

Carbon-rich organometallics: synthesis and characterization of new ferrocenyl end-capped bis(butadiynyl) fluorene derivatives

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Abstract

A new series of ferrocenyl end-capped bis(butadiynyl) fluorene complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}\equiv\text{CC}\equiv\text{C}(\text{R})\text{C}\equiv\text{CC}\equiv\text{C}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$ (R = fluoren-9-one-2,7-diyl, **1**; 9,9-dihexylfluorene-2,7-diyl, **2**; 9-ferrocenylmethylenefluorene-2,7-diyl, **3**; 9-ferrocenylphenylmethylenefluorene-2,7-diyl, **4**) have been synthesized in moderate yields by the oxidative coupling reactions of ethynylferrocene with half equivalents of the appropriate diethynylfluorene derivatives. All the new complexes have been characterized by FTIR, NMR and UV–vis spectroscopies and fast atom bombardment mass spectrometry. The molecular structures of selected molecules have been determined by X-ray crystallographic techniques. The electronic absorption and redox properties of these carbon-rich molecules were investigated and the data were compared with those for the corresponding 2,7-bis(ferrocenylethynyl)fluorene counterparts. Cyclic voltammetry indicates that the half-wave potential of the terminal ferrocenyl moieties becomes more anodic when the number of ethynyl units increases and when the 9-substituent of the central fluorene ring changes from an electron-donating group to an electron-deficient group.

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1. Introduction

The past few decades have witnessed an increasing research interest in developing carbon-rich organometallic systems containing rigid, π -conjugated fragments [1]. Molecules containing long unsaturated carbon atom chains capable of transmitting electrons have been proposed for use as molecular wires for the construction of nanoscale electronic devices [2]. It has been shown that molecular wires comprising mixed-valence bimetallic units or remote electroactive organometallic components linked by all-carbon chains could be used in molecular electronics, optoelectronics and chemical sensing devices [3]. Since the first report of the mixed-valence ion of diferrocenylacetylene in the early 1974 [4],

interest in ferrocenyl-coordinated conjugated di- and polyynes as models for materially useful compounds becomes very intense and much research efforts have been devoted to the molecular design of ferrocene-derived homo- and heterometallic molecular scaffolds spaced by various aromatic and heteroaromatic units [5]. Recent works to prepare and evaluate the properties of molecular wires have provided some very promising results [6]. Among these, Adams et al. [7] have studied extensively the coordination chemistry of various ferrocenyl-capped oligoynes towards metal cluster complexes and the electrocommunication between ferrocenyl groups in these compounds.

Our research group has recently developed rational synthetic routes to some well-defined bis(ferrocenylethynyl) complexes and their heterometallic analogues with bridging units such as oligothiophenes and functionalized 2,7-fluorenes [8]. X-ray crystal structures of several

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of these molecules in the solid-state were determined in which iron-iron through-space separations of ca. 32–42 Å can be obtained [8b,c,d]. While previous work in this area only highlighted on the use of monoalkynyl unit, it seemed an attractive goal to us to develop new molecular architectures based on the more extended 1,3-butadiynyl C_4 chain, and such a study will act as a spur to synthetic chemists working on the design of carbon-rich organometallics. In view of the fact that alkynyl ligands can offer structural rigidity and have great potentials to allow electronic communication between redox-active terminal end groups through delocalized bonds [9], we report in this article the synthesis, characterization, redox and structural properties of a new series of carbon-rich ferrocenyl-capped bis(butadiynyl) complexes containing various fluorene-based spacers. The spectroscopy and electrochemistry of these compounds were discussed as a function of the length of alkynyl bridges and the electronic effect of the Z moiety of fluorene unit (Chart 1).

2. Results and discussion

2.1. Synthesis

Following the classical Hay- or Eglinton-type synthetic procedures [10], the oxidative coupling reaction of 4-ethynylferrocene with a series of 2,7-diethynylfluorene derivatives in a feed mole ratio of 2:1 under a $Cu(OAc)_2/O_2$ /pyridine system gave 2,7-bis(ferrocenylbutadiynyl)fluoren-9-one (**1**), 2,7-bis(ferrocenylbutadiynyl)-9,9-dihexylfluorene (**2**), 2,7-bis(ferrocenylbutadiynyl)-9-ferrocenylmethylenefluorene (**3**) and 2,7-bis(ferrocenylbutadiynyl)-9-ferrocenylphenylmethylenefluorene (**4**) as the major products, accompanied by the inevitable formation of 1,4-bis(ferrocenyl)butadiyne as a side product under such aerobic experimental conditions (Scheme 1). However, attempts to make a similar complex with the unsubstituted fluorene ring using 2,7-diethynylfluorene have met with little success and only compound **1** can be isolated probably due to the simultaneous oxidation of fluorene to fluoren-9-one under such air atmosphere. To evaluate the effect of $-(C\equiv C)_n-$ units ($n = 1, 2$) on the molecular properties, we have also prepared some 2,7-bis(ferrocenylethynyl)fluorene counterparts **5–8** ($n = 1$) similar to **1–4** ($n = 2$) using the Sonogashira coupling of ethynylferrocene with the corresponding dibromofluorene derivatives (Scheme 2) [5b,8]. The synthesis of 2,7-bis(ferrocenylethynyl)fluoren-9-one (**5**) and 2,7-bis(ferrocenylethynyl)-9-ferrocenylmethylenefluorene (**7**) was known [8a]. New compounds, 2,7-bis(ferrocenylethynyl)-9,9-dihexylfluorene (**6**) and 2,7-bis(ferrocenylethynyl)-9-ferrocenylphenylmethylenefluorene (**8**) can be isolated similarly in good yields in the present work. In the preparation of **8**, another monosubstituted product 2-bromo-7-ferrocenylethynyl-9-ferrocenylphenylmethylenefluorene (**9**) was also formed in 23% yield. Each of these reactions was readily monitored by thin-layer chromatography (TLC) and solution IR spectroscopy. These products can be purified by preparative TLC on silica and exhibit good air stability and solubility in common organic solvents. The proposed formulations of the new complexes were all in accord with their analytical and spectroscopic (FTIR, NMR and MS) data and the molecular structures of **1**, **4** and **9** have been studied by single-crystal X-ray analyses.

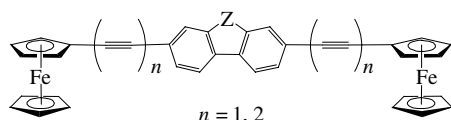
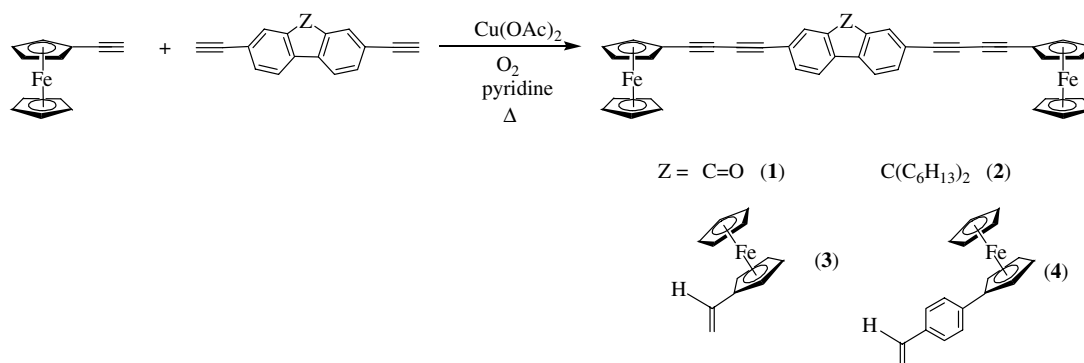


Chart 1.

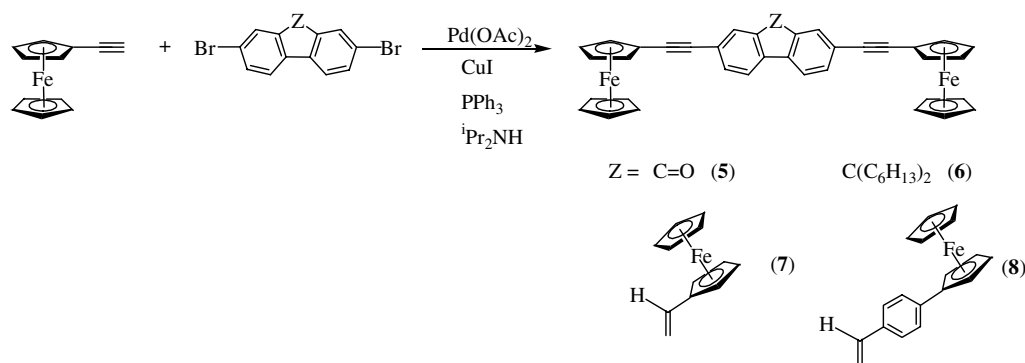


Scheme 1.

nyl)-9-ferrocenylmethylenefluorene (**3**) and 2,7-bis(ferrocenylbutadiynyl)-9-ferrocenylphenylmethylenefluorene (**4**) as the major products, accompanied by the inevitable formation of 1,4-bis(ferrocenyl)butadiyne as a side product under such aerobic experimental conditions (Scheme 1). However, attempts to make a similar complex with the unsubstituted fluorene ring using 2,7-diethynylfluorene have met with little success and only compound **1** can be isolated probably due to the simultaneous oxidation of fluorene to fluoren-9-one under such air atmosphere. To evaluate the effect of $-(C\equiv C)_n-$ units ($n = 1, 2$) on the molecular properties, we have also prepared some 2,7-bis(ferrocenylethynyl)fluorene counterparts **5–8** ($n = 1$) similar to **1–4** ($n = 2$) using the Sonogashira coupling of ethynylferrocene with the corresponding dibromofluorene derivatives (Scheme 2) [5b,8]. The synthesis of 2,7-bis(ferrocenylethynyl)fluoren-9-one (**5**) and 2,7-bis(ferrocenylethynyl)-9-ferrocenylmethylenefluorene (**7**) was known [8a]. New compounds, 2,7-bis(ferrocenylethynyl)-9,9-dihexylfluorene (**6**) and 2,7-bis(ferrocenylethynyl)-9-ferrocenylphenylmethylenefluorene (**8**) can be isolated similarly in good yields in the present work. In the preparation of **8**, another monosubstituted product 2-bromo-7-ferrocenylethynyl-9-ferrocenylphenylmethylenefluorene (**9**) was also formed in 23% yield. Each of these reactions was readily monitored by thin-layer chromatography (TLC) and solution IR spectroscopy. These products can be purified by preparative TLC on silica and exhibit good air stability and solubility in common organic solvents. The proposed formulations of the new complexes were all in accord with their analytical and spectroscopic (FTIR, NMR and MS) data and the molecular structures of **1**, **4** and **9** have been studied by single-crystal X-ray analyses.

2.2. Spectroscopic and structural characterization

All the butadiynyl compounds **1–4** display two weak to moderate $\nu(C\equiv C)$ absorptions in their IR spectra at around 2144 and 2213 cm^{-1} , which is obviously different



Scheme 2.

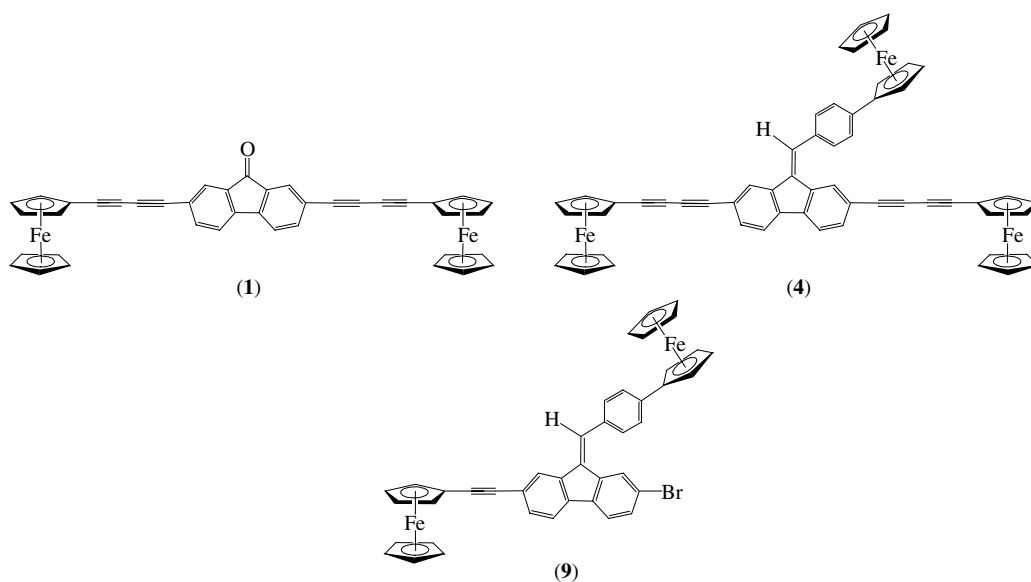


Chart 2.

from the monoyne counterparts **5–8** where only one $\nu(\text{C}\equiv\text{C})$ peak at about 2207 cm^{-1} is observed in each case. The symmetrical nature of complexes **1**, **2**, **5** and **6** was evident from their ^1H NMR spectral pattern and proton signals stemming from the ferrocenyl and fluorenyl groups were clearly noted. The ^1H NMR spectral features of the triferrocenyl molecules **3**, **4**, **7** and **8** showed the presence of ferrocenyl, fluorenyl and vinyl protons in an unsymmetrical environment. The chemical structures of selected compounds were also confirmed by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy which show four resonances of sp carbon atoms. The fast atom bombardment mass spectrometry (FABMS) and elemental analytical data further support the formulae of these compounds.

Single-crystal X-ray analyses were carried out for **1**, **4** and **9** to affirm their solid-state geometries (Chart 2). A perspective view of the molecular structure of **1** is depicted in Fig. 1, which includes the atom-numbering scheme. Important bond parameters along with selected dihedral angles are tabulated in Table 1. The structure

of **1** consists of two ferrocenyl-1,3-butadiyne end groups appended to the central fluorenone unit at the 2,7-positions via C(14)–C(15) and C(21)–C(28) bonds. To our knowledge, this represents the first structurally characterized example of such bis(ferrocenylbutadiynyl)arylene species in the literature. An iron–iron through-space separation of ca. 21.9 \AA was estimated in **1** which was found to be longer than that of 17.5 \AA in **5** by 4.4 \AA [8a]. The two 1,3-butadiyne linear chains are essentially linear with C–C–C bond angles lying within $175.9(3)$ – $177.2(3)^\circ$. The C–C triple bonds spanning the narrow range of $1.182(3)$ – $1.195(3)\text{ \AA}$ are of the order of those observed in 1,4-diferrocenyl-1,3-butadiyne ($1.198(4)\text{ \AA}$) [11], 1,4-bis(4-ferrocenylphenyl)butadiyne ($1.184(8)\text{ \AA}$) [8d] and 1,12-bis(ferrocenyl)-1,3,5,7,9,11-dodecaheptyne ($1.196(9)$ – $1.224(10)\text{ \AA}$) [7d]. The fluorenone diyl ring system is planar with a mean deviation from the plane of 0.009 \AA . In both ferrocenyl moieties, the C_5 rings are essentially parallel, inclined by 3.0° for Fe(1) and 2.4° for Fe(2). The deviation of the five-membered

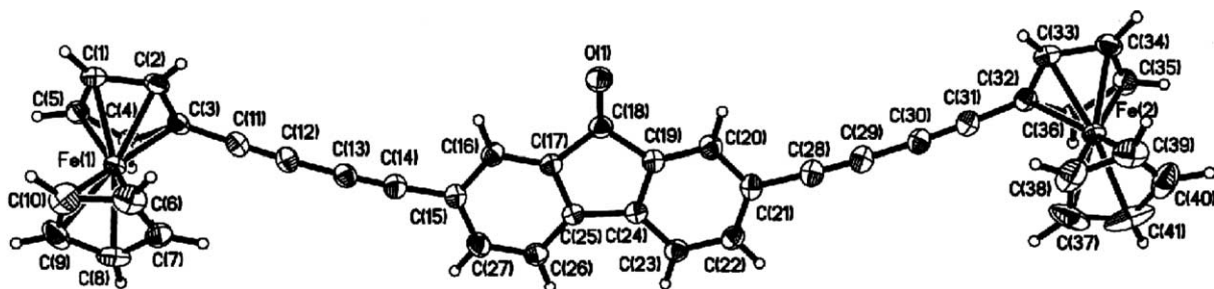


Fig. 1. A perspective view of **1**, showing the atomic labelling scheme.

Table 1
Selected bond lengths (Å) and angles (°) for complex **1**

Fe(1)–C ₅ H ₅	1.6517	Fe(1)–C ₅ H ₄	1.6374
Fe(2)–C ₅ H ₅	1.6495	Fe(2)–C ₅ H ₄	1.6415
C(11)–C(12)	1.195(3)	C(13)–C(14)	1.182(3)
C(28)–C(29)	1.188(3)	C(30)–C(31)	1.188(3)
C(11)–C(12)–C(13)	176.4(3)	C(12)–C(13)–C(14)	175.9(3)
C(28)–C(29)–C(30)	176.7(3)	C(29)–C(30)–C(31)	177.2(3)

Dihedral angles (°) between planes

A and B	3.0	A and C	25.0
B and C	25.4	C and D	23.6
C and E	22.0	D and E	2.4

Planes: A, C(1)–C(2)–C(3)–C(4)–C(5); B, C(6)–C(7)–C(8)–C(9)–C(10); C, C(15)–C(16)–C(17)–C(18)–C(19)–C(20)–C(21)–C(22)–C(23)–C(24)–C(25)–C(26)–C(27). D, C(32)–C(33)–C(34)–C(35)–C(36); E, C(37)–C(38)–C(39)–C(40)–C(41).

rings from the eclipsed conformation in the Fe(1) unit is 6.5° while the corresponding angle in the Fe(2) unit is considerably larger at 19.4°. The Fe–C(cyclopentadienyl) distances vary from 2.006(3) to 2.047(2) Å. However, there are no apparent short intermolecular contacts between the fluorenyl rings in the crystal lattice.

A partial structural determination of the molecular structure of **4** was made and a perspective drawing of **4** is depicted in Fig. 2. Preliminary X-ray study is consistent with the proposed triferrocenyl structure but

the poor quality of the data due to the small size and weakly diffracting nature of the crystals precludes satisfactory discussion of the structural details. But, we feel that the structure is correct and unambiguous. Generally speaking, the structure of **4** is very similar to that of **1**, except that fluorene-9-one-2,7-diyl group is being replaced by 9-ferrocenylphenylmethylenefluorene-2,7-diyl moiety and the structural parameters are rather analogous to those observed for **1**. An estimation of the iron–iron distance of about 22 Å was made in this case.

Structurally, compound **9** contains one ferrocenylethynyl unit substituted at the 7-position of the fluorene nucleus while the bromo group remains intact at the 2-position such that the ferrocenylphenylmethylen moiety is arranged on the opposite side to that of the terminal ferrocene group on steric grounds. The cyclopentadienyl rings of both ferrocenyl groups are essentially planar and the tilt angles are 3.0° and 0.8° for the two C₅ rings in the Fe(1) and Fe(2) ferrocenyl units, respectively. An eclipsed nature of the C₅ rings in the structure of **2** is confirmed with deviation angles of ca. 4.3° and 2.1°. The C≡C bond in the ethynyl bridge is fairly typical at 1.171(7) Å in **9**. The exo double bond C(23)–C(26) is only slightly distorted from planarity by 1.6° (defined by C(1)–C(13)–C(14)–C(15)) in **9**. The C(23)–C(26) double bond length is typical at 1.330(6) Å, which compares well with those in [(η⁵-C₅H₅)Fe(η⁵-C₅H₄CH=Ar)] (Ar =

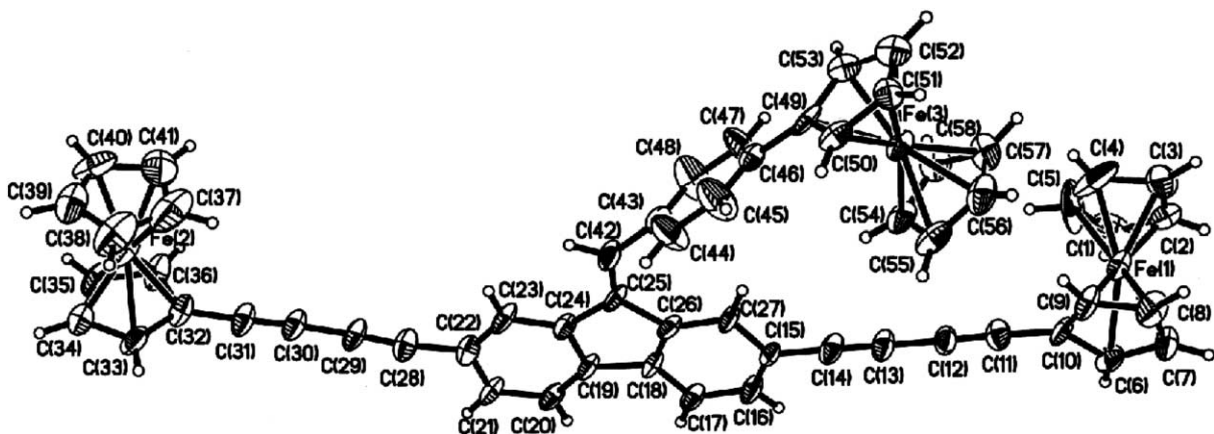


Fig. 2. A perspective view of **4**, showing the atomic labelling scheme.

2-formyl-9-fluorenyl 1.354(6) Å [12], 2,7-diformyl-9-fluorenyl 1.340(3) Å [12], 2,7-diethynyl-9-fluorenyl 1.348(3) Å [13]), *trans*-[Ph(Et₃P)₂PtC≡CArC≡CPt(PEt₃)₂Ph] (Ar = 9-(ferrocenylmethylene)fluorene-2,7-diyl 1.37(2) Å [13], 9-(dicyanomethylene)fluorene-2,7-diyl 1.348(9) Å [14], 2,4,5,7-tetranitro-9-[cyano(dimethylamino)methylene]fluorene (1.388(4) Å) [15], 2,7-dibromo-9-[cyano(ethynyl)methylene]fluorene derivatives (1.361(8) and 1.363(7) Å) [16] and other polynitrosubstituted 9-(dicyanomethylene)fluorenes [17]. There is a lengthening of the C(23)–C(26) bond (1.330(6) Å) and shortening of the C(26)–C(27) bond (1.469(7) Å), in line with the presence of π -conjugation along the fragment C(23)–C(26)–C(27) (see Fig. 3 and Table 2).

2.3. Optical and redox properties

Table 3 collects the absorption, emission and redox data of our new complexes recorded in CH₂Cl₂. Each of them essentially displays several structureless absorption bands in the near UV region which are mainly due to π – π^* electronic transitions of the associated organic group [8]. The fluorenone-containing compounds also display broad low-energy features beyond 400 nm. It is clear that an increase in the number of ethynyl units from $n = 1$ (for **5–8**) to $n = 2$ (for **1–4**) leads to a bathochromic shift in the absorption maxima, consistent with the more extended π -conjugation for **1–4**. All these fluorene-based ferrocenyl complexes are found to be emissive in fluid solutions at room temperature. The emission features follow the same trend as the absorption spectra, and the emission wavelengths are generally red-shifted from **5–8** to **1–4** for

Table 2
Selected bond lengths (Å) and angles (°) for complex **9**

Fe(1)–C ₅ H ₅	1.6500	Fe(1)–C ₅ H ₄	1.6415
Fe(2)–C ₅ H ₅	1.6478	Fe(2)–C ₅ H ₄	1.6447
C(11)–C(12)	1.171(7)	C(23)–C(26)	1.330(6)
C(11)–C(12)–C(13)	177.9(6)	C(23)–C(26)–C(27)	126.9(4)
C(24)–C(23)–C(26)	125.3(4)		
Dihedral angles (°) between planes			
A and B	3.0	A and C	91.3
B and C	91.2	C and D	101.9
C and E	92.6	C and F	93.0
D and E	9.7	D and F	9.6
E and F	0.8		

Planes: A, C(1)–C(2)–C(3)–C(4)–C(5); B, C(6)–C(7)–C(8)–C(9)–C(10); C, C(13)–C(14)–C(15)–C(16)–C(17)–C(18)–C(19)–C(20)–C(21)–C(22)–C(23)–C(24)–C(25); D, C(27)–C(28)–C(29)–C(30)–C(31)–C(32); E, C(33)–C(34)–C(35)–C(36)–C(37); F, C(38)–C(39)–C(40)–C(41)–C(42).

each corresponding fluorene spacer. With reference to the spectroscopic studies in previous systems [8d], these luminescence bands probably arise from ligand-dominating emissive states and can be attributed to the intraligand π – π^* transitions.

Cyclic voltammetric measurements in CH₂Cl₂ at room temperature show that each of **1–9** is characterized by one quasi-reversible oxidation wave due to the ferrocenyl electrophore that is present. An anodic shift of the ferrocene–ferrocenium couple relative to the ferrocene standard is caused by the unsaturation of the alkyne units which makes the removal of electrons more difficult than pure ferrocene. While no significant electronic interaction between terminal ferrocenyl moieties was detected in each case, we observe that those

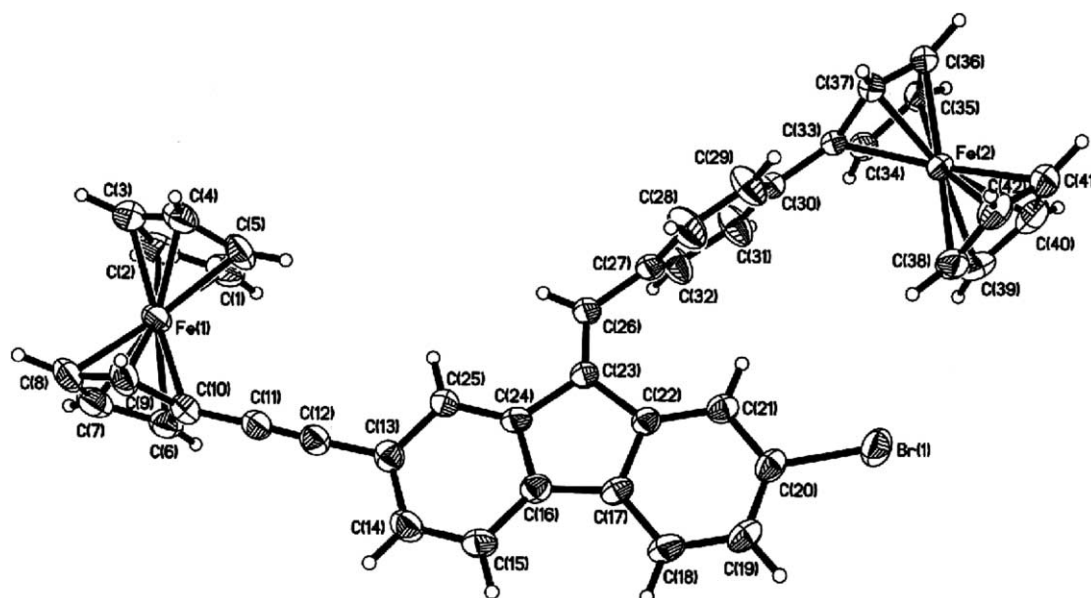


Fig. 3. A perspective view of **9**, showing the atomic labelling scheme.

Table 3
Photophysical and redox data for compounds **1–9** in CH₂Cl₂

Complex	λ_{max} (nm) ^a	λ_{em} (nm) ^b	$E_{1/2}$ (V) ^c
1	304 (1.5), 354 (1.1), 365 (1.1), 486br (0.2)	429 (360)	0.25 (130)
2	385 (1.8), 410 (1.7)	426, 449 (385)	0.16 (148)
3	274 (1.6), 365 (1.3)	390 (350)	0.15 (180)
4	267 (0.6), 275 (0.9), 365 (0.7)	416 (365)	0.17 (198)
5	288 (8.7), 349 (4.7), 493br (0.8) ^d	404 (350)	0.14 (159) ^d
6	344 (4.0)	402, 428 (344)	0.02 (122)
7	275 (4.6), 348 (6.1) ^d	365 (345)	0.03 (219) ^d
8	267 (0.9), 275 (1.1), 339 (0.6), 364 (0.5)	377 (335)	0.05 (196)
9	267 (1.0), 275 (1.1), 327 (1.0), 341 (1.0)	353 (327)	0.06 (192)

^a Extinction coefficients ($\epsilon \times 10^{-4}$ dm³ mol⁻¹ cm⁻¹) are shown in parentheses.

^b Excitation wavelengths are shown in parentheses.

^c Scan rate = 100 mV s⁻¹, half-wave potential values $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ for reversible ferrocenyl oxidation, $E_{\text{p}} = E_{\text{pa}} - E_{\text{pc}}$ (in mV) for reversible waves are given in parentheses, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

^d Data taken from [8a].

diferrocenyl complexes **1**, **2**, **5** and **6** (or triferrocenyl complexes **3**, **4**, **7** and **8**) only undergo a single-step two- (or three-) electron oxidation involving the concomitant oxidation of the two (or three) ferrocenyl subunits at the experimental scan rate of 100 mV s⁻¹. Similar non-interacting multiferoecenyl-substituted molecules are not unprecedented and, in fact, are quite common [8,18]. It is worthwhile to note that the half-wave potential of the terminal ferrocenyl units follows the order **1** > **3** \approx **4** and **5** > **7** \approx **8** when the substituent at the 9-position of the central fluorene spacer varies from an electron-accepting fluorene-9-one to an electron-donating ferrocenyl group. This is in line with the loss of electron density from the ferrocenyl group to the net electron-withdrawing fluorenone via the ethynyl or butadiynyl bridges. The much lower $E_{1/2}$ values in the triferrocenyl species indicate the electron-richness of these compounds. When the conjugation is extended from **5–8** to **1–4** upon incorporating an additional C \equiv C unit on each side of fluorene group, the increased unsaturation of the conjugated backbone tends to increase the ferrocene-based oxidation potentials in **1–4**.

3. Concluding remarks

We have successfully extended the chemistry of bis(ethynylferrocene) complexes with aromatic spacers to their bis(butadiynyl) congeners through the oxidative coupling reactions between two acetylenic precursors. A new family of carbon-rich bis(butadiynylferrocene) organometallic complexes were prepared in satisfactory

yields. The spectroscopic, structural and electrochemical properties of these compounds were examined in terms of the electronic nature of the 9-substituents of fluorene and the length of the C_n-bridges. We are currently expanding this system in the guest for a new series of rigid-rod multimetallic assemblies of nano-sized dimensions.

4. Experimental

4.1. General procedures

The preparations of compounds **5–9** were carried out under a nitrogen atmosphere with the use of standard inert atmosphere and Schlenk techniques, but no special precautions were taken to exclude oxygen during work-up. Solvents were predried and distilled from appropriate drying agents. All chemicals, unless otherwise stated, were obtained from commercial sources and used as received. Preparative TLC was performed on 0.7 mm silica plates (Merck Kieselgel 60 GF₂₅₄) prepared in our laboratory. The starting compound ethynylferrocene [19], 2,7-diethynylfluorene-9-one [20], 9,9-diethynyl-2,7-dihexylfluorene [21], 2,7-diethynyl-9-ferrocenylmethylenefluorene [13], 2,7-diethynyl-9-ferrocenylphenylmethylenefluorene [22], 2,7-dibromo-9,9-dihexylfluorene [21], 2,7-dibromo-9-ferrocenylmethylenefluorene [12] and 2,7-dibromo-9-ferrocenylphenylmethylenefluorene [22] were prepared by the reported procedures. Infrared spectra were recorded as CH₂Cl₂ solutions in a CaF₂ cell (0.5 mm path length) on a Perkin–Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer. Proton NMR spectra were measured in CDCl₃ on a Jeol EX270 or a Varian INOVA 400 MHz FT NMR spectrometer. Chemical shifts were quoted relative to SiMe₄ ($\delta = 0$). Fast atom bombardment mass spectra were recorded on a Finnigan MAT SSQ710 mass spectrometer. Electronic absorption spectra were obtained with a Hewlett–Packard 8453 UV–vis spectrometer and steady-state visible luminescence spectra on a Photon Technology International (PTI) Alphascan spectrofluorimeter. Cyclic voltammetry experiments were done with a Princeton Applied Research (PAR) model 273A potentiostat. A conventional three-electrode configuration consisting of a glassy-carbon working electrode, a Pt-wire counter electrode and a Ag/AgNO₃ reference electrode (0.1 M in acetonitrile) was used. The solvent in all measurements was deoxygenated CH₂Cl₂ and the supporting electrolyte was 0.1 M [Bu₄N]PF₆. Ferrocene was added as a calibrant after each set of measurements and all potentials reported were quoted with reference to the ferrocene–ferrocenium couple (taken as $E_{1/2} = +0.17$ V relative to Ag/AgNO₃). The number of electrons transferred for each compound was estimated by comparing the peak height of the respective ferrocene oxidation wave with an equal concentration of

the ferrocene standard added in the same system, in which one-electron oxidation was assumed.

4.2. Preparations of complexes

4.2.1. Synthesis of 2,7-bis(ferrocenylbutadiynyl)fluoren-9-one (**1**)

A mixture of 2,7-diethynylfluoren-9-one (25.2 mg, 0.11 mmol), ethynylferrocene (46.2 mg, 0.22 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (71.7 mg, 0.36 mmol) and pyridine (5 cm^3) was charged into a 10 cm^3 round-bottomed flask and the resulting slurry was heated to 90 °C overnight in air. After the volatile components were removed under reduced pressure, the residue was concentrated and subjected to silica gel TLC separation using a solvent mixture of hexane– CH_2Cl_2 (2:1, v/v) as the eluent. The first brown band was characterized to be the known compound bis(ferrocenylethynyl)-1,3-butadiyne (10.0 mg, 22%) and the title product **1** was isolated from the second red band ($R_f = 0.66$) as a red solid in 46% yield (32.6 mg). IR (CH_2Cl_2): 2214, 2146 $\nu(\text{C}\equiv\text{C})$, 1719 $\nu(\text{C}=\text{O})$ cm^{-1} . ^1H NMR (CDCl_3): δ 4.27–4.29 (m, 14H, Cp), 4.54 (t, 4H, $J_{\text{H-H}} = 1.8$ Hz, Cp), 7.49 (d, 2H, $J_{\text{H-H}} = 7.6$ Hz, Ar), 7.64 (dd, 2H, $J_{\text{H-H}} = 1.4$, 7.6 Hz, Ar) and 7.77 (d, 2H, $J_{\text{H-H}} = 1.4$ Hz, Ar). ^{13}C NMR (CDCl_3): δ 69.12, 69.55, 70.22, 72.29 (Cp), 77.13, 78.67, 85.15, 86.25 (C \equiv C), 120.61, 127.88, 129.46, 131.59, 138.50, 144.37 (Ar) and 184.45 (C=O). FABMS: m/z 644 (M^+). Anal. Found: C, 76.20; H, 3.55. Calc. for $\text{C}_{41}\text{H}_{24}\text{Fe}_2\text{O}$: C, 76.43; H, 3.75%.

4.2.2. Synthesis of 2,7-bis(ferrocenylbutadiynyl)-9,9-dihexylfluorene (**2**)

A similar procedure as illustrated for **1** was employed using 2,7-diethynyl-9,9-dihexylfluorene (42.1 mg, 0.11 mmol) instead of 2,7-diethynylfluoren-9-one. The crude product was worked-up, as before, and the residue was purified by TLC on silica ($R_f = 0.35$) using hexane– CH_2Cl_2 (2:1, v/v) as eluent to yield **2** as an orange-red solid (38.7 mg, 44%). IR (CH_2Cl_2): 2212, 2146 $\nu(\text{C}\equiv\text{C})$ cm^{-1} . ^1H NMR (CDCl_3): δ 0.58 (m, 4H, CH_2CH_3), 0.79 (t, 6H, $J_{\text{H-H}} = 7.0$ Hz, CH_3), 1.06 (m, 12H, $(\text{CH}_2)_3$), 1.94 (m, 4H, $\text{CH}_2(\text{CH}_2)_3$), 4.24–4.28 (m, 14H, Cp), 4.51 (t, 2H, $J_{\text{H-H}} = 1.9$ Hz, Cp), 7.48–7.54 (m, 4H, Ar) and 7.61–7.68 (m, 2H, Ar). ^{13}C NMR (CDCl_3): δ 13.99, 22.59, 23.67, 29.64, 31.45, 40.15 (C_6H_{13}), 55.17 (quat. C), 62.98, 69.33, 70.12, 72.14 (Cp), 75.19, 79.72, 82.98, 86.87 (C \equiv C), 120.00, 120.81, 126.64, 131.37, 141.09 and 150.96 (Ar). FABMS: m/z 799 (M^+). Anal. Found: C, 79.62; H, 6.15. Calc. for $\text{C}_{53}\text{H}_{50}\text{Fe}_2$: C, 79.70; H, 6.31%.

4.2.3. Synthesis of 2,7-bis(ferrocenylbutadiynyl)-9-ferrocenylmethylenefluorene (**3**)

Compound **3** was prepared similarly from 2,7-diethynyl-9-ferrocenylmethylenefluorene (45.1 mg, 0.11

mmol) and it was isolated as a red solid in 35% yield (31.8 mg) after preparative TLC on silica ($R_f = 0.64$) eluting with hexane– CH_2Cl_2 (2:1, v/v). IR (CH_2Cl_2): 2213, 2142 $\nu(\text{C}\equiv\text{C})$ cm^{-1} . ^1H NMR (CDCl_3): δ 4.20–4.30 (m, 19H, Cp), 4.54 (t, 2H, $J_{\text{H-H}} = 1.6$ Hz, Cp), 4.56 (t, 2H, $J_{\text{H-H}} = 1.6$ Hz, Cp), 4.58 (t, 2H, $J_{\text{H-H}} = 1.6$ Hz, Cp), 4.75 (t, 2H, $J_{\text{H-H}} = 1.6$ Hz, Cp), 7.49–7.55 (m, 3H, Ar + vinyl CH), 7.66–7.72 (m, 2H, Ar), 7.96 (m, 1H, Ar) and 8.40 (m, 1H, Ar). FABMS: m/z 826 (M^+). Anal. Found: C, 75.20; H, 4.02. Calc. for $\text{C}_{52}\text{H}_{34}\text{Fe}_3$: C, 75.58; H, 4.15%.

4.2.4. Synthesis of 2,7-bis(ferrocenylbutadiynyl)-9-ferrocenylphenylmethylenefluorene (**4**)

Compound **4**, synthesized from 2,7-diethynyl-9-ferrocenylphenylmethylenefluorene (53.5 mg, 0.11 mmol), was isolated as an orange-red solid in 42% yield (41.7 mg) after preparative TLC on silica (eluent: hexane– CH_2Cl_2 , 2:1, v/v, $R_f = 0.57$). IR (CH_2Cl_2): 2214, 2144 $\nu(\text{C}\equiv\text{C})$ cm^{-1} . ^1H NMR (CDCl_3): δ 4.15–4.30 (m, 17H, Cp), 4.39–4.42 (m, 4H, Cp), 4.56 (t, 2H, $J_{\text{H-H}} = 2.0$ Hz, Cp), 4.64 (t, 2H, $J_{\text{H-H}} = 2.0$ Hz, Cp), 4.78 (t, 2H, $J_{\text{H-H}} = 2.0$ Hz, Cp), 7.48–7.56 (m, 3H, Ar + vinyl CH), 7.61–7.63 (m, 2H, Ar), 7.67–7.73 (m, 2H, Ar), 7.89 (m, 1H, Ar) and 7.95 (m, 1H, Ar). FABMS: m/z 902 (M^+). Anal. Found: C, 76.88; H, 4.10. Calc. for $\text{C}_{58}\text{H}_{38}\text{Fe}_3$: C, 77.19; H, 4.24%.

4.2.5. Synthesis of 2,7-bis(ferrocenylethynyl)-9,9-dihexylfluorene (**6**)

2,7-Dibromo-9,9-dihexylfluorene (54.2 mg, 0.11 mmol), ethynylferrocene (46.2 mg, 0.22 mmol) and $^i\text{Pr}_2\text{NH}$ (10 cm^3) were mixed under N_2 with catalytic amounts of $\text{Pd}(\text{OAc})_2$ (9 mg), CuI (10 mg) and PPh_3 (24 mg). The mixture was allowed to reflux for a period of 15 h, after which all volatile components were removed under reduced pressure. The residue was redissolved in CH_2Cl_2 and subsequently filtered through a short silica column. The filtrate was concentrated and subjected to preparative TLC separation using hexane– CH_2Cl_2 (2:1, v/v) as eluent. From the major red band ($R_f = 0.52$), the title compound was obtained as an orange-red powder in 80% yield (66.0 mg). IR (CH_2Cl_2): 2207 $\nu(\text{C}\equiv\text{C})$ cm^{-1} . ^1H NMR (CDCl_3): δ 0.61 (m, 4H, CH_2CH_3), 0.78 (t, 6H, $J_{\text{H-H}} = 7.2$ Hz, CH_3), 1.06 (m, 12H, $(\text{CH}_2)_3$), 1.97 (m, 4H, $\text{CH}_2(\text{CH}_2)_3$), 4.26 (t, 4H, $J_{\text{H-H}} = 1.8$ Hz, Cp), 4.28 (s, 10H, Cp), 4.54 (t, 4H, $J_{\text{H-H}} = 1.8$ Hz, Cp), 7.44 (d, 2H, $J_{\text{H-H}} = 1.2$ Hz, Ar), 7.47 (dd, 2H, $J_{\text{H-H}} = 1.8$, 8.0 Hz, Ar) and 7.63 (d, 2H, $J_{\text{H-H}} = 8.0$ Hz, Ar). ^{13}C NMR (CDCl_3): δ 14.14, 22.72, 23.78, 29.80, 31.63, 40.45 (C_6H_{13}), 55.20 (quat. C), 65.45, 68.85, 69.97, 71.38 (Cp), 86.74, 88.47 (C \equiv C), 119.67, 122.33, 125.56, 130.46, 140.12 and 150.84 (Ar). FABMS: m/z 751 (M^+). Anal. Found: C, 78.25; H, 6.65. Calc. for $\text{C}_{49}\text{H}_{50}\text{Fe}_2$: C, 78.41; H, 6.71%.

4.2.6. Synthesis of 2,7-bis(ferrocenylethynyl)-9-ferrocenylphenylmethylenefluorene (**8**) and 2-bromo-7-ferrocenylethynyl-9-ferrocenylphenylmethylenefluorene (**9**)

A similar procedure as illustrated for **6** was employed using 2,7-dibromo-9-ferrocenylphenylmethylenefluorene (65.6 mg, 0.11 mmol) instead of 2,7-dibromo-9,9-dihexylfluorene. The crude product was worked-up, as before, and the residue was purified by TLC on silica using hexane–CH₂Cl₂ (4:1, v/v) as eluent to yield analytically pure samples of **8** ($R_f = 0.27$) and **9** ($R_f = 0.37$) as orange solids in 40 and 23% yields, respectively. **8**: IR (CH₂Cl₂): 2208 $\nu(\text{C}\equiv\text{C})$ cm⁻¹. ¹H NMR (CDCl₃): δ 4.10–4.11 (m, 5H, Cp), 4.16–4.17 (m, 5H, Cp), 4.27–4.28 (m, 7H, Cp), 4.36 (m, 2H, Cp), 4.39 (m, 2H, Cp), 4.54 (m, 2H, Cp), 4.72 (m, 2H, Cp), 4.75 (m, 2H, Cp), 7.45 (m, 1H, Ar), 7.48–7.63 (m, 6H, Ar + vinyl CH), 7.67 (m, 1H, Ar), 7.73 (m, 1H, Ar), 7.84 (m, 1H, Ar) and 7.92 (m, 1H, Ar). FABMS: m/z 854 (M⁺). Anal. Found: C, 75.80; H, 4.20. Calc. for C₅₄H₃₈Fe₃: C, 75.91; H, 4.48%. **9**: IR (CH₂Cl₂): 2207 $\nu(\text{C}\equiv\text{C})$ cm⁻¹. ¹H NMR (CDCl₃): δ 4.11 (s, 5H, Cp), 4.16 (m, 2H, Cp), 4.27 (s, 5H, Cp), 4.39 (t, 2H, $J_{\text{H-H}} = 1.9$ Hz, Cp), 4.54 (t, 2H, $J_{\text{H-H}} = 1.9$ Hz, Cp), 4.75 (t, 2H, $J_{\text{H-H}} = 1.9$ Hz, Cp), 7.45–7.53 (m, 5H, Ar + vinyl CH), 7.56–7.61 (m, 2H, Ar), 7.63–7.66 (m, 1H, Ar), 7.74 (m, 1H, Ar), 7.84 (m, 1H, Ar) and 7.91 (m, 1H, Ar). FABMS: m/z 726 (M⁺). Anal. Found: C, 69.38; H, 3.85. Calc. for C₄₂H₂₉BrFe₂: C, 69.55; H, 4.03%.

5. Crystallography

Single crystals of **1**, **4**·CH₂Cl₂ and **9** suitable for X-ray crystallographic analyses were grown by slow evaporation of their respective solutions in CH₂Cl₂–hexane at room temperature (r.t.). The crystals were chosen and mounted on a glass fiber using epoxy resin. Crystal data, data collection parameters and results of the analyses are listed in Table 4. (For **4**, only the cell parameters and some details of the refinement are given.) The diffraction experiments were carried out at r.t. on a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The raw intensity data frames were integrated with the SAINT+ program using a narrow-frame integration algorithm [23]. Corrections for Lorentz and polarization effects were also applied by SAINT. For each analysis an empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS [24]. The structures were solved by direct methods, and expanded by difference Fourier syntheses using the software SHELXTL [25]. Structure refinements were made on F^2 by the full-matrix least-squares technique. In each case, all the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in their ideal positions but not refined.

Table 4
Summary of crystal structure data for complexes **1**, **4** and **9**

	1	4 ·CH ₂ Cl ₂	9
Empirical formula	C ₄₁ H ₂₄ Fe ₂ O	C ₅₉ H ₄₀ Cl ₂ Fe ₃	C ₄₂ H ₂₉ BrFe ₂
Molecular weight	644.30	987.36	725.26
Crystal size (mm)	0.29 × 0.14 × 0.08	0.25 × 0.10 × 0.07	0.29 × 0.12 × 0.10
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	7.7660(11)	7.892(5)	7.7761(7)
b (Å)	9.6487(13)	12.938(8)	26.278(2)
c (Å)	19.987(3)	23.759(15)	15.6556(14)
α (°)	94.258(3)	100.639(13)	
β (°)	99.953(2)	97.464(12)	99.339(2)
γ (°)	96.016(3)	101.664(14)	
U (Å ³)	1460.4(3)	2300(2)	3156.7(5)
$\mu(\text{Mo-K}\alpha)$ (mm ⁻¹)	1.027	1.090	2.215
D_{calc} (g cm ⁻³)	1.465	1.426	1.526
Z	2	2	4
$F(000)$	660	1012	1472
θ range (°)	2.08–27.57	1.77–25.00	2.03–25.00
Reflections collected	8678	11 659	15 809
Unique reflections	6289	7987	5561
R_{int}	0.0143		0.0750
Observed reflections [$I > 2\sigma(I)$]	4781	2948	2736
No. of parameters	398		406
R_1, wR_2 [$I > 2\sigma(I)$]	0.0373, 0.1020	0.1468, 0.3458	0.0460, 0.1009
R_1, wR_2 (all data)	0.0516, 0.1113		0.1170, 0.1254
Goodness-of-fit on F^2	1.019	1.020	0.867
Residual extrema in final diff. map (e Å ⁻³)	0.378 to -0.219	1.230 to -0.941	0.382 to -0.413

6. Supplementary material

Crystallographic data (comprising hydrogen atom coordinates, thermal parameters and full tables of bond lengths and angles) for the structural analysis has been deposited with the Cambridge Crystallographic Centre (Deposition Nos. 247733–247734). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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