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Synthesis, structures and electrochemistry of bis(alkynylferrocene) complexes with fluorene spacers

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Abstract

New bis(alkynylferrocene) complexes with fluorenyl-based spacers $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)C{\equiv}CRC{\equiv}C(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ (R = fluoren-9-one-2,7-diyl, **1**; fluorene-2,7-diyl, **2**; 9-ferrocenylmethylenefluorene-2,7-diyl, **3**) have been prepared in excellent yields by the Sonogashira coupling reactions of ethynylferrocene with half an equivalent of the corresponding dibromofluorene derivatives BrRBr. All the compounds have been characterized by FTIR, ^{1}H-NMR and UV–vis spectroscopies and fast atom bombardment mass spectrometry (FABMS). The molecular structures of **1** and **2** have been elucidated by single-crystal X-ray analyses. The redox chemistry of these fluorene-linked biferrocenes has been investigated by cyclic voltammetry and the interaction between the ferrocene units is rather weak in each case. The half-wave potential of the terminal ferrocenyl moieties increases progressively in the order $\mathbf{3} < \mathbf{2} < \mathbf{1}$ when the substituent at the 9-position of the central spacer changes from an electron-donating ferrocenyl group (as in **3**) to an electron-deficient oxo group (as in **1**). This is consistent with the loss of electron density from the ferrocenyl unit to the net electron-accepting fluorenone through the ethynyl bridge in **1**. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Alkynyl complexes; Crystal structures; Ferrocene; Fluorene; Cyclic voltammetry

1. Introduction

Conjugated organometallic systems that contain electronically coupled photo- and/or redox-active sites across an unsaturated organic bridge are of considerable current interest [1,2]. Special attention has been paid to the π-conjugated bi- or multi-metallic assemblies capable of intermetallic electron- or energy-transfer processes [2]. With regards to this goal, tremendous efforts have been devoted to the design and synthesis of ferrocene-based materials with π-conjugation [3]. Systems incorporating ferrocene entities are known with spacers such as oligoene, oligoyne, thiophene, furan, phenylene, phenyleneyne, thienyl ethynyl and furanyl vinyl units [3,4]. These ferrocene-containing molecules have been shown to exhibit a variety of intriguing electronic, optical, redox and structural properties [3,4]. The significance of ferrocenyl derivatives in homo- or hetero-bimetallic mixed-valence species has been demonstrated [5]. The development of this class of ferrocenyl chemistry has found potential applications in areas including molecular sensors [6], molecular electronics [7] and non-linear optics [8].

In continuation of our interest in the study of organometallic σ-acetylide compounds, we set out to prepare new alkynylferrocene complexes with different organic linkers. To the best of our knowledge, fluorene-linked ferrocenyl acetylide complexes are not known in the literature. Recent reports on the importance of fluorenyl derivatives in bimetallic and polymeric metallic species have encouraged us to undertake a program to design a new system featuring this characteristic [3k,9]. In this contribution, we report a series of new bis(alkynylferrocene) complexes bridged by some 2,7-disubstituted fluorene functionalities **I**–**III** possessing tunable electronic properties. Among these, 9-oxo- and 9-ferrocenylmethylene-substituted fluorenes serve as an electron-withdrawing and an electron-donating moieties, respectively, between the ferrocenyl units.

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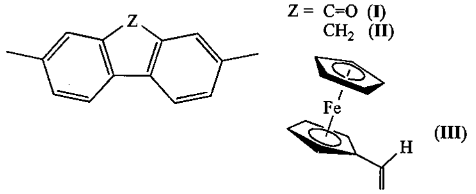


2. Results and discussion

2.1. Synthesis

The new fluorene-linked alkynylferrocene compounds 2,7-bis(ferrocenylethynyl)fluoren-9-one (**1**), 2,7-bis(ferrocenylethynyl)fluorene (**2**) and 9-ferrocenylmethylene-2,7-bis(ferrocenylethynyl)fluorene (**3**) were prepared by the Sonogashira coupling reactions of ethynylferrocene with the corresponding dibromofluorene derivatives in a 2:1 molar ratio [4a] (Scheme 1). The reactions were monitored readily by thin-layer chromatography (TLC) and solution IR spectroscopy. The product yields of **1**–**3** are very high (> 90%) and we were able to circumvent the formation of the homocoupling compound, namely, 1,4-diferrocenylbutadiyne, under strictly anaerobic conditions [3f,10]. All the complexes were purified by preparative TLC on silica using a hexane–CH_2Cl_2 mixture as eluent and they were isolated as air-stable orange to red solids in high purity. Complexes **1**–**3** are soluble in common organic solvents and have been characterized by satisfactory microanalysis, fast atom bombardment mass spectrometry (FABMS), IR and NMR spectroscopies.

2.2. Spectroscopic properties

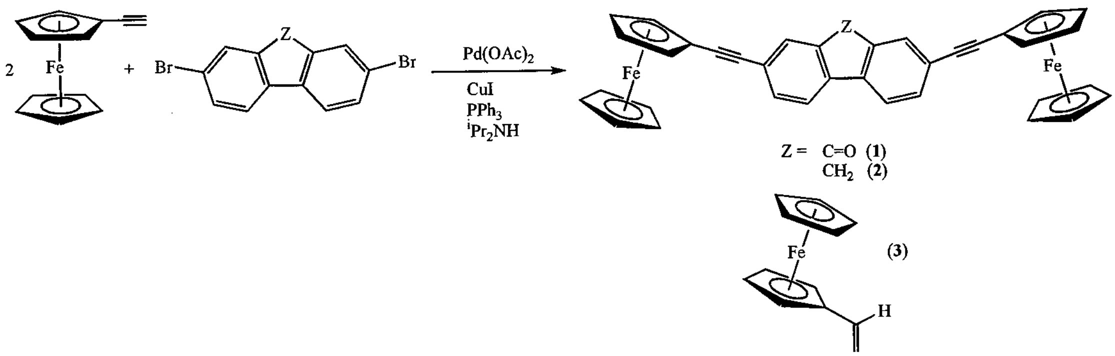
Table 1 summarizes the main spectroscopic data for all the new compounds in this study. In the solution IR spectra, the $\nu(C{\equiv}C)$ vibrational modes are diagnostic and represent a useful monitoring tool. The $\nu(C{\equiv}C)$ values in the range 2207–2211 cm^{-1} indicate the presence of $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)C{\equiv}C$ moiety which compare well with those previously reported in other ferrocenyl acetylide compounds [3c]. The $C{\equiv}C\text{–}H$ stretching band in the starting complex is absent and the alkynyl unit is bound to the fluorenyl ring system. For **1**, characteristic $\nu(C{=}O)$ IR vibration due to the fluorenone unit was also observed at 1720 cm^{-1} [9a].

The symmetrical nature of complexes **1** and **2** was evident from the ^1H-NMR spectral pattern and proton signals stemming from the ferrocenyl and organic groups were observed clearly. The ^1H-NMR spectral features of the triferrocenyl compound **3** showed the presence of ferrocenyl, fluorenyl and vinyl protons in an unsymmetrical environment. In all cases, the ferrocenyl moieties give rise to the expected patterns where the unsubstituted C_5H_5 ring shows up as a strong singlet and the monosubstituted C_5H_4 ring gives an unsymmetrical pair of ‘pseudo’-triplets corresponding to the spectrum of an A_2B_2 case with J(adjacent) $\cong J$(cross). Hence, three separate singlets and six triplets in close proximity were noticed for the non-equivalent ferrocenyl protons in **3**. The formulae of **1**–**3** were also established successfully by positive FABMS and the respective molecular ion peak was detected in each case.

The electronic absorption spectra of our complexes **1**–**3** were recorded in CH_2Cl_2 and the data are presented in Table 2. Each of them displays two to three prominent absorption bands. Reminiscent of other ferrocenyl species, the lower energy weak absorption may be ascribed to the d–d transition, whereas the higher energy intense band(s) below 400 nm arises from π–π* electronic transition of the organic segment [4a,11]. For **2** and **3**, the broad low-energy features appear as shoulders at 429 and 478 nm, respectively, which account for the orange and red colors of these compounds.

2.3. Electrochemistry

An electrochemical approach has been used widely to investigate the possibility of electronic interactions be-



Scheme 1.

Table 1
Spectroscopic data for complexes **1**–**3**

Complex	IR (cm^{-1}) [a]	^1H-NMR δ (ppm) (J, Hz) [b]	FABMS (m/z) [c]
1	2211m $\nu(C\equiv C)$, 1720s $\nu(C=O)$	4.26 (s, 10H, C_5H_5) 4.28 (t, 4H, $J_{H-H} = 2.0$, C_5H_4) 4.52 (t, 4H, $J_{H-H} = 2.0$, C_5H_4) 7.47 (dd, 2H, $J_{H-H} = 0.4$, 7.6, $H_{4,5}$) 7.60 (dd, 2H, $J_{H-H} = 1.6$, 7.6, $H_{3,6}$) 7.76 (dd, 2H, $J_{H-H} = 0.4$, 1.6, $H_{1,8}$)	596 (596)
2	2208m $\nu(C\equiv C)$	3.91 (s, 2H, CH_2) 4.25 (t, 4H, $J_{H-H} = 2.0$, C_5H_4) 4.26 (s, 10H, C_5H_5) 4.53 (t, 4H, $J_{H-H} = 2.0$, C_5H_4) 7.52 (d, 2H, $J_{H-H} = 8.0$, $H_{3,6}$) 7.67 (s, 2H, $H_{1,8}$) 7.72 (d, 2H, $J_{H-H} = 8.0$, $H_{4,5}$)	582 (582)
3	2207m $\nu(C\equiv C)$	4.24 (t, 2H, $J_{H-H} = 2.0$, C_5H_4) 4.25 (s, 5H, C_5H_5) 4.26 (s, 5H, C_5H_5) 4.28 (t, 2H, $J_{H-H} = 2.0$, C_5H_4) 4.29 (s, 5H, C_5H_5) 4.51 (t, 2H, $J_{H-H} = 2.0$, C_5H_4) 4.54 (t, 2H, $J_{H-H} = 2.0$, C_5H_4) 4.56 (t, 2H, $J_{H-H} = 2.0$, C_5H_4) 4.78 (t, 2H, $J_{H-H} = 2.0$, C_5H_4) 7.47 (dd, 1H, $J_{H-H} = 1.6$, 7.6, H_3 or H_6) 7.50 (dd, 1H, $J_{H-H} = 1.6$, 7.6, H_3 or H_6) 7.54 (s, 1H, vinyl CH) 7.67 (d, 1H, $J_{H-H} = 7.6$, H_4 or H_5) 7.68 (d, 1H, $J_{H-H} = 7.6$, H_4 or H_5) 7.89 (s, 1H, H_1 or H_8) 8.42 (s, 1H, H_1 or H_8)	778 (778)

[a] Recorded in CH_2Cl_2.
[b] Recorded in $CDCl_3$.
[c] Calculated values in parentheses.

tween redox centers in π-conjugated organometallic systems [12]. Hence, the redox properties of complexes **1**–**3** were studied in CH_2Cl_2 at room temperature by cyclic voltammetry. Results of the study are given in Table 2. The two metal centers that are interacting in an electrochemical sense would show two distinct reversible couples with a potential separation determined by the extent of the interaction [12]. However, in our present case, only one quasi-reversible oxidation wave due to the ferrocenyl electrophores was observed for each complex. These waves exhibited significant peak broadening as revealed from the large ΔE_p values, indicative of two closely spaced redox waves (Fig. 1). Therefore, the two ferrocenyl end groups only weakly communicate through the fluorenyl ring system. Considering the relative peak heights with respect to the added ferrocene standard in the cyclic voltammograms, both complexes **1** and **2** were found to undergo a single-step two-electron oxidation involving the concomitant oxidation of the two ferrocenyl subunits whereas complex **3** showed a one-step three-electron oxidation when these compounds were subjected to the electrochemical measurements with a scan rate of 100 mV s^{-1}. It is interesting to find that the half-wave potential of the terminal ferrocenyl units shows a gradual increase in the order $\mathbf{3} < \mathbf{2} < \mathbf{1}$ upon changing the substituent at the 9-position of the fluorenyl ring from the electron-donating ferrocenyl group (as in **3**) to an electron-withdrawing oxo group (as in **1**) [3k]. The potential is shifted anodically by ca. 110 mV from **3** to **1** and the low value for the oxidation potential in **3** shows that such a triferrocenyl species is electron rich.

Table 2
UV–vis and electrochemical data for complexes **1**–**3** in CH_2Cl_2

Complex	λ_{max} (nm) [a]	$E_{1/2}$ (V) [b]
1	288 (8.7), 349 (4.7), 493 (0.8)	0.14 (159), −0.95 [c]
2	342 (5.5), 429sh (0.3)	0.08 (120)
3	275 (4.6), 348 (6.1), 478sh (0.7)	0.03 (219)

[a] Extinction coefficients ($\varepsilon \times 10^{-4}$ $dm^3\ mol^{-1}\ cm^{-1}$) are shown in parentheses.
[b] Scan rate = 100 mV s^{-1}, half-wave potential values $E_{1/2} = (E_{pa} + E_{pc})/2$ for reversible oxidation, $\Delta E_p = E_{pa} - E_{pc}$ (in mV) for reversible waves are given in parentheses, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.
[c] Irreversible wave.

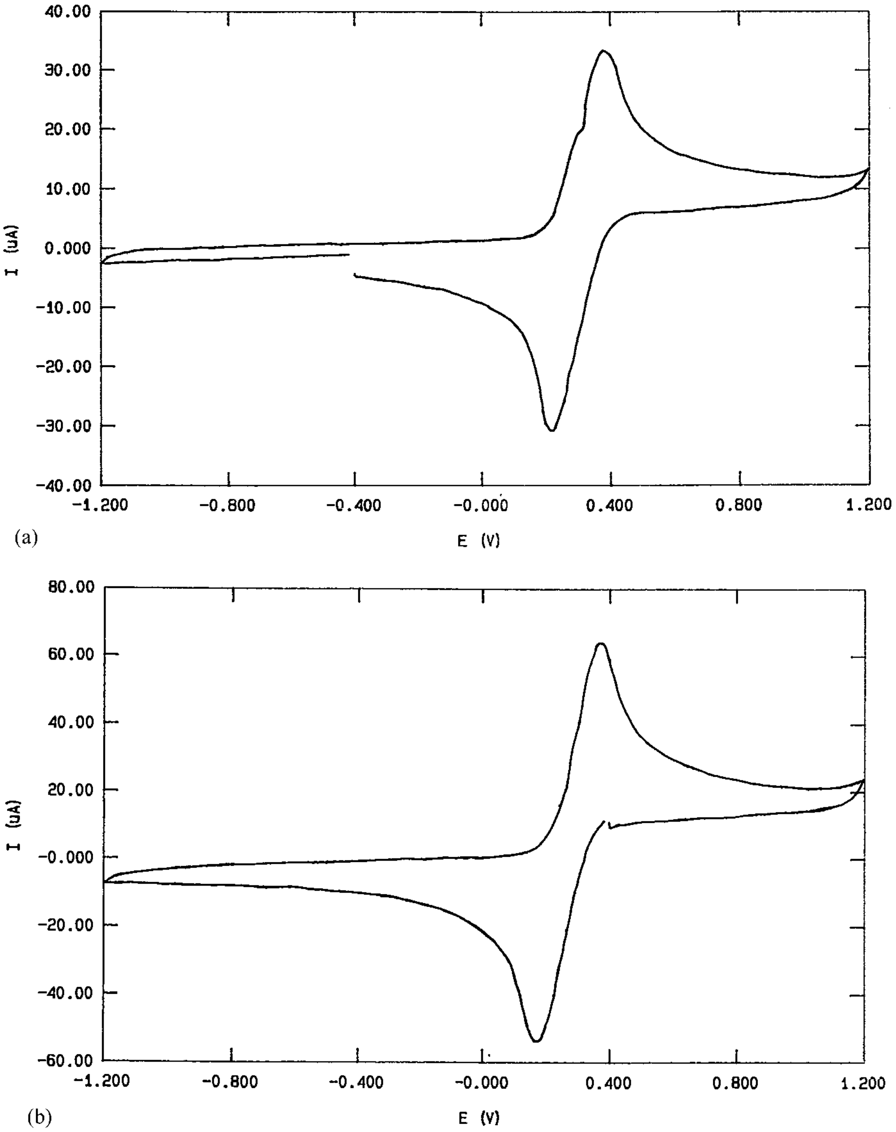


Fig. 1. Cyclic voltammograms of complexes: (a) **1** and (b) **3**.

Loss of electron density from the ferrocenyl donor unit to the net electron-accepting fluorenone moiety through the alkynyl linking unit makes the oxidation wave appear at a more positive potential in **1**. For **1**, an additional irreversible wave was also observed at −0.95 V, which was attributable to the reduction of the central fluorenone moiety.

2.4. Crystal structure analyses

The molecular structures of complexes **1** and **2**, as shown crystallographically, are depicted in Figs. 2 and 3, respectively. Some important bond parameters are listed and compared in Table 3. In the solid state, the molecule of complex **1** consists of two alkynylferrocene

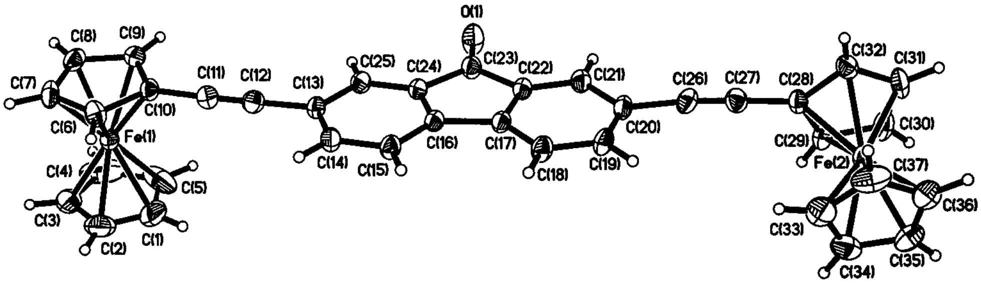


Fig. 2. Molecular structure of **1**, showing the atomic labelling scheme. Ellipsoids are shown at the 25% probability level.

end groups appended to the central fluorenone unit at the 2,7-positions via C(12)–C(13) and C(20)–C(26) bonds. The fluorenonediyl ring system is planar with a mean deviation from the plane of 0.016 Å. The cyclopentadienyl rings of both ferrocenyl groups are essentially planar and the tilt angles are 2.3 and 2.1° for the two C_5 rings in the Fe(1) and Fe(2) ferrocenyl units, respectively. The deviation of the five-membered rings from the eclipsed conformation in the Fe(1) unit is 15.3° while the corresponding angle in the Fe(2) unit is considerably smaller at 2.0°. The mean Fe–C(cyclopentadienyl) bond length is 2.034(4) Å and the cyclopentadienyl rings produce an average distance of 1.647 Å from their centroids. One of the substituted C_5H_4 rings is nearly coplanar with the fluorenyl plane (dihedral angle 2.9°) while the other C_5H_4 ring is rotated by 76.0° relative to the plane of the attached fluorenone about the alkynyl bond. The X-ray analysis of complex **2** shows the molecule to adopt a conformation in which the two ferrocenyl units are positioned on the opposite side over the plane of the central fluorene spacer. In both ferrocenyl moieties, the C_5 rings are essentially parallel, inclined by 1.9° for Fe(1) and 2.7° for Fe(2). An eclipsed nature of the C_5 rings in the structure of **2** is confirmed with deviation angles of ca. 4.5 and 4.0°. The fluorenediyl unit does not deviate

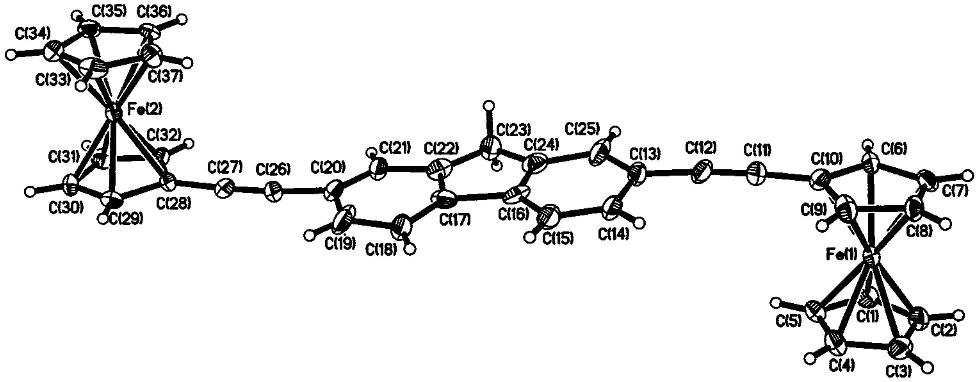


Fig. 3. Molecular structure of **2**, showing the atomic labelling scheme. Ellipsoids are shown at the 25% probability level.

Table 3
Selected bond lengths (Å) and bond angles (°) for complexes **1** and **2**

	1	**2**		**1**	**2**
Fe(1)–C(1)	2.034(4)	2.053(8)	Fe(1)–C(2)	2.039(4)	2.056(7)
Fe(1)–C(3)	2.025(4)	2.069(7)	Fe(1)–C(4)	2.014(4)	2.041(7)
Fe(1)–C(5)	2.018(4)	2.017(7)	Fe(1)–C(6)	2.031(3)	2.069(6)
Fe(1)–C(7)	2.026(3)	2.045(6)	Fe(1)–C(8)	2.037(3)	2.058(7)
Fe(1)–C(9)	2.044(3)	2.029(8)	Fe(1)–C(10)	2.044(3)	2.059(6)
Fe(1)–ring(C_5H_5)	1.657	1.650	Fe(1)–ring(C_5H_4)	1.642	1.652
Fe(2)–C(28)	2.031(3)	2.025(6)	Fe(2)–C(29)	2.040(3)	2.014(5)
Fe(2)–C(30)	2.039(3)	2.041(7)	Fe(2)–C(31)	2.029(3)	2.047(7)
Fe(2)–C(32)	2.037(4)	2.051(7)	Fe(2)–C(33)	2.018(4)	2.022(8)
Fe(2)–C(34)	2.044(4)	2.033(7)	Fe(2)–C(35)	2.047(4)	2.025(6)
Fe(2)–C(36)	2.042(4)	2.034(6)	Fe(2)–C(37)	2.034(4)	2.039(7)
Fe(2)–ring(C_5H_5)	1.653	1.646	Fe(2)–ring(C_5H_4)	1.637	1.644
C(11)–C(12)	1.126(4)	1.20(1)	C(26)–C(27)	1.133(4)	1.179(9)
C(23)–O(1)	1.211(4)				
C(10)–C(11)–C(12)	177.0(4)	174.7(8)	C(11)–C(12)–C(13)	176.4(4)	171.8(9)
C(20)–C(26)–C(27)	175.1(4)	175.2(7)	C(26)–C(27)–C(28)	178.0(4)	174.1(8)
Dihedral angles (°) between planes					
A and B	2.3	1.9	A and C	0.6	7.9
A and D	76.6	3.1	A and E	77.8	1.8
B and C	2.9	6.0	B and D	78.9	1.2
B and E	80.0	2.0	C and D	76.0	4.9
C and E	77.2	6.8	D and E	2.1	2.7

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(28)–C(29)–C(30)–C(31)–C(32); E, C(33)–C(34)–C(35)–C(36)–C(37).

significantly from planarity (mean deviation 0.015 Å) and makes small dihedral angles of 6.0 and 4.9° with the substituted C_5H_4 rings. The Fe–C(cyclopentadienyl) distances vary from 2.014(4) to 2.053(8) Å. The C≡C bonds in the ethynyl bridge to both ferrocenyl units are fairly typical at 1.20(1) and 1.179(9) Å in **2** and do not differ significantly from those seen in, for example, *trans*-[Ph(Et_3P)$_2$PtC≡C(η^5-C_5H_4)Fe(η^5-C_5H_4)C≡CPt-(PEt_3)$_2$Ph] (1.203(7) Å) [3d], *trans*-[Ph(Et_3P)$_2$PtC≡C{(η^5-C_5H_4)Fe(η^5-C_5H_4)$_2$Fe(η^5-C_5H_4)}C≡CPt(PEt_3)$_2$-Ph] (1.21(1) Å) [3d], *trans*-[{(η^5-C_5H_5)Fe(η^5-C_5H_4)C≡C}$_2$$C_6H_3${C≡CRu(dppm)$_2$Cl}] (1.20(2) and 1.21(2) Å) [3c] and *trans*-[Ph(Et_3P)$_2$PtC≡CRC≡CPt(PEt_3)$_2$Ph] (R = fluorene-2,7-diyl) (1.17(2) and 1.18(2) Å) [3k]. However, the C≡C bond distances in **1** are slightly shorter at 1.126(4) and 1.133(4) Å. The average bond angles of 177.5(4)° (**1**) and 174.4(8)° (**2**) for the fragment $C_5H_4C≡C$ conform to the linear geometry of the alkynylferrocenyl complexes.

3. Conclusions

A new class of biferrocenes bearing some fluorene-based spacers covalently appended to the redox-active ferrocenyl center via an ethynyl bridge has been prepared and characterized. These bis(alkynyl) species are electrochemically active and cyclic voltammetric studies in CH_2Cl_2 solutions reveal that each complex undergoes a concomitant oxidation of the ferrocenyl subunits that are present, the $E_{1/2}$ value of which is influenced by the electronic effect of the substituent at the periphery of the central fluorenyl moiety. However, there is only a very weak electronic communication between the terminal ferrocenyl electrophores.

4. Experimental

4.1. General procedures

All reactions were carried out under N_2 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 [13]. 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 GF_{254}) prepared in our laboratory. The starting materials ethynylferrocene [10,14] and 9-ferrocenylmethylene-2,7-dibromofluorene [9c] were prepared by reported procedures. Infrared spectra were recorded as CH_2Cl_2 solutions in a CaF_2 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 $CDCl_3$ on a Varian Inova 400 MHz FTNMR spectrometer. Chemical shifts were quoted relative to Me_4Si ($\delta = 0$). 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. 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 | $AgNO_3$ reference electrode (0.1 M in MeCN) was used. The solvent in all measurements was deoxygenated CH_2Cl_2 and the supporting electrolyte was 0.1 M [Bu_4N]PF_6. 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 | $AgNO_3$). 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 ***1–3***

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

2,7-Dibromofluoren-9-one (34 mg, 0.10 mmol), ethynylferrocene (46 mg, 0.22 mmol) and diisopropylamine (5 cm^3) were mixed under N_2 with catalytic amounts of Pd(OAc)$_2$ (1 mg), CuI (1 mg) and PPh_3 (2 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 (1:1, v/v) as eluent. From the major deep red band, the title compound was obtained as a dark red powder in 95% yield (57 mg). Anal. Found: C, 74.35; H, 4.00. Calc. for $C_{37}H_{24}Fe_2O$: C, 74.53; H, 4.06%.

4.2.2. Synthesis of 2,7-bis(ferrocenylethynyl)fluorene ***(2)***

A similar procedure as illustrated for **1** was employed using 2,7-dibromofluorene (32 mg, 0.10 mmol) instead of 2,7-dibromofluoren-9-one. The crude product was worked-up, as before, and the residue was purified by TLC on silica using hexane–CH_2Cl_2 (3:1, v/v) as eluent to yield 55 mg (95%) of analytically pure sample of **2** as an orange solid. Anal. Found: C, 76.02; H, 4.34. Calc. for $C_{37}H_{26}Fe_2$: C, 76.32; H, 4.50%.

Table 4
Summary of crystal structure data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{37}H_{24}Fe_2O$	$C_{37}H_{26}Fe_2$
Molecular weight	596.26	582.28
Crystal size (mm)	$0.38\times0.26\times0.21$	$0.35\times0.19\times0.14$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	Pc
Unit cell dimensions		
a (Å)	10.048(4)	12.205(1)
b (Å)	11.418(5)	10.1006(8)
c (Å)	13.252(6)	11.766(1)
α (°)	73.701(8)	90
β (°)	69.021(7)	114.451(1)
γ (°)	86.483(8)	90
U (Å^3)	1361(1)	1320.3(2)
D_{calc} (g cm^{-3})	1.455	1.465
Z	2	2
μ (Mo–Kα) (cm^{-1})	10.95	11.24
F(000)	612	600
θ Range (°)	1.71–27.73	1.83–27.52
Reflections collected	8134	7557
Unique reflections	5875	3788
R_{int}	0.0203	0.0368
Observed reflections [$I>2.0\sigma(I)$]	5875	3788
Number of parameters	361	353
R_1	0.0505	0.0341
wR_2	0.1543	0.0856
Goodness-of-fit on F^2	1.088	1.010
Residual extrema in final difference map (e Å^{-3})	0.722 to -0.463	0.477 to -0.347

*4.2.3. Synthesis of 9-ferrocenylmethylene-2,7-bis-(ferrocenylethynyl)fluorene (**3**)*

This complex was synthesized using the conditions described above for **1** but 9-ferrocenylmethylene-2,7-dibromofluorene (52 mg, 0.10 mmol) was used instead to produce a deep red solid of **3** in 93% yield (72 mg) after TLC purification using hexane–CH_2Cl_2 (3:1, v/v) as eluent. Anal. Found: C, 73.98; H, 4.25. Calc. for $C_{48}H_{34}Fe_3$: C, 74.07; H, 4.40%.

5. Crystallography

Single crystals of **1** and **2** suitable for X-ray crystallographic analyses were chosen and mounted on a glass fiber using epoxy resin. Crystal data and other experimental details are summarized in Table 4. The diffraction experiments were carried out at room temperature on a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å). Cell parameters and orientation matrix for both complexes were obtained from the least-squares refinement of reflections measured in three different sets of 15 frames each. At the end of data collection, no crystal decay was observed. The collected frames were processed with the software SAINT [15a], and an absorption correction was applied (SADABS) [15b] to the collected reflections. The space groups for all crystals were determined from a combination of Laue symmetry check and their systematic absences, which were then confirmed by successful refinement of the structures. Both structures were solved by direct methods, and expanded by difference Fourier syntheses using the software SHELTXL [16]. 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 and not refined.

6. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 154124 and 154125 for compounds **1** and **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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