dryness, the residue was washed with dilute HCl, Na_2CO_3 (10%), and water and then subjected to column chromatography on alumina using a hexane−dichloromethane (4:1) solvent system. Successive bands of orange **1** (0.037 g, 36%), orange **2** (0.048 g, 36%), and orange-red **3** (0.020 g, 12%) were subsequently obtained as microcrystalline solids after removal of the solvent *in vacuo*.

Table 3. Crystal Data and Data Collection and Refinement Parameters for 1 and 3[a]

data	**1**	**3**
formula	$C_{18}H_{12}Br_2Fe$	$C_{42}H_{30}Fe_3$
solvent		0.5 PhH
fw	444.0	741.3
color, habit	orange-red prisms	thin yellow plates
cryst size (mm)	0.27 × 0.20 × 0.15	0.13 × 0.10 × 0.02
lattice type	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$
cell dimens		
a (Å)	9.352(1)	21.628(7)
b (Å)	14.165(1)	12.750(2)
c (Å)	11.856(1)	25.880(4)
β (deg)	93.39(1)	110.01(2)
V (Å^3)	1567.9(3)	6706(3)
Z	4	8
D_c (g cm^{-3})	1.881	1.468
$F(000)$	864	3048
radiation used	Mo Kα	Cu Kα[b]
μ (mm^{-1})	6.05	10.51
θ range (deg)	2.2−25.0	3.6−60.0
no. of unique reflns		
measd	2730	4591
obsd, $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	1572	2580
abs cor	semiempirical	semiempirical
max, min transmissn	0.27, 0.20	0.91, 0.48
no. of variables	190	431
R1[c]	0.049	0.072
wR2[d]	0.089	0.155
weighting factors A, B[e]	0.034, 0.217	0.064, 30.103
largest diff peak, hole (e Å^{-3})	0.44, −0.38	0.60, −0.68

[a] Details in common: graphite-monochromated radiation, ω-scans, Siemens P4 diffractometer, 293 K, refinement based on F^2. [b] Rotating-anode source. [c] $R1 = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [e] $w^{-1} = \sigma^2(F_o^2) + (AP)^2 + BP$.

1: mp 189−191 °C. Anal. Calcd for $C_{18}H_{12}FeBr_2$: C, 48.71; H, 2.73. Found: C, 48.64; H, 2.81. ν (C≡C) (cm^{-1}): 2211 (CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 4.25 (s, 5H, C_5H_5 ring), 4.28 (t, J = 2.0 Hz; 2H, H_3, H_4 Cp ring), 4.50 (t, J = 2.0 Hz; 2H, H_2, H_5 Cp ring), 7.55 (d, J = 1.3 Hz; 2H, H_2, H_6 Ph ring), 7.60 (d, J = 1.3 Hz; 1H, H_4 Ph ring). MS (FAB + ve): m/z (relative intensity, %) 444 (M$^+$, 40).

2: mp 217−220 °C dec. Anal. Calcd for $C_{30}H_{21}Fe_2Br$: C, 62.98; H, 3.77. Found: C, 63.30; H, 4.01. ν (C≡C) (cm^{-1}): 2216 (CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 4.24 (s, 10H, C_5H_5 ring), 4.25 (t, J = 2.0 Hz; 4H, H_3, H_4 Cp ring), 4.89 (t, J = 2.0 Hz; 4H, H_2, H_5 Cp ring), 7.51 (d, J = 1.3 Hz; 1H, H_4 Ph ring), 7.53 (d, J = 1.3 Hz; 2H, H_2, H_6 Ph ring). MS (FAB + ve): m/z (relative intensity, %) 574 (M$^+$, 4).

3: mp 254−256 °C dec. Anal. Calcd for $C_{42}H_{30}Fe_3$: C, 71.82; H, 4.34. Found: C, 71.70; H, 4.25. ν (C≡C) (cm^{-1}): 2214 (CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 4.24 (m, 21H, C_5H_5 rings and H_2, H_5 Cp ring), 4.49 (t, J = 2.0 Hz; 6H, H_3, H_4 Cp ring), 7.51 (s, 3H, H_2, H_4, and H_6 Ph ring). MS (FAB + ve): m/z (relative intensity, %) 702 (M$^+$, 3).

X-ray Crystallography. Table 3 provides a summary of the crystal data, data collection, and refinement parameters for **1** and **3**, which were solved by direct methods and the heavy-atom method, respectively. Except for the disordered solvent molecules in **3**, where the carbon atoms were refined isotropically, all of the non-hydrogen atoms in both structures were refined anistropically using full-matrix least squares based on F^2. All of the C−H hydrogen atoms in each structure were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system.[28]

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The crystallographic data (excluding structure factors) for the structures reported in Table 3 have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB12 1EZ U.K. (Fax, Int. code + (1223)336-033; e-mail, teched@chemcrys.cam.ac.uk.).

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Supporting Information Available: Tables of crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles for **1** and **3** (14 pages). Ordering information is given on any current masthead page.

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