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Synthesis and characterisation of monomeric, dimeric and polymeric ferrocenylacetylides. Crystal structure of 1,1′-bis(phenylethynyl)ferrocene

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Abstract

The reactions of alkynyltrimethylstannanes with 1,1′-dilithioferrocene have given several ferrocenylacetylides, namely 1-phenylethynyl-1′-iodo-ferrocene (1) 1,1′-bis(phenylethynyl)ferrocene (2), 1,4-di(1′-iodoferrocenylethynyl)benzene (3) and poly[1,4-(1′-ferrocenylethynyl)ethynylbenzene] (4). The versatility of this reaction for the formation of ferrocenylacetylides is demonstrated. The crystal structure of **2** has been determined, and shown to involve a linear array of the groups with a *cis* arrangement of the phenylethynyl ligands.

Key words: Ferrocene; Tin; Alkyne; Crystal structure; Polymer

1. Introduction

There is currently great interest in ferrocene-containing complexes owing to the rapid growth of material science. Metallocenes, and in particular ferrocene, have been of use in molecular ferromagnets [1,2], molecular sensors [3,4], electrochemical agents [5], and nonlinear optics [6,7]. Following our development of alkynyltrimethylstannanes as alkynylating reagents for formation of a wide range of transition metal acetylide complexes [8], our attention has focused on the synthesis of ferrocene-containing acetylides. Interest in ferrocenylacetylides has spanned several decades, mainly because of their use in the synthesis of more complicated organometallic compounds. Several methods [9–11] involve acetyl- or diacetyl-ferrocene as the starting material and conversion of the ketone group into an acetylenic one by various organic reactions. Coupling of iodo- and 1,1′-diiodo-ferrocene with cuprous phenylacetylide [9] or trimethylsilylacetylene [12] has also proved successful.

The synthesis of mono-, di- and poly-meric ferrocenylacetylides by use of alkynyltrimethylstannanes is reported below, along with the crystal structure of **2**, a ferrocenyl species with a phenylethynyl group attached to each cyclopentadienyl ring. It is hoped that the syntheses described will lead to greater versatility in the formation of ferrocenylacetylides.

2. Results and discussion

Over the last few years, reactions have been developed involving alkynyltrimethylstannanes and metal halides in order to form transition metal σ-acetylide mono-, oligo- and poly-meric complexes [8]. This route has proved to be very successful and we decided to extend this approach to the preparation of ferrocenyl halides in order to permit a study of the role of the metallocenyl fragments in the acetylide species.

The known compounds, 1-phenylethynyl-1′-iodo-ferrocene (1) and 1,1′-bis(phenylethynyl)ferrocene (2), were made in good yield from a reaction of 1,1′-diiodoferrocene with phenylalkynyltrimethylstannane in the presence of a palladium catalyst (Scheme 1). Depending on which compound is required, the choice of reaction time and/or quantities of reactants can be used to direct the reaction in either direction to result in an improved yield of the desired product. It should be noted that the reaction does not proceed when

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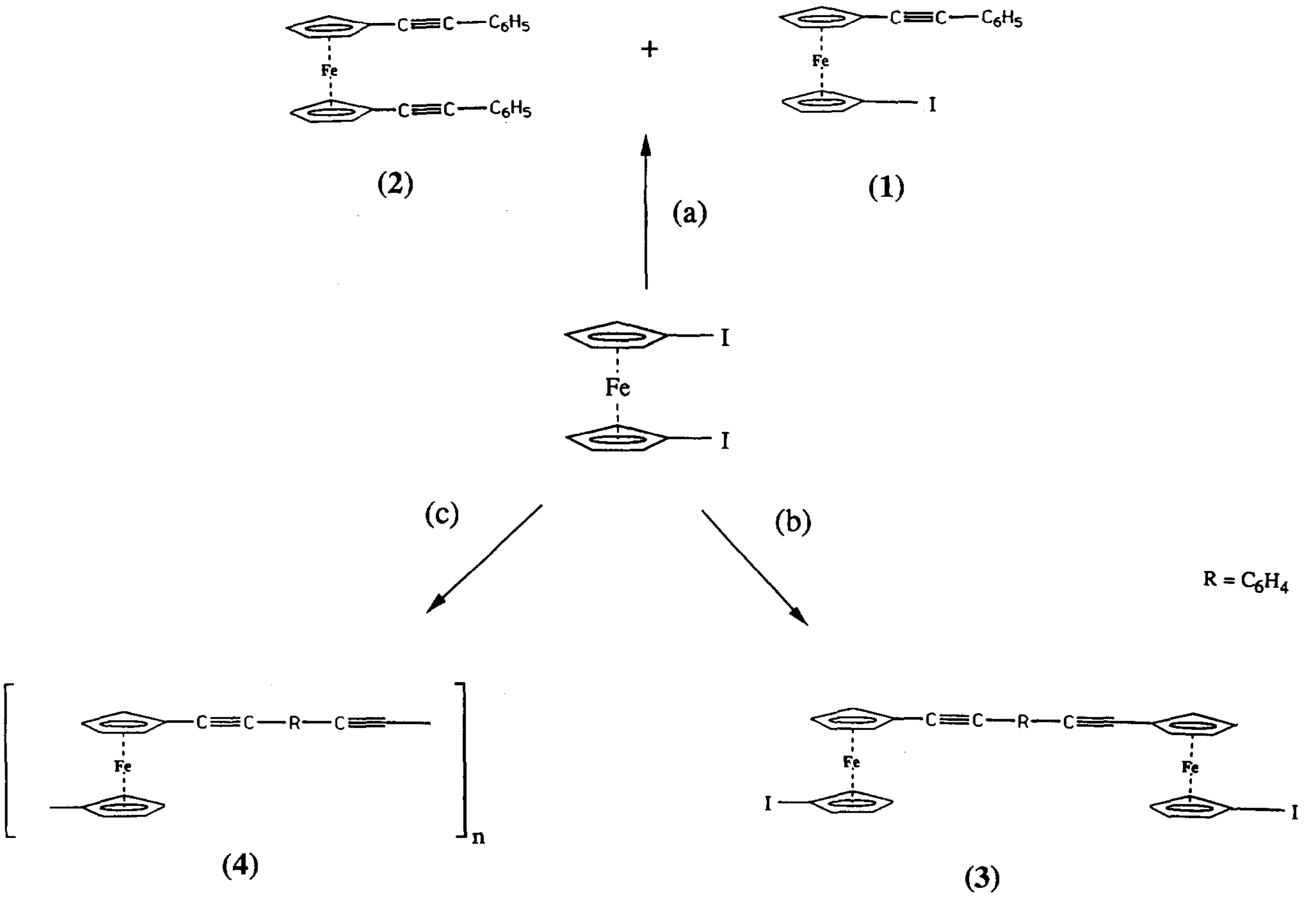

Scheme 1. (a) 2.5 equiv. $Me_3SnC{\equiv}CPh$ + $[Pd(PPh_3)_4]$ (2 mole-%); (b) 0.3 equiv. $Me_3SnC{\equiv}CC_6H_4C{\equiv}CSnMe_3$ + $[Pd(PPh_3)_4]$ (2 mole-%); (c) 1.0 equiv. $Me_3SnC{\equiv}CC_6H_4C{\equiv}CSnMe_3$ + $[Pd(PPh_3)_4]$ (2 mole-%).

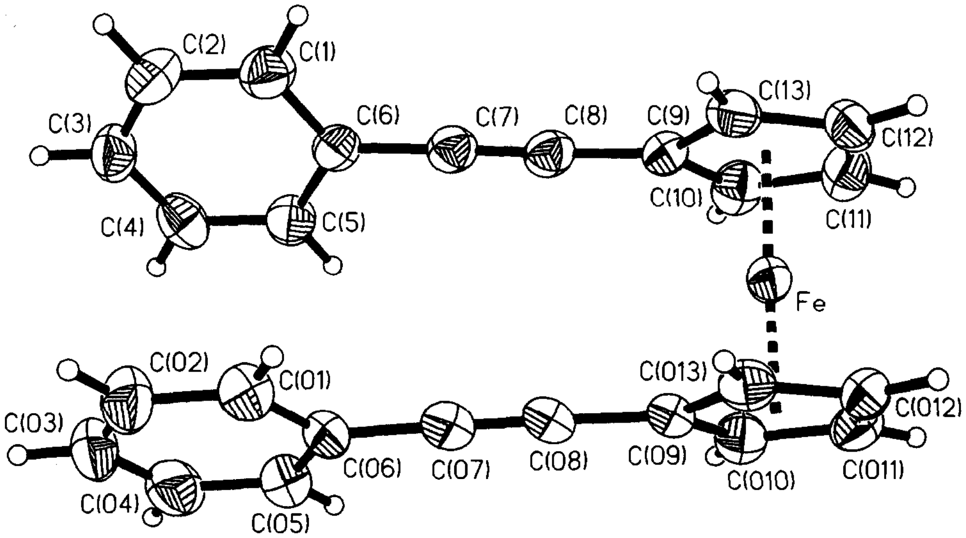

Fig. 1. Structure of 1,1′-bis(phenylethynyl)ferrocene (2).

bromoferrocene is used, although the nature of the halogen seems not to have presented a problem in the analogous reactions between alkynyltrimethylstannanes and transition metal halides.

In the preparation of 3, variation of the reaction conditions and quantities of reagents can again be used to direct the reaction to the preferred product. Compound **3** (and the following polymers **4**) is likely to be linear, since the benzene ring in the bis(acetylide) ligand ($Me_3SnC{\equiv}CC_6H_4C{\equiv}CSnMe_3$) is known to be substituted in the 1- and 4-positions. All the compounds (**1–3**) were characterised from their analytical data and mass, NMR and IR spectra. They are fairly stable, soluble in common organic solvents, and can be purified by column chromatography, but they should be stored under nitrogen as a precaution.

The reaction giving rise to formation of the polymeric products **4** appears to be very sensitive to the purity and relative quantities of the reactants and the reaction time. The temperature of the reaction mixture is no doubt also a factor, though this has yet to be fully investigated. The ratio of reagents has to be exactly 1 : 1, but if the reaction is carried out for 72 h a large amount of insoluble material is obtained. Reaction for a shorter time, such as 24, 6, or 3 h proved more fruitful and although the values of n are not large, the polymers show excellent solubility, and there is scope for a study of the optimum reaction conditions. The single, strong, $\nu(C{\equiv}C)$ absorption, though slightly broadened, indicates a *trans* orientation of the acetylenic units around the ferrocenyl moiety. Characterisation of these polymers and investigation of their physical properties is in progress.

The molecular structure of 1,1′-bis(phenylethynyl)ferrocene (**2**) is shown in Fig. 1. The relevant atomic coordinates, displacement parameters and bond distances and angles are listed in Tables 1–3. The structure consists of the ferrocenyl moiety containing two phenylethynyl-substituted cyclopentadienyl rings in a *cis* orientation. This is, perhaps, unexpected when considered in terms of steric hindrance, since a *trans* orientation of the phenylacetylide groups would involve less interaction and so should be preferred (this is obviously the case for the polymeric system). However, there is not a large tilting of the phenyl groups from the planes of the cyclopentadienyl rings, as illustrated in Fig. 2. The angles between the various ring planes are as follows: (a) phenyl ring [C(1)–C(6)] and cyclopentadienyl ring [C(9)–C(13)], 26.6(2)°; (b) phenyl ring [C(01)–C(06)] and cyclopentadienyl ring [(C(09)–C(13)], 11.2(2)°; (c) phenyl rings, 16.6(2)° and (d) cyclopentadienyl rings, 2.0(4)°. It seems that crystal packing forces result in adoption of the observed structure. The cyclopentadienyl rings are totally eclipsed and, as expected, both these and the phenyl rings are planar. In solution, of course, the phenyl and cyclopentadienyl rings are free to rotate.

TABLE 1. Atomic coordinates and equivalent isotropic displacement coefficients ($Å^2$) for $[Fe(CpCCPh)_2]$

	x	y	z	U_{eq}
Fe	0.11976(3)	−0.19212(4)	0.30315(4)	0.03297(14)
C(1)	0.2465(2)	0.3591(3)	0.5067(3)	0.0486(8)
C(2)	0.2996(2)	0.4438(3)	0.5805(3)	0.0525(9)
C(3)	0.3240(2)	0.4233(3)	0.7034(3)	0.0489(8)
C(4)	0.2954(2)	0.3192(3)	0.7525(3)	0.0487(8)
C(5)	0.2438(2)	0.2325(3)	0.6799(3)	0.0422(8)
C(6)	0.2193(2)	0.2507(3)	0.5548(3)	0.0364(7)
C(7)	0.1689(2)	0.1575(3)	0.4777(3)	0.0387(7)
C(8)	0.1303(2)	0.0776(3)	0.4129(3)	0.0382(7)
C(9)	0.0819(2)	−0.0129(3)	0.3333(3)	0.0360(7)
C(10)	0.0207(2)	−0.1011(3)	0.3626(3)	0.0450(8)
C(11)	−0.0146(2)	−0.1707(3)	0.2568(3)	0.0515(9)
C(12)	0.0238(2)	−0.1281(3)	0.1621(3)	0.0489(9)
C(13)	0.0837(2)	−0.0314(3)	0.2075(3)	0.0408(7)
C(01)	0.4506(2)	0.1079(3)	0.5914(3)	0.0491(9)
C(02)	0.5028(2)	0.1884(3)	0.6709(4)	0.0604(10)
C(03)	0.5074(2)	0.1799(3)	0.7934(4)	0.0628(11)
C(04)	0.4586(2)	0.0911(3)	0.8378(3)	0.0600(10)
C(05)	0.4052(2)	0.0103(3)	0.7597(3)	0.0500(8)
C(06)	0.4006(2)	0.0171(3)	0.6347(3)	0.0407(7)
C(07)	0.3445(2)	−0.0667(3)	0.5521(3)	0.0425(8)
C(08)	0.2993(2)	−0.1370(3)	0.4849(3)	0.0393(7)
C(09)	0.2447(2)	−0.2240(3)	0.4062(3)	0.0343(7)
C(010)	0.1810(2)	−0.3056(3)	0.4406(3)	0.0427(7)
C(011)	0.1422(2)	−0.3778(3)	0.3369(3)	0.0475(8)
C(012)	0.1801(2)	−0.3404(3)	0.2394(3)	0.0433(8)
C(013)	0.2424(2)	−0.2453(3)	0.2806(3)	0.0389(7)

The carbon–carbon distances in the cyclopentadienyl rings vary from 1.403(5) to 1.435(4) Å and the C–C–C angles range between 106.9(2) and 108.6(3)°. Both sets of values agree well with those for other ferrocenyl compounds [13–15], as do the iron–carbon distances (2.035(3)–2.063(3) Å).

The acetylide bonds have lengths of 1.199(4) and 1.185(4) Å, and are in accord with those observed for

TABLE 2. Bond lengths (Å) for $[Fe(CpCCPh)_2]$

Fe–C(010)	2.035(3)	C(3)–C(4)	1.364(5)	C(02)–C(03)	1.367(5)
Fe–C(11)	2.040(3)	C(4)–C(5)	1.375(4)	C(03)–C(04)	1.376(5)
Fe–C(12)	2.042(3)	C(5)–C(6)	1.390(4)	C(04)–C(05)	1.375(5)
Fe–C(013)	2.045(3)	C(6)–C(7)	1.438(4)	C(05)–C(06)	1.394(4)
Fe–C(10)	2.045(3)	C(7)–C(8)	1.199(4)	C(06)–C(07)	1.441(4)
Fe–C(011)	2.048(3)	C(8)–C(9)	1.420(4)	C(07)–C(08)	1.185(4)
Fe–C(13)	2.049(3)	C(9)–C(10)	1.427(4)	C(08)–C(09)	1.430(4)
Fe–C(012)	2.052(3)	C(9)–C(13)	1.435(4)	C(09)–C(013)	1.424(4)
Fe–C(09)	2.053(3)	C(10)–C(11)	1.412(4)	C(09)–C(010)	1.432(4)
Fe–C(9)	2.063(3)	C(11)–C(12)	1.403(5)	C(010)–C(011)	1.421(4)
C(1)–C(2)	1.377(4)	C(12)–C(13)	1.412(4)	C(011)–C(012)	1.408(5)
C(1)–C(6)	1.388(4)	C(01)–C(02)	1.374(5)	C(012)–C(013)	1.412(4)
C(2)–C(3)	1.370(5)	C(01)–C(06)	1.396(4)		

the iron(II) and ruthenium(II) bis-acetylide complexes previously reported [16–18]. This indicates that the bond length is much the same whether the acetylenic group is bonded to a metal or to a cyclopentadienyl ring in a metallocene.

We are now in a position to synthesise more ferrocenyl systems containing acetylenic bonds. Current investigations include studies of (a) donor–acceptor systems for second order non-linear optics, where the ferrocenyl group acts as an electron donor, and (b) transition metal σ-acetylide systems incorporating ferrocenyl moieties, in the hope of introducing useful properties in respect of stability and photo- and electro-chemical behaviour.

3. Experimental details

3.1. General

All preparations were carried out by standard Schlenk techniques [19]. All solvents were freshly distilled, dried and degassed before use and all reactions were performed under purified nitrogen. The following compounds were prepared by published methods; 1,1′-diiodoferrocene [20], $Me_3SnC{\equiv}CPh$ [21] and $Me_3SnC{\equiv}CC_6H_4C{\equiv}CSnMe_3$ [22]. $[Pd(PPh_3)_4]$ was purchased (Strem).

Infrared and mass spectra were recorded with CH_2Cl_2 solutions on a Perkin-Elmer 1710 Fourier transform spectrometer and a Kratos MS890 spectrometer, respectively. ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer for $CDCl_3$ solutions, with solvent resonances used as references. Elemental analyses were carried out in this Department. Molecular weights were determined by Gel Permeation Chromatography [23].

3.2. Synthesis of Compounds

3.2.1. 1-phenylethynyl-1′-iodo-ferrocene (1) and 1,1′-bis(phenylethynyl)ferrocene (2)

To a stirred (orange) solution of 1,1′-diiodoferrocene (0.25 g, 0.57 mmol) in tetrahydrofuran (20 ml) was

TABLE 3. Bond angles (°) for $[Fe(CpCCPh)_2]$

C(010)–Fe–C(11)	122.81(14)	C(13)–Fe–C(09)	123.58(12)	C(11)–C(12)–Fe	69.8(2)
C(010)–Fe–C(12)	158.80(13)	C(012)–Fe–C(09)	68.02(12)	C(13)–C(12)–Fe	70.0(2)
C(11)–Fe–C(12)	40.19(14)	C(010)–Fe–C(9)	122.49(12)	C(12)–C(13)–C(9)	107.9(3)
C(010)–Fe–C(013)	68.66(13)	C(11)–Fe–C(9)	68.16(12)	C(12)–C(13)–Fe	69.6(2)
C(11)–Fe–C(013)	156.54(13)	C(12)–Fe–C(9)	68.20(12)	C(9)–C(13)–Fe	70.1(2)
C(12)–Fe–C(013)	122.25(14)	C(013)–Fe–C(9)	125.74(12)	C(02)–C(01)–C(06)	120.3(3)
C(010)–Fe–C(10)	107.21(14)	C(10)–Fe–C(9)	40.64(12)	C(03)–C(02)–C(01)	120.6(4)
C(11)–Fe–C(10)	40.44(13)	C(011)–Fe–C(9)	157.38(13)	C(02)–C(03)–C(04)	119.9(3)
C(12)–Fe–C(10)	67.95(14)	C(13)–Fe–C(9)	40.84(11)	C(05)–C(04)–C(03)	120.5(4)
C(013)–Fe–C(10)	162.09(12)	C(012)–Fe–C(9)	161.65(13)	C(04)–C(05)–C(06)	120.3(3)
C(010)–Fe–C(011)	40.74(12)	C(09)–Fe–C(9)	109.16(11)	C(05)–C(06)–C(01)	118.5(3)
C(11)–Fe–C(011)	106.25(14)	C(2)–C(1)–C(6)	120.8(3)	C(05)–C(06)–C(07)	120.7(3)
C(12)–Fe–C(011)	122.56(13)	C(3)–C(2)–C(1)	120.3	C(01)–C(06)–C(07)	120.8(3)
C(013)–Fe–C(011)	68.05(13)	C(4)–C(3)–C(2)	119.9(3)	C(08)–C(07)–C(06)	179.0(3)
C(10)–Fe–C(011)	120.97(14)	C(3)–C(4)–C(5)	120.93	C(07)–C(08)–C(09)	178.5(3)
C(010)–Fe–C(13)	159.05(12)	C(4)–C(5)–C(6)	120.1(3)	C(013)–C(09)–C(08)	127.1(3)
C(11)–Fe–C(13)	67.94(14)	C(1)–C(6)–C(5)	118.3(3)	C(013)–C(09)–C(010)	107.3(3)
C(12)–Fe–C(13)	40.38(12)	C(1)–C(6)–C(7)	121.4(3)	C(08)–C(09)–C(010)	125.5(3)
C(013)–Fe–C(13)	108.93(13)	C(5)–C(6)–C(7)	120.3(3)	C(013)–C(09)–Fe	69.3(2)
C(10)–Fe–C(13)	68.32(13)	C(8)–C(7)–C(6)	177.2(3)	C(08)–C(09)–Fe	126.6(2)
C(011)–Fe–C(13)	159.38(13)	C(7)–C(8)–C(9)	177.4(3)	C(010)–C(09)–Fe	68.8(2)
C(010)–Fe–C(012)	68.16(13)	C(8)–C(9)–C(10)	126.4(3)	C(011)–C(010)–C(09)	107.8(3)
C(11)–Fe–C(012)	120.77(13)	C(8)–C(9)–C(13)	126.6(3)	C(011)–C(010)–Fe	70.1(2)
C(12)–Fe–C(012)	107.37(13)	C(10)–C(9)–C(13)	106.9(3)	C(09)–C(010)–Fe	70.2(2)
C(013)–Fe–C(012)	40.32(12)	C(8)–C(9)–Fe	127.92	C(012)–C(011)–C(010)	108.13
C(10)–Fe–C(012)	155.99(13)	C(10)–C(9)–Fe	69.0(2)	C(012)–C(011)–Fe	70.1(2)
C(011)–Fe–C(012)	40.16(13)	C(13)–C(9)–Fe	69.0(2)	C(010)–C(011)–Fe	69.2(2)
C(13)–Fe–C(012)	124.37(13)	C(11)–C(10)–C(9)	108.2(3)	C(011)–C(012)–C(013)	108.6(3)
C(010)–Fe–C(09)	41.00(12)	C(11)–C(10)–Fe	69.6(2)	C(011)–C(012)–Fe	69.8(2)
C(11)–Fe–C(09)	160.49(14)	C(9)–C(10)–Fe	70.4(2)	C(013)–C(012)–Fe	69.5(2)
C(12)–Fe–C(09)	158.50(13)	C(12)–C(11)–C(10)	108.5(3)	C(012)–C(013)–C(09)	108.1(3)
C(013)–Fe–C(09)	40.68(11)	C(12)–C(11)–Fe	70.0(2)	C(012)–C(013)–Fe	70.1(2)
C(10)–Fe–C(09)	124.92(12)	C(10)–C(11)–Fe	70.0(2)	C(09)–C(013)–Fe	70.0(2)
C(011)–Fe–C(09)	68.38(12)	C(11)–C(12)–C(13)	108.5(3)		

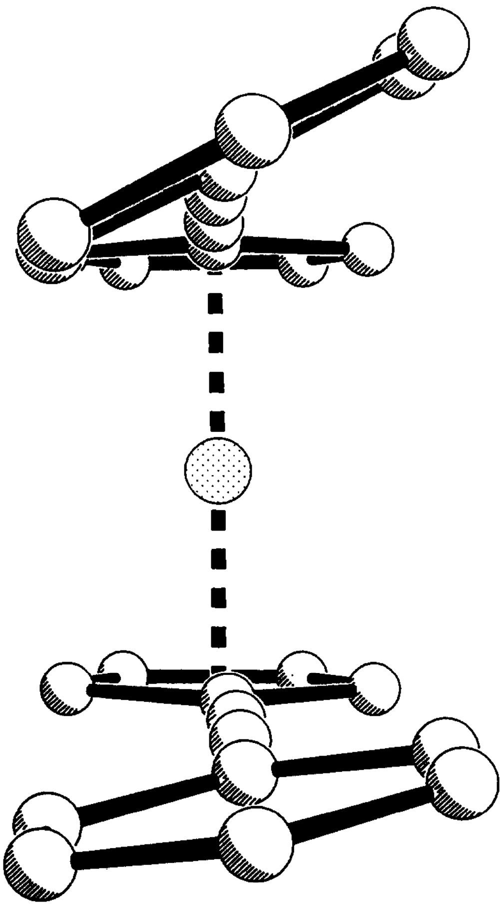

Fig. 2. Another view of the structure of 2, showing the planes of the rings.

added $Me_3SnC{\equiv}CPh$ (0.37 g, 1.40 mmol) followed by $Pd(PPh_3)_4$ (0.013 g, 0.0113 mmol (2% molar)). The mixture was stirred at 75°C for 20 h during which the solution darkened and gave a dark red-brown suspension. The suspension was evaporated to dryness, then subjected to dry column chromatography on neutral grade II alumina. Elution with hexane gave an orange band containing unchanged starting material 1,1'-diiodoferrocene. Elution with hexane : dichloromethane (75 : 25) then gave a yellow-orange band, which was evaporated to dryness to leave **1**, an orange oil (0.082 g, 35%). Anal. Found: C, 54.32; H, 3.51. $C_{18}H_{13}FeI$ calc.: C, 52.43; H, 3.16%. Mass Spectrum (EI) M^+ 412. IR $\nu(C{\equiv}C)$ (CH_2Cl_2) 2209 cm^{-1}. ^1H NMR $(CDCl_3)$ 4.22 (2H, t, $^3J(H-H)$ 1.84 Hz, C_5H_4), 4.25 (2H, t, $^3J(H-H)$ 1.87, C_5H_4), 4.44 (2H, t, $^3J(H-H)$ 1.81, C_5H_4), 4.47 (2H, t, $^3J(H-H)$ 1.89, C_5H_4), 7.30–7.34 (3H, m, C_6H_5) and 7.49–7.53 (2H, m, C_6H_5).

Continued elution with hexane : dichloromethane (75 : 25) produced another orange band, which was collected and evaporated to dryness to leave **2**, an orange-red solid (0.112 g, 51%) m.p. 173–174°C. Anal. Found: C, 80.60; H, 4.62. $C_{26}H_{18}Fe$ calc.: C, 80.83; H, 4.66%. Mass Spectrum (EI) M^+ 386. IR $\nu(C{\equiv}C)$ (CH_2Cl_2) 2210 cm^{-1}. ^1H NMR $(CDCl_3)$ 4.32 (4H, t, $^3J(H-H)$ 1.80 Hz, C_5H_4), 4.54 (4H, t, $^3J(H-H)$ 1.79, C_5H_4), 7.28–7.30 (6H, m, C_6H_5) and 7.40–7.46 (4H, m, C_6H_5).

3.2.2. *1,4-di(1'-iodoferrocenylethynyl)benzene (3)*

The procedure used here was very similar to that described in 3.2.1, except that a 3 : 1 mol ratio of 1,1'-diiodoferrocene to $1,4\text{-}(Me_3SnC{\equiv}C)C_6H_4$ bisacetylide ligand was used. After 20 h, the crude mixture was again subjected to dry column chromatography on neutral grade II alumina. On elution with hexane, the first band contained unchanged starting material. Further elution with hexane gave a yellow band which was collected and evaporated to dryness to leave an orange solid (0.025 g, 14%). Analytical, mass spectral, infrared and ^1H NMR data indicated that this compound was an unexpected product resulting from a rearrangement of the catalyst and had formula $[Fe(\eta\text{-}C_5H_5)_2C{\equiv}CC_6H_4C{\equiv}CC_6H_5]$ (since neither the mechanism for this reaction nor the reproducibility of this reaction are known, it will not be discussed here). Elution with hexane : dichloromethane (75 : 25) gave an orange band, which was evaporated to dryness to leave **3**, an orange-red solid (0.128 g, 57%) m.p. 195–200°C (decomp.). Anal. Found: C, 48.50; H, 2.74. $C_{30}H_{20}FeI_2$ calc.: C, 48.26; H, 2.68%. Mass Spectrum (EI) M^+ 746. IR $\nu(C{\equiv}C)$ (CH_2Cl_2) 2206 cm^{-1}. ^1H NMR $(CDCl_3)$ 4.26 (4H, t, $^3J(H-H)$ 1.85 Hz, C_5H_4), 4.30 (4H, t, $^3J(H-H)$ 1.85, C_5H_4), 4.46 (4H, t, $^3J(H-H)$ 1.83, C_5H_4), 4.48 (4H, t, $^3J(H-H)$ 1.85, C_5H_4) and 7.47 (4H, s, C_6H_4).

3.2.3. *Poly[1,4-(1'-ferrocenylethynyl)ethynylbenzene] (4)*

To a stirred solution of 1,1'-diiodoferrocene (0.088 g, 0.2 mmol) in tetrahydrofuran (20 ml) was added $Me_3SnC{\equiv}CC_6H_4C{\equiv}CSnMe_3$ (0.090 g, 0.2 mmol) followed by $Pd(PPh_3)_4$ (0.005 g, 0.004 mmol (2% molar)). The mixture was stirred at 75°C for 24 h and the resulting red-brown suspension was then evaporated to dryness. The residue was dissolved in CH_2Cl_2 the solution was filtered and the filtrate was concentrated *in vacuo* to small volume. After repeated precipitation with hexane, an orange-brown solid (**4**) was obtained (0.048 g, 78%). m.p. 220–230°C (decomp.), * IR $\nu(C{\equiv}C)$

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* Analyses obtained for these ferrocenyl polymers were unsatisfactory. However, this is a common occurrence [24] with the carbon values notoriously low due to incomplete oxidation and formation of carbides and ceramics in the analytical process.

(CH_2Cl_2) 2208–2210 cm^{-1} (broad). $M_w = 4692$ (n = 15). ^1H NMR ($CDCl_3$) 4.23–4.55 (8H, m, C_5H_4) and 7.27–7.67 (4H, m, C_6H_4).

The reaction time was varied to give different lengths of polymers; (a) 3 days, no soluble polymeric species, (b) 6 h, $M_w = 1978$, (c) 3 h, $M_w = 5491$.

3.3. Crystal structure determination

The crystals of **2** used for X-ray diffraction were grown by two-layer crystallisation from a hexane : dichloromethane (1 : 1) mixture.

Crystal data for $C_{26}H_{18}Fe$: $M = 386.25$, monoclinic, space group $P2_1/c$, $a = 15.434(3)$, $b = 10.754(2)$, $c = 11.246(2)$ Å, $\beta = 102.46(3)°$, $V = 1822.6(6)$ Å^3, $Z = 4$, $D_c = 1.408$ g cm^{-3}, $F(000) = 800$, λ(Mo-Kα) = 0.034 mm^{-1}.

An orange block shaped crystal of approximate dimensions 0.10 × 0.40 × 0.40 mm was mounted on a glass fibre. Accurate lattice parameters were determined from 25 reflections ($\theta = 22.50–24.13°$). Intensity data were measured with a Rigaku AFC7R diffractometer using monochromated Mo-K_α radiation and $\omega/2\theta$ scan mode to a maximum value for θ of 25.0°. Three standard reflections were monitored after every 100 reflections and showed a decrease in standard intensity during the data collection time of 6.78%, this decay was corrected by assuming linear decay. A total of 3391 reflections were measured within the range $-18 \le h \le 17, -12 \le k \le 0, 0 \le l \le 13$ and averaged to yield 3212 unique reflections ($R_{int} = 0.0372$) of which 2198 were judged as significant by the criterion that ${F_{obs}}^2 > 2\sigma({F_{obs}}^2)$. Corrections for Lorentz and polarisation effects were applied. Absorption corrections were applied by the use of semi-empirical ψ scans (minimum and maximum transmission coefficients 0.789 and 0.998 respectively). Structure solution was by a combination of Patterson methods and Fourier techniques. Hydrogen atoms were placed in calculated positions with the thermal parameters free to refine. Anisotropic thermal motion was assumed for all non-hydrogen atoms. Full matrix least-squares refinement on ${F_{obs}}^2$ for 3212 data and 262 parameters converged to $wR2 = 0.0973$ (all data), conventional $R1 = 0.0354$ (observed data), $(\Delta/\sigma)_{max} = 0.001$, GOF (all data) = 1.027. The function minimised was $\Sigma w({F_{obs}}^2 - {F_{calc}}^2)^2$, $w = 1/[\sigma^2({F_{obs}}^2) + (0.0387P)^2 + 0.7051P]$ where $P = ({F_{obs}}^2 + 2{F_{calc}}^2)/3$ and σ was obtained from counting statistics. A final difference electron density Fourier synthesis revealed maximum and minimum residual electron density peaks of 0.321 and -0.255 e Å^{-3}.

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