

Synthesis, structures and properties of platinum(II) complexes of oligothiophene-functionalized ferrocenylacetylene

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A series of rigid-rod alkynylferrocenyl precursors with oligothiophene (from thiophene to terthiophene) linkage units in the backbone, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}\equiv\text{C}(\text{C}_4\text{H}_2\text{S})_m\text{Br}]$ **2a–2c**, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}\equiv\text{C}(\text{C}_4\text{H}_2\text{S})_m\text{C}\equiv\text{CSiMe}_3]$ **3a–3c** and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}\equiv\text{C}(\text{C}_4\text{H}_2\text{S})_m\text{C}\equiv\text{CH}]$ **4a–4c** ($m = 1\text{--}3$), have been prepared in moderate to good yields. The ferrocenylacetylene complexes **4a–4c** can be used to form a range of stable platinum(II) alkynyl and bis(alkynyl) compounds *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}\equiv\text{C}(\text{C}_4\text{H}_2\text{S})_m\text{C}\equiv\text{C}(\text{Pt}(\text{PEt}_3)_2\text{Ph})]$ **5a–5c** and *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}\equiv\text{C}(\text{C}_4\text{H}_2\text{S})_m\text{C}\equiv\text{C}(\text{Pt}(\text{PBU}_3)_2\text{C}\equiv\text{C}(\text{C}_4\text{H}_2\text{S})_m\text{C}\equiv\text{C}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5))]$ **6a–6c** ($m = 1\text{--}3$). All these new compounds have been fully characterized by analytical and spectroscopic methods and the molecular structures of the bithienyl-linked complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{C}\equiv\text{C}(\text{C}_4\text{H}_2\text{S})_2\text{C}\equiv\text{C}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]$, **2b**, **4b**, **5b** and **6b** have been established by X-ray crystallography. Structural analysis of **6b** confirms its rigid-rod structural motif, featuring coplanar bithienyl rings and a *trans* arrangement of the two bithiophene groups. An iron–iron through-space distance of *ca.* 32 Å is observed in **6b**. Although there is no significant metallocene–metallocene interaction through the alkynyl–platinum–oligothiophene bridge, a slight negative shift of the ferrocene–ferrocenium redox potential in the platinum-containing species indicates some degree of electron delocalization into the platinum segment, in line with the results from theoretical studies. Oxidation of the thiophene units is facilitated by the presence of the platinum centre and increased conjugation in the chain.

Introduction

There is a flurry of research interest in the development of carbon-rich organometallics containing rigid, π -conjugated chains due to their widespread applications in the syntheses of unsaturated organic species,¹ organometallic polymers,² and π -conjugated bi- or multi-metallic systems.³ These organometallic assemblies are important design targets for the investigation of electron-transfer processes,⁴ the formation of liquid crystalline materials,⁵ the construction of molecular devices,⁶ and the generation of conjugated dendrimers.⁷ In particular, the polyynyls $[\text{L}_n\text{M}-(\text{C}\equiv\text{C})_m\text{R}]$ and polyynediyls $[\text{L}_n\text{M}-(\text{C}\equiv\text{C})_m\text{M}'\text{L}_n]$ ($m = 1, 2, \dots$; $\text{M} = \text{M}'$, $\text{M} \neq \text{M}'$) are attractive candidates for use in the preparation of molecular wires and in the assembly of nano-scale electronic devices, by virtue of the possible charge delocalization along the entire conjugated backbone.⁸ Molecular wires comprising mixed-valence bi-metallic fragments or remote redox-active organometallic building blocks assembled with all-carbon chains could be used in molecular electronics, optoelectronic devices and chemical sensing appliances.^{6b,9} Since the first report of diferrocenylacetylene,¹⁰ the interest in these metal-capped linear polycarbon chains as models for materially useful compounds has dramatically increased.¹¹ Two models are commonly employed to evaluate the capability of electronic communication between two terminal metal centres “ M_1 ” made possible by an organic spacer “ $\text{M}_1\text{--spacer--M}_1$ ”, and the influence of an organometallic fragment “ M_2 ” in a conjugated organic chain “ $\text{M}_1\text{--spacer--M}_2\text{--spacer--M}_1$ ”.^{11a,12} In several cases, redox active sites are strongly coupled electronically through the polyynyl fragments.¹² It has also been demonstrated that a metal bis(acetylide) unit allows a significant ground-state interaction between terminal redox-active groups in some multimetallic systems.^{12b,i}

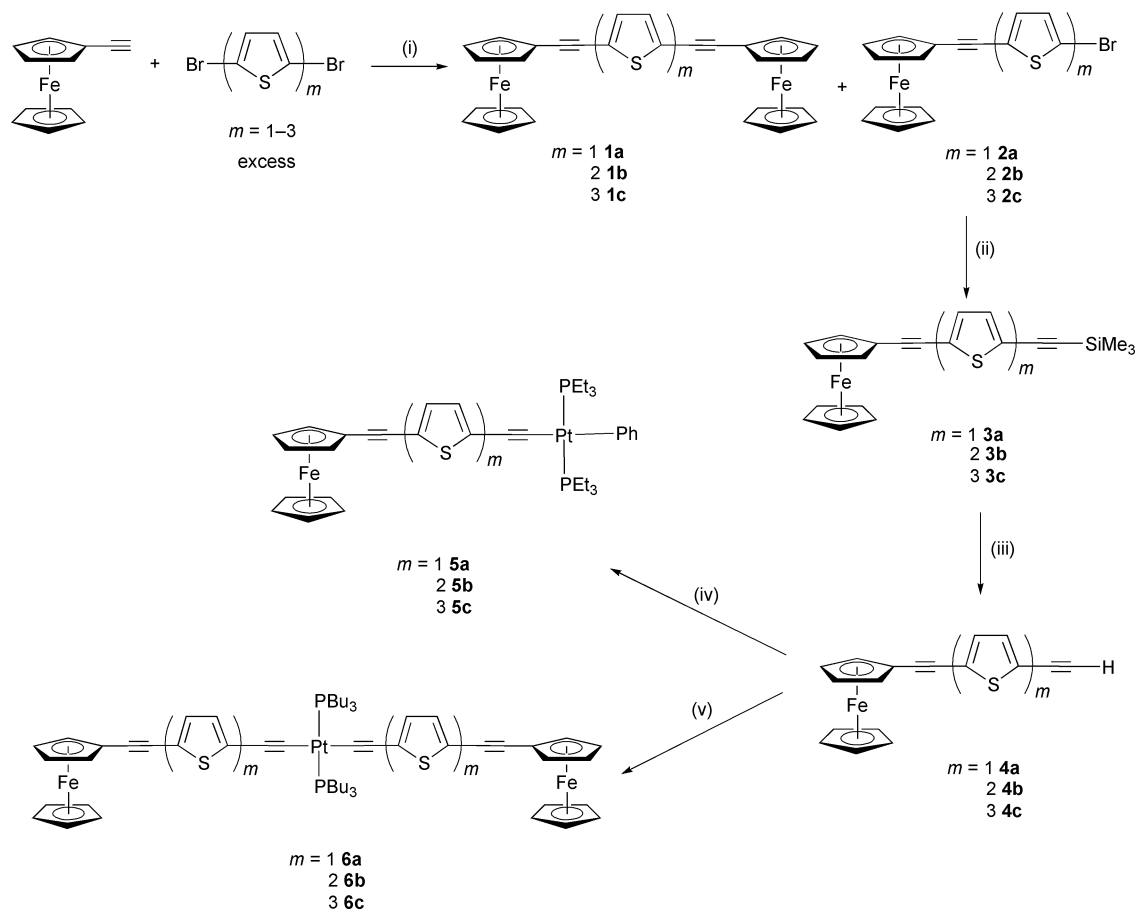
Within this research framework, the use of ferrocenyl

electrophores and their derivatives offers fascinating perspectives for the design and realization of such molecular wires, due to its stability in both the neutral and oxidized forms. Tremendous efforts have been devoted to the synthesis of ferrocene-based materials with π -conjugation.^{2a,12b,i,13} Although the 1,4-diethynylbenzene $\text{--C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C--}$ unit has been extensively used as the π -spacer in organic and homo- and hetero-metallic oligomers and polymers,¹⁴ increasing attention is currently being paid to materials based on oligothiophenes and polythiophenes because of their remarkable electronic and optoelectronic properties.¹⁵ The ease of modification and knowledge of the structure–property relationship of polythiophenes continue to make the synthesis of oligo- and polythiophenes a critical subject in the development of new advanced materials.^{15,16} Especially, π -conjugation of organometallic moieties into the oligothiophene chain should provide interesting models that possess unique properties which are not accessible in the classical organic counterparts.^{2,17} Insertion of these metal groups may promote or inhibit electron delocalization in such conjugated systems. Evidence indicates that metal acetylide polymers containing oligothiophenyl bridges may be good candidates for conducting materials.^{15b,18} Following our recent reports of the synthesis and optical properties of dimeric and polymeric platinum acetylide compounds with oligothiophenyl bridges,¹⁹ we have expanded this system to the alkynylferrocenyl complexes in the quest for new ferrocene-containing materials. We describe here the chemistry of a series of platinum(II) complexes of oligothiophene-functionalized ferrocenylacetylene.

Results and discussion

Synthesis

Scheme 1 summarizes the reaction steps leading to the new ferrocenyl compounds in this study. 2-Bromo-5-(2-ferrocenylethynyl)-



Scheme 1 Reagents and conditions: (i) NHPr^t_2 , $\text{Pd}(\text{OAc})_2$, PPh_3 , CuI ; (ii) $\text{Me}_3\text{SiC}\equiv\text{CH}$, NHPr^t_2 , $\text{Pd}(\text{OAc})_2$, PPh_3 , CuI ; (iii) K_2CO_3 , MeOH ; (iv) *trans*-[Pt(PEt₃)₂PhCl], NHPr^t_2 , CuI ; (v) *trans*-[Pt(PBu₃)₂Cl₂], NHPr^t_2 , CuI .

thiophene **2a**, 5'-bromo-5-(2-ferrocenylethynyl)[2,2']bithiophene **2b** and 5''-bromo-5-(2-ferrocenylethynyl)[2,2':5',2'']terthiophene **2c** were prepared in good yields as orange solids by the Sonogashira coupling reactions of ethynylferrocene with an excess of the corresponding dibromothiophenes.^{13b,20} The previously reported diferrocenyl bis(alkynyl) complexes **1a–1c** were also formed as minor products in these preparations and can hardly be avoided.^{13b} We were able to circumvent the formation of 1,4-diferrocenylbutadiyne under strictly anaerobic conditions.^{13b,21} Analogous Pd(II)/CuI-catalyzed cross-coupling reactions of **2a–2c** with trimethylsilylacetylene readily afforded the Me₃Si-substituted ferrocenyl species **3a–3c** in reasonable yields.^{19a,20} Removal of the Me₃Si groups in **3a–3c** to form **4a–4c** was accomplished by treatment with K₂CO₃ in MeOH^{20c} and these complexes with the free alkyne group can be used as key starting products for access to the hetero-bimetallic and trimetallic systems. The classical dehydrohalogenation reactions between **4a–4c** and *trans*-[Pt(PEt₃)₂PhCl] or *trans*-[Pt(PBu₃)₂Cl₂] under the CuI–NHPr^t₂ conditions provided the alkynyl and bis(alkynyl) platinum(II) complexes *trans*-[(η⁵-C₅H₅)Fe(η⁵-C₅H₄)C≡C(C₄H₂S)_mC≡CPt(PEt₃)₂Ph] **5a–5c** and *trans*-[(η⁵-C₅H₅)Fe(η⁵-C₅H₄)C≡C(C₄H₂S)_mC≡CPt(PBu₃)₂Cl] **6a–6c** (*m* = 1–3), respectively,^{19,22} and they were isolated as air-stable red crystalline solids in high yields. In all cases, the desired products were purified by preparative TLC on silica using a mixture of hexane and CH₂Cl₂ as eluent and obtained as solids in high purity. They exhibit moderate to good solubilities in common chlorinated solvents such as CH₂Cl₂ and CHCl₃. Satisfactory analytical and spectroscopic (FTIR, NMR and MS) data readily establish the exact identity of each compound and the molecular structures of selected complexes have been determined unequivocally by single-crystal X-ray analyses.

Spectroscopic and structural characterization

All the compounds show weak IR stretching vibrations for the C≡C groups in the range 2077–2229 cm^{−1} and a characteristic C≡C–H stretching mode is apparent as an intense peak around 3270 cm^{−1} for **4a–4c**. Essentially, two ν_{C≡C} bands are observed in the spectra for **3–6**. Those at the higher frequencies appear at similar energies for the whole series, and the lower frequency ν_{C≡C} bands are lower in energy for **5** and **6** than the corresponding absorptions for **3** and **4**, demonstrating the effect of back-bonding of the Pt(II) centre to the acetylide. The proton signals due to the heteroaromatic and other organic groups were clearly evident from the ¹H NMR spectra. In most cases, the expected ferrocenyl spectral pattern can be observed where the unsubstituted C₅H₅ ring resonates as a strong singlet and the monosubstituted C₅H₄ ring gives an unsymmetrical pair of 'pseudo' triplets corresponding to the A₂B₂ spectrum with *J*(adjacent) ≅ *J*(cross). For **6a–6c**, the symmetrical arrangement of the central platinum bis(acetylide) fragment was noted. The room-temperature ³¹P NMR signal of the platinum-containing species is observed as a sharp singlet accompanied by platinum satellites in each case. This is consistent with a *trans* configuration of the coordinated phosphine units around the platinum centre, which was further confirmed by X-ray structural determinations for **5b** and **6b** (*vide infra*). The ¹J_{P–Pt} values range from 2622–2626 Hz for **5a–5c** and 2316–2325 Hz for **6a–6c**, as expected for related *trans*-PtP₂ systems.^{19,22} The formulae of these new compounds were also established by the appearance of intense molecular ion peaks in the respective positive FAB mass spectra.

Although compound **1b** is known in the literature,^{13b} its structural characterization is not yet reported. The molecular structures of the bithienyl derivatives **1b**, **2b**, **4b**, **5b** and **6b** were determined and are illustrated in Figs. 1–5, respectively, and

pertinent bond parameters along with dihedral angles are collected in Tables 1–5. For **1b**, two halves of the molecules are related by the centre of symmetry at the midpoint of the C(16)–C(16A) bond. Reminiscent of other transition metal oligothiophenyl acetylide complexes reported such as *trans*-[Ph(Et₃P)₂PtC≡CRC≡CPTt(PEt₃)₂Ph]^{19a} and *trans*-[Ru(dppm)₂(C≡CR)₂] (R = terthiophenediyl),²³ the two thiophene rings display a *trans* arrangement in order to minimize steric repulsions between the lone pairs on both sulfur atoms. The iron–iron through-space distance is estimated to be *ca.* 17 Å in **1b**. The ethynyl bond is fairly typical at 1.189(3) Å and the linear rigid-rod nature of the molecule was shown by the C(10)–C(11)–C(12) bond angle of 174.3(3)°. The structures of **2b** and **4b** both reveal a *trans*

geometry with respect to the two thiophene groups. The C(11)–C(12) bonds are 1.177(3) and 1.197(3) Å, respectively, and the free alkyne C≡C bond distance is 1.169(4) Å in **4b** with the bond angle C(20)–C(21)–C(22) (179.3(3)°) close to linearity. In all the above three cases, the cyclopentadienyl rings of the ferrocenyl group are essentially planar and the tilt angles lie within the narrow range 0.8–1.4°. The ferrocenyl moieties have nearly staggered conformations for the five-membered rings with an angle deviation of *ca.* 3.0° in each case. The substituted cyclopentadienyl rings are more or less coplanar with the 2,5-disubstituted bithiophene nucleus and the complete list of dihedral angles between the planes passing through the thiophene and the C₅H₄ rings are tabulated in Tables 1–3.

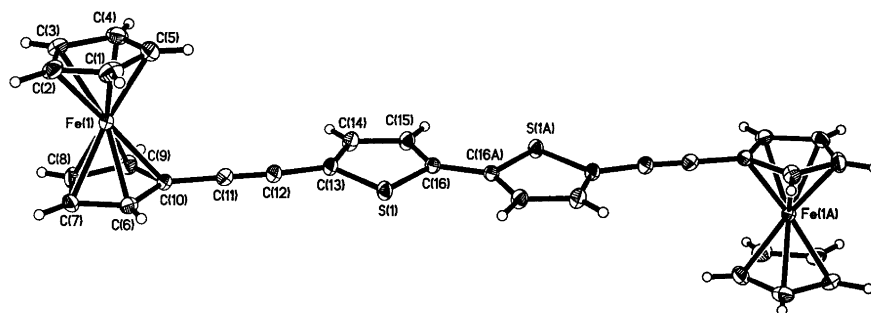


Fig. 1 A perspective drawing of compound **1b**.

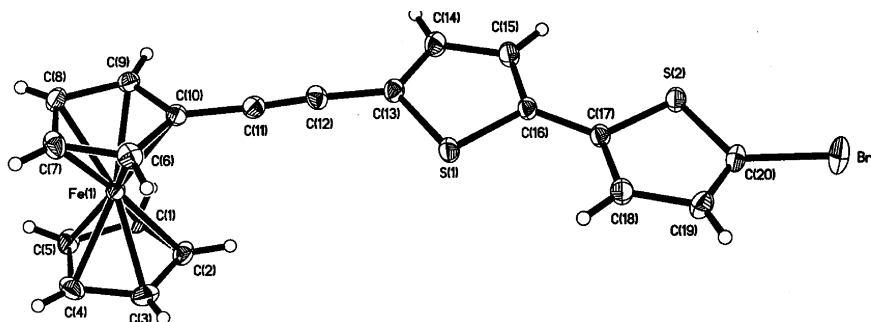


Fig. 2 A perspective drawing of compound **2b**.

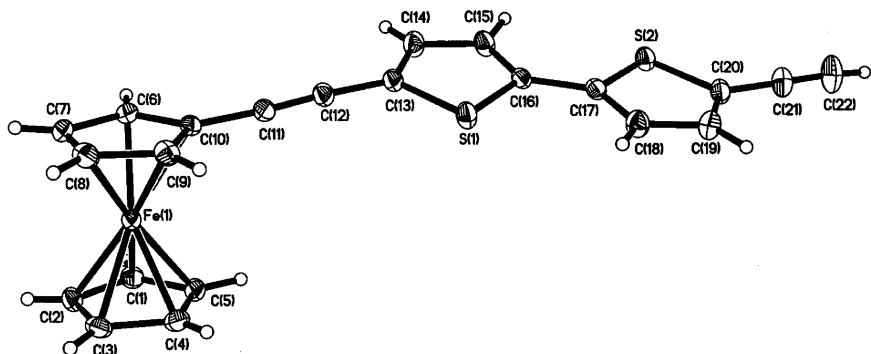


Fig. 3 A perspective drawing of compound **4b**.

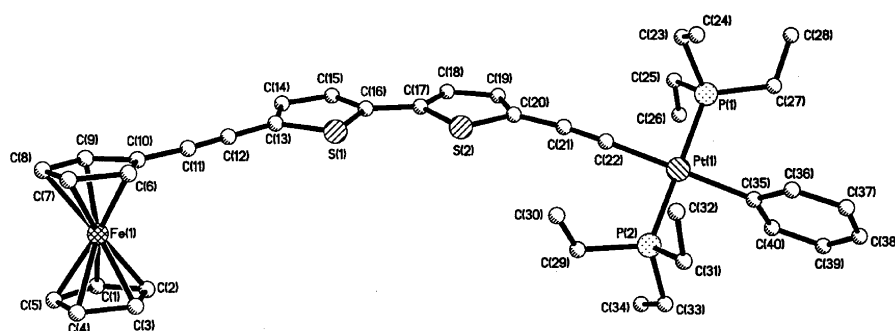
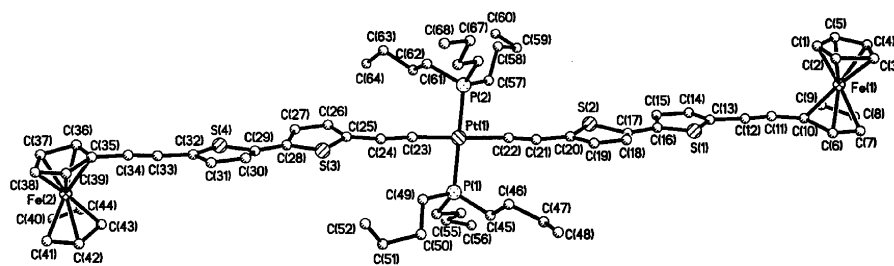


Fig. 4 A perspective drawing of compound **5b**.

Fig. 5 A perspective drawing of compound **6b**.**Table 1** Selected bond lengths (Å) and angles (°) for complex **1b**

Fe(1)–Cp	1.6556	Fe(1)–C ₅ H ₄	1.6536
C(10)–C(11)	1.427(3)	C(11)–C(12)	1.189(3)
C(12)–C(13)	1.423(3)	C(16)–C(16A)	1.448(4)
C(10)–C(11)–C(12)	174.3(3)	C(11)–C(12)–C(13)	176.1(2)
Dihedral angles (°) between planes ^a			
A and B	0.8	A and C	6.0
B and C	5.8		

^a Planes: A, defined by C(1)–C(2)–C(3)–C(4)–C(5); B, C(6)–C(7)–C(8)–C(9)–C(10); C, S(1)–C(13)–C(14)–C(15)–C(16).

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

Fe(1)–Cp	1.6480	Fe(1)–C ₅ H ₄	1.6463
C(10)–C(11)	1.426(3)	C(11)–C(12)	1.177(3)
C(12)–C(13)	1.436(3)	C(16)–C(17)	1.453(3)
Br(1)–C(20)	1.870(2)		
C(10)–C(11)–C(12)	176.0(3)	C(11)–C(12)–C(13)	176.6(3)
Br(1)–C(20)–S(2)	120.2(2)		
Dihedral angles (°) between planes ^a			
A and B	1.4	A and C	15.9
B and C	14.5	B and D	10.4
A and D	11.8	C and D	4.6

^a Planes: A, defined by C(1)–C(2)–C(3)–C(4)–C(5); B, C(6)–C(7)–C(8)–C(9)–C(10); C, S(1)–C(13)–C(14)–C(15)–C(16); D, S(2)–C(17)–C(18)–C(19)–C(20).

Table 3 Selected bond lengths (Å) and angles (°) for complex **4b**

Fe(1)–Cp	1.6525	Fe(1)–C ₅ H ₄	1.6492
C(10)–C(11)	1.433(3)	C(11)–C(12)	1.197(3)
C(12)–C(13)	1.421(3)	C(16)–C(17)	1.454(3)
C(20)–C(21)	1.421(3)	C(21)–C(22)	1.169(4)
C(10)–C(11)–C(12)	176.2(2)	C(11)–C(12)–C(13)	177.1(2)
C(20)–C(21)–C(22)	179.3(3)		
Dihedral angles (°) between planes ^a			
A and B	1.3	A and C	16.8
B and C	15.5	B and D	12.5
A and D	13.8	C and D	3.9

^a Planes: A, defined by C(1)–C(2)–C(3)–C(4)–C(5); B, C(6)–C(7)–C(8)–C(9)–C(10); C, S(1)–C(13)–C(14)–C(15)–C(16); D, S(2)–C(17)–C(18)–C(19)–C(20).

For **5b**, the bithiophenediyl-spaced bis(alkynyl) ligand links a ferrocenyl unit at one end and a Pt(PEt₃)₂Ph unit at the other extreme. The two PEt₃ groups adopt a *trans* geometry at the platinum centre with unexceptional coordination distances. Unlike the free precursor **4b**, the two sulfur atoms in the bithiophene fragment are arranged on the same side in **5b**, presumably due to solid-state packing effects. An almost staggered conformation is observed for the cyclopentadienyl rings in **5b** with a twist angle of 2.0°. All four five-membered rings within the molecule are nearly coplanar (dihedral angles 0.1–11.4°) and the phenyl ring is inclined by *ca.* 52° to the S(2)

Table 4 Selected bond lengths (Å) and angles (°) for complex **5b**

Fe(1)–Cp	1.6456	Fe(1)–C ₅ H ₄	1.6429
C(10)–C(11)	1.425(6)	C(11)–C(12)	1.195(6)
C(12)–C(13)	1.412(6)	C(16)–C(17)	1.460(5)
C(20)–C(21)	1.424(5)	C(21)–C(22)	1.197(6)
Pt(1)–C(22)	2.014(4)	Pt(1)–P(1)	2.288(1)
Pt(1)–P(2)	2.291(1)	Pt(1)–C(35)	2.074(4)
C(10)–C(11)–C(12)	176.9(5)	C(11)–C(12)–C(13)	178.6(5)
C(20)–C(21)–C(22)	174.6(5)	Pt(1)–C(22)–C(21)	174.7(4)
C(22)–Pt(1)–C(35)	175.9(2)	C(22)–Pt(1)–P(1)	87.1(1)
C(22)–Pt(1)–P(2)	92.6(1)		
Dihedral angles (°) between planes ^a			
A and B	0.1	A and C	10.7
A and E	44.4	B and C	10.6
B and E	44.6	C and D	3.3
D and E	52.2	A and D	11.4
		B and D	11.3
		C and E	53.6

^a Planes: A, defined by C(1)–C(2)–C(3)–C(4)–C(5); B, C(6)–C(7)–C(8)–C(9)–C(10); C, S(1)–C(13)–C(14)–C(15)–C(16); D, S(2)–C(17)–C(18)–C(19)–C(20); E, C(35)–C(36)–C(37)–C(38)–C(39)–C(40).

Table 5 Selected bond lengths (Å) and angles (°) for complex **6b**

Fe(1)–Cp	1.6204	Fe(1)–C ₅ H ₄	1.6706
Fe(2)–Cp	1.7031	Fe(2)–C ₅ H ₄	1.5897
C(10)–C(11)	1.40(1)	C(11)–C(12)	1.19(2)
C(12)–C(13)	1.47(2)	C(16)–C(17)	1.54(2)
C(20)–C(21)	1.44(1)	C(21)–C(22)	1.15(2)
Pt(1)–C(22)	2.07(1)	Pt(1)–P(1)	2.325(3)
Pt(1)–P(2)	2.282(4)	Pt(1)–C(23)	1.92(1)
C(23)–C(24)	1.30(2)	C(24)–C(25)	1.51(2)
C(28)–C(29)	1.42(1)	C(32)–C(33)	1.43(2)
C(33)–C(34)	1.24(2)	C(34)–C(35)	1.48(2)
C(10)–C(11)–C(12)	168(1)	C(11)–C(12)–C(13)	159(1)
C(20)–C(21)–C(22)	158(1)	Pt(1)–C(22)–C(21)	173(1)
C(22)–Pt(1)–P(1)	93.4(3)	C(22)–Pt(1)–P(2)	86.2(3)
C(22)–Pt(1)–C(23)	178.3(6)	Pt(1)–C(23)–C(24)	174(1)
C(23)–C(24)–C(25)	162(1)	C(32)–C(33)–C(34)	159(1)
C(33)–C(34)–C(35)	173(1)		
Dihedral angles (°) between planes ^a			
A and B	1.3	A and C	9.9
A and E	5.8	A and F	15.2
A and H	8.9	B and C	10.5
B and E	6.3	B and F	15.9
B and H	7.6	C and D	1.6
C and F	5.5	C and G	10.6
D and E	5.8	D and F	4.0
D and H	15.8	E and F	9.6
E and H	11.2	F and G	15.6
G and H	4.1	A and D	11.5
		A and G	7.3
		B and D	12.1
		B and G	6.3
		C and E	4.1
		C and H	14.6
		D and G	11.7
		E and G	7.5
		F and H	19.7

^a Planes: A, defined by C(1)–C(2)–C(3)–C(4)–C(5); B, C(6)–C(7)–C(8)–C(9)–C(10); C, S(1)–C(13)–C(14)–C(15)–C(16); D, S(2)–C(17)–C(18)–C(19)–C(20); E, S(3)–C(25)–C(26)–C(27)–C(28); F, S(4)–C(29)–C(30)–C(31)–C(32); G, C(35)–C(36)–C(37)–C(38)–C(39); H, C(40)–C(41)–C(42)–C(43)–C(44).

thienyl mean plane. The alkynyl bond distances C(11)–C(12) and C(21)–C(22) are 1.195(6) and 1.197(6) Å, respectively, and do not differ significantly from those seen in, for example,

trans-[Ph(Et₃P)₂PtC≡C(η⁵-C₅H₄)Fe(η⁵-C₅H₄)C≡CPt(PEt₃)₂Ph] (1.203(7) Å),^{22f} *trans*-[Ph(Et₃P)₂PtC≡C{(η⁵-C₅H₄)Fe(η⁵-C₅H₄)₂-Fe(η⁵-C₅H₄)C≡CPt(PEt₃)₂Ph} (1.21(1) Å),^{22f} *trans*-[{(η⁵-C₅H₅)Fe(η⁵-C₅H₄)C≡C}₂C₆H₃{C≡CRu(dppm)₂Cl}] (1.20(2) and 1.21(2) Å),²⁴ *trans*-[Ph(Et₃P)₂PtC≡C(R)C≡CPt(PEt₃)₂Ph] (R = fluorene-2,7-diyl) (1.17(2) and 1.18(2) Å),²⁵ *trans*-[Ph(Et₃P)₂PtC≡C(R)C≡CPt(PEt₃)₂Ph] (R = 9-ferrocenylmethylenefluorene-2,7-diyl) (1.22(2) and 1.21(2) Å)²⁵ and *trans*-[{(η⁵-C₅H₅)Fe(η⁵-C₅H₄)C≡C}₂Ru(dppm)₂] (1.184(8) Å).^{12h,i} The bond angles C(10)–C(11)–C(12) (176.9(5)°) and Pt(1)–C(22)–C(21) (174.7(4)°) are close to 180° for the alkynyl fragments.

For **6b**, the crystal structure shows a diferrocenyl end-capped molecule in which the two acetylide linkages are bonded to the central platinum centre in a *trans* orientation with normal bond parameters. The platinum atom is surrounded by four ligands in a square planar geometry. Within each ferrocenyl subunit, the cyclopentadienyl rings have a slightly staggered (*ca.* 6.4–6.9°) conformation, the rings being almost parallel to within 1.3–4.1°. On steric grounds, the bithienyl systems exhibit a *trans* conformation for the sulfur atoms and do not deviate significantly from planarity (mean deviation of *ca.* 0.019–0.035 Å). A slight lengthening of the alkynyl bond lengths (mean distance = 1.22(2) Å) suggests π -conjugation along the main chain. The rigidity of the complex is confirmed with four C≡C bonds and four thienyl rings connecting the organometallic entities to afford an iron–iron through-space separation of *ca.* 32 Å. The average through-space Fe–Pt distance is 16 Å. However, there are no intermolecular interactions of note.

Absorption properties

The electronic absorption spectra of all new complexes were measured in CH₂Cl₂ solutions and the data are collected in Table 6. In general, the absorption spectra of the ferrocenyl precursor complexes **1–4** show intense, relatively high-energy bands in the near UV and visible region, which arise from the π – π^* transition of the oligothiophene fragments.^{12c,13b,19,26} This assignment is in agreement with the fact that an increase in the extent of π -conjugation with additional thienyl units from one to three results in a bathochromic shift of the π – π^* transition and a notable increase in the molar absorption coefficients (Fig. 6).^{13b} Increasing the number of thienyl units in the main chain stabilizes the lowest unoccupied molecular orbitals of the oligothiophene linkage. The electronic spectra of the platinum-containing complexes **5** and **6** are also dominated by the structureless π – π^* transition bands of the corresponding oligothiophene bridges.¹⁹ The effect of attachment of the platinum(II) moiety is found to lower the transition energies and to increase the absorption intensity, indicating an enhancement in the degree of π -delocalization through the platinum conjugated system. These observations also provide evidence for the additional charge-transfer character due to the platinum centre,²⁷ which was further supported by molecular orbital calculations (*vide infra*). Again, increasing conjugation through more thienyl units leads to a decreased transition energy for **5a–5c** as well as **6a–6c**. Thus, a red shift of *ca.* 61 nm is observed from **5a** to **5c**, whereas the shift is 57 nm from **6a** to **6c** (Fig. 6). We note that λ_{max} decreases according to the sequence **6** > **5** > **1** > **3** > **4** > **2**. However, the extent of bathochromic shifts induced by the end substitution of organometallic groups is less pronounced with increasing number of thienyl rings. This substituent effect diminishes progressively as more thienyl units are added and there would be little benefit in increasing the number of thiophene units above 5 or 6. Such chain length dependence of the optical properties can be rationalized from the plot of $\Delta\lambda$ against *n* (Fig. 7) where $\Delta\lambda$ corresponds to the red shift in wavelength between the organometallic end-substituted complexes **1**, **5** and **6** and the free alkynes **4** in the absence of metal groups, and *n* is the number of thiophene units per ferrocenyl end group in the main chain. From the plot, it is obvious that the shift is

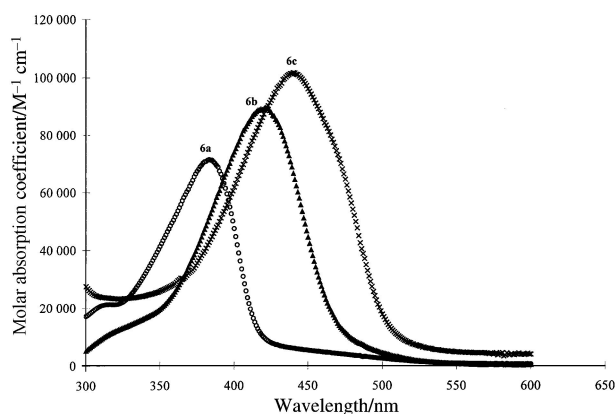


Fig. 6 Absorption spectra of compounds **6a–6c**.

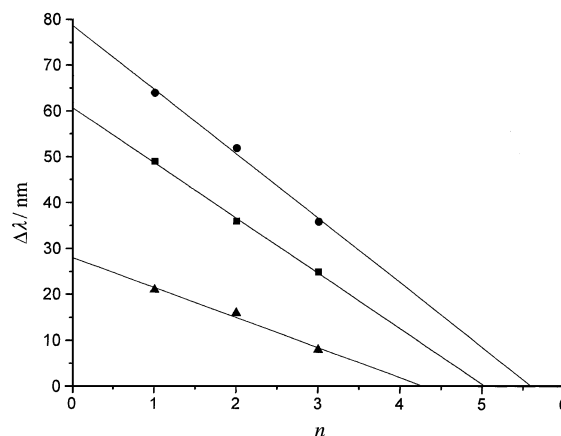


Fig. 7 Bathochromic shifts of the absorption maximum induced by the end ferrocenyl substitution (▲), end –Pt(PEt₃)₂Ph substitution (■) and end –Pt(PBu₃)₂– substitution (●), relative to the number of thiophene units of the chain; the optical data for **1a–1c** are taken from ref. 13b.

the largest for the bis(alkynyl) platinum(II) complexes **6a–6c** at the same value of *n*.

Electrochemistry

The electrochemical behaviour of our complexes were studied by cyclic voltammetry in CH₂Cl₂ at room temperature and the results are given in Table 6. In each case, the cyclic voltammogram is characterized by a single quasi-reversible oxidation wave due to the ferrocenyl electrophore that is present in the complex. An anodic shift of the ferrocene–ferrocenium couple with respect to the ferrocene standard is in line with the unsaturation of the ethynyl bridge which makes the removal of electrons more difficult than for pure ferrocene.²⁸ Clearly, a small negative shift of the ferrocenyl redox potential occurs upon progressive insertion of thienyl rings because of the increased electron density in the ferrocene vicinity induced by the electron-rich thiophene groups. When the conjugation length is increased, oxidation is favoured by the delocalization of charge along the system which renders the ferrocenyl oxidation easier. Likewise, the slight but notable cathodic shift of the Fe(III)/Fe(II) couple for **5** and **6** can be attributed to the electron delocalization into the platinum segment through a $d\pi \rightarrow p\pi$ interaction.^{12c} It was also found that the first oxidation wave for each of the diferrocenyl compounds **6a–6c** corresponds to a single-step two-electron oxidation involving the concomitant oxidation of the two terminal ferrocenyl moieties.^{13b,29} Analogous to **1b**, these two ferrocenyl end groups only exhibit sparse electronic communication in **6a–6c**.^{13b} It has also been reported that there is very little electronic interaction between the redox-active iron cores through the metal ethynyl

Table 6 Electronic absorption and redox data for ferrocenyl compounds

Compound	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^{-3}/\text{M}^{-1} \text{cm}^{-1}$) ^a	Optical gap ^b /eV	E_{ox} (ΔE_{p}) ^c
2a	311 (5.0), 445 sh (0.3)	3.12	0.15 (119)
2b	355 (14.4), 460 sh (1.2)	3.03	0.12 (119)
2c	394 (43.3)	2.74	0.11 (119), 0.82 ^d
3a	327 (17.1), 442 sh (1.0)	3.04	0.16 (160)
3b	374 (30.1)	2.90	0.11 (139)
3c	405 (39.3)	2.63	0.10 (80), 0.80 ^d
4a	319 (7.1), 429 sh (0.6)	2.99	0.16 (139)
4b	369 (29.0)	2.92	0.11 (99)
4c	404 (40.7)	2.64	0.08 (119), 0.72 ^d
5a	368 (24.3), 421 (1.4)	2.93	0.12 (99), 0.67 ^d
5b	405 (32.9)	2.75	0.10 (119), 0.53 ^d
5c	429 (35.9)	2.49	0.06 (119), 0.38, ^d 0.70 ^d
6a	383 (71.3)	2.90	0.07 (99), 0.65 ^d
6b	421 (89.4)	2.57	0.04 (116), 0.51 ^d
6c	440 (101.5)	2.44	0.02 (120), 0.35, ^d 0.61 ^d
1a	340 (26.7), 445 sh (3.4) ^e	2.91	^e
1b	385 (32.4) ^e	2.72	^e
1c	412 (44.7) ^e	2.46	^e

^a All absorption spectra were recorded in CH_2Cl_2 at 293 K. ^b Estimated from the absorption edge. ^c All the potential values are with reference to the external ferrocene standard. $E_{\text{ox}} = (E_{\text{pc}} + E_{\text{pa}})/2$ for reversible oxidation, and peak potential is reported for irreversible oxidation (in volts). ΔE_{p} in mV. Scan rate = 100 mV s^{-1} . ^d Irreversible wave. ^e Ref. 13b.

bridge in a series of complexes of the type *trans*-[(η^5 -C₅H₅)-Fe(η^5 -C₅H₄)C≡C]Pt(PR₃)₂C≡C-(η^5 -C₅H₄)Fe(η^5 -C₅H₅)]³⁰ and *trans*-[Pd(PBu₃)₂{C≡CC₆H₄C≡C(η^5 -C₅H₄)Fe(η^5 -C₅H₅)}₂]^{11a}

Another redox event was also observed at higher positive potentials in several compounds due to the oxidation of the thienyl fragments. No such anodic wave was associated with compounds **2a**, **2b**, **3a**, **3b**, **4a** and **4b** with one or two thiophene units but without Pt(II) functionality. However, complexes **2c**, **3c** and **4c** with an increased oligothiophenyl chain length were found to undergo an irreversible thienyl oxidation peaking at 0.82, 0.80 and 0.72 V, respectively, which agrees with the common phenomenon that formation of the heteroaromatic cation radicals is favoured by the presence of electron-donating end groups³¹ and increased in the conjugation in the chain.^{26b} It is well-documented that electrooxidation of oligothiophenes is often an irreversible process because the electrogenerated radical cations readily undergo rapid coupling reactions leading to higher oligomers or polymers. The stability of these radical cations increases when the oligomeric chain becomes longer.^{26b} Insertion of platinum(II) moieties in **5** and **6** also tends to facilitate the oxidation processes of the thienyl core. For complexes **5a–5c** or **6a–6c**, each of them displays an irreversible thienyl oxidation wave within 0.38–0.67 V for **5** and 0.35–0.65 V for **6**, and a second irreversible oxidation of the thiophene moiety also occurs at 0.70 and 0.61 V for **5c** and **6c**, respectively (Fig. 8). The waves become more reversible at higher scan rates (>100 mV s^{-1}). Lowering of the redox potential of the thiophene units on increasing the chain length can be verified for **5a–5c** as well as **6a–6c**, which is a manifestation of a more π delocalized system in the terthienyl congeners. As observed for some thienylenevinylene oligomers, it is likely that the first thienyl oxidation step is generally followed by chemical reactions or the formation of a polymer.^{16c}

Theoretical studies

To study the electronic structures of these newly synthesized ferrocenyl complexes, we have carried out molecular orbital calculations at the B3LYP level of density functional theory for **1b**, **2b**, **4b**, **5b** and **6b** based on their experimental geometries obtained from the crystallographic studies.³² For theoretical simplicity, PH₃ was used to replace the phosphines bonded to the Pt(II) centre in the calculations. Examining the characteristics of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals for these complexes, we found that they are commonly related to π and π^* of the bithiophene

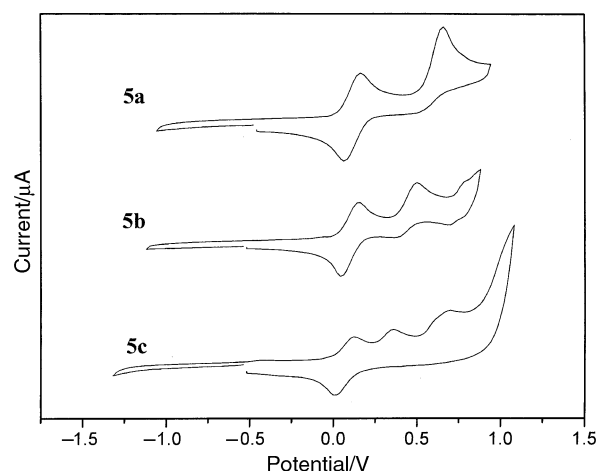


Fig. 8 Cyclic voltammetric traces of compounds **5a–5c** measured in CH_2Cl_2 solution (scan rate 100 mV s^{-1}).

structural unit(s). To better understand this common feature, we plot a correlation diagram, depicted in Fig. 9, showing the frontier molecular orbitals for 5,5'-diethynyl[2,2']bithiophene and compound **4b**.³³ From Fig. 9, we can see clearly the common feature that the HOMO and LUMO correspond to π and π^* of the bithiophene aromatic unit. The HOMO–LUMO gap for **4b** is smaller in comparison to the parent bithiophene without the terminal ferrocenyl moiety. This is consistent with the presence of the metal coordination which enhances the delocalization in the conjugated structural backbone. The main contribution to the second and third HOMOs is mainly from the Fe centre, corresponding to the d_{xy} and $d_{x^2-y^2}$ orbitals of Fe, if we define the Cp–Fe–Cp axis as the z -axis of the Cartesian system (Fig. 9).

Fig. 10 shows the molecular orbitals in the frontier region for all five complexes studied. For each of them, the HOMO–LUMO transition is related to the π – π^* excitation within the bithiophene structural unit(s). There are two Fe d orbitals immediately below the HOMO which may give rise to a high-energy Fe(d)-to-ligand(π^*) charge-transfer transition. For complexes **5b** and **6b** containing square-planar Pt(II) coordination, the energy levels are complicated because of the presence of Pt–L(σ^*) components and the Pt's empty p orbital in the LUMO region. We expect that ligand(π)-to-Pt charge transfer is also accessible in the UV/VIS spectra at high energies. The

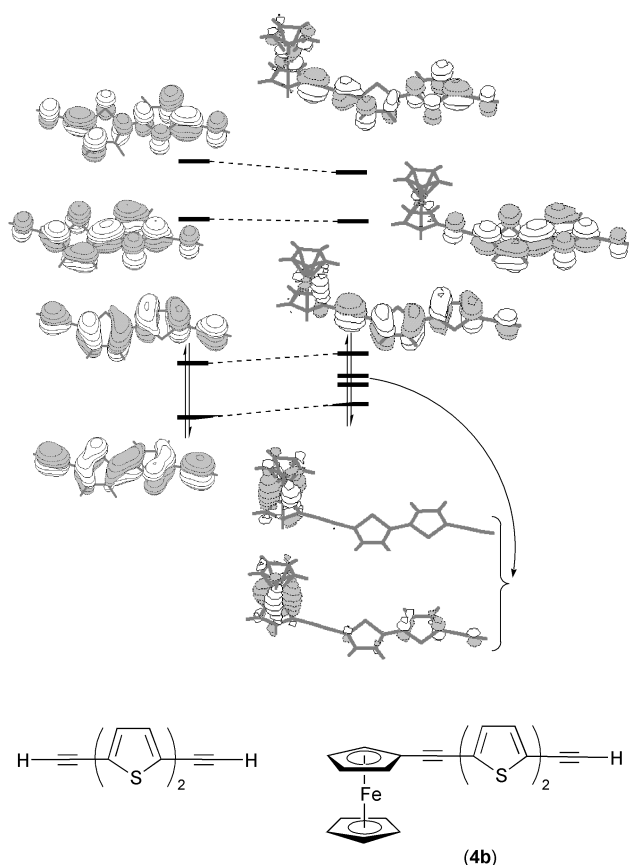


Fig. 9 The frontier molecular orbitals for compound **4b** and the parent 5,5'-diethynyl[2,2']bithiophene.

HOMO–LUMO gaps shown in Fig. 10 are closely correlated to the extent of delocalization in the π -conjugation for the complexes. The increase of the π -delocalization by extending the conjugation system or introducing the metal coordination results in a smaller optical gap. The calculated relative HOMO–LUMO gaps are consistent with the experimental energy gap order **2b** > **4b** > **5b** > **1b** > **6b** (Table 6) and complex **6b** absorbs at the longest wavelength among the homologous bithiophene family.

Concluding remarks

In summary, a new series of soluble oligothiophene-substituted alkynylferrocene complexes have been prepared in good yields and their use in the generation of novel rigid-rod platinum(II) complexes has been pursued. Electronic absorption and electrochemical studies of these hetero-bimetallic and trimetallic complexes have been investigated as a function of the oligothiophenyl chain length. Addition of Pt(II) decreases the energy of the π – π^* transition in the oligothiophenyl bridges which is consistent with the theoretical calculations, and increases the absorption intensity. Electrochemical oxidation of the thiophene moiety can be facilitated and stabilized by increased conjugation length and incorporation of a Pt centre. It is likely that the redox behaviour of this class of materials can be modulated and improved by using 3,4-disubstituted thiophene segments that can exert a stabilizing effect induced by the substituents on the ionized states. Work in this direction and in extending this synthetic protocol to design other conjugated ferrocenyl heterometallic systems incorporating different spacer units or organometallic fragments is in progress.

Experimental

General

All reactions were carried out under a nitrogen atmosphere

with the use of standard 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 materials ethynylferrocene,³⁴ *trans*-[Pt(PEt₃)₂PhCl]³⁵ and *trans*-[Pt(PBu₃)₂Cl]₂³⁶ were prepared by the literature methods. IR spectra were recorded in CH₂Cl₂ using a Perkin-Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in appropriate solvents on a JEOL EX270 or a Varian INOVA 400 MHz FT-NMR spectrometer, with ¹H NMR chemical shifts quoted relative to SiMe₄ and ³¹P chemical shifts relative to an 85% H₃PO₄ external standard. Fast atom bombardment (FAB) 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/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]BF₄. Ferrocene was added as a calibrant after each set of measurements and all potentials reported were quoted with reference to the ferrocene–ferrocenium couple. The number of electrons transferred for compounds **6a–6c** 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. For density functional calculations at the B3LYP level, the basis set used for C and H atoms was 6-31G while effective core potentials with a LanL2DZ basis set were employed for P, S, Br, Fe and Pt atoms. Polarization functions were added for P, S and Br atoms ($\xi_d(\text{P}) = 0.340$, $\xi_d(\text{S}) = 0.421$ and $\xi_d(\text{Br}) = 0.389$).

Synthetic procedures

2-Bromo-5-(2-ferrocenylethynyl)thiophene 2a. 2,5-Dibromothiophene (0.11 cm³, 1.00 mmol), ethynylferrocene (105 mg, 0.50 mmol) and NHPr₄⁺ (10 cm³) were mixed under N₂ with catalytic amounts of Pd(OAc)₂ (1 mg), CuI (1 mg) and PPh₃ (2 mg). The mixture was stirred under reflux for 17 h, after which all volatile components were removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and the red solution filtered through a short silica column. The filtrate was concentrated and subjected to preparative TLC separation on silica using hexane–CH₂Cl₂ (6 : 1, v/v) as eluent. The orange product **2a** (*R*_f = 0.53) was obtained in 60% yield (111 mg), accompanied by 15% of the known compound 2,5-bis(ferrocenylethynyl)thiophene **1a** (*R*_f = 0.23). (Found: C, 51.50; H, 2.86. C₁₆H₁₁BrFeS requires C, 51.79; H, 2.99%). IR (CH₂Cl₂): 2207 cm^{−1} ($\nu_{\text{C}\equiv\text{C}}$). ¹H NMR (CDCl₃): δ 6.94 (d, *J*_{H–H} = 4.0 Hz, 1H, thienyl), 6.91 (d, *J*_{H–H} = 4.0 Hz, 1H, thienyl), 4.48 (t, *J*_{H–H} = 1.9 Hz, 2H, C₅H₄), 4.25 (t, *J*_{H–H} = 1.9 Hz, 2H, C₅H₄) and 4.24 (s, 5H, Cp). MS (FAB): *m/z* 371 (calc. M⁺ 371).

5'-Bromo-5-(2-ferrocenylethynyl)[2,2']bithiophene 2b. Compound **2b** was prepared using the conditions described above for **2a** but 5,5'-dibromo[2,2']bithiophene (324 mg, 1.00 mmol) and ethynylferrocene (105 mg, 0.50 mmol) were used instead to afford an orange powder of **2b** (*R*_f = 0.30) in 45% yield (102 mg) along with 5,5'-bis(ferrocenylethynyl)[2,2']bithiophene **1b** (*R*_f = 0.15, 14%) after silica TLC purification using hexane–CH₂Cl₂ (9 : 1, v/v) as eluent. (Found: C, 52.80; H, 2.81. C₂₀H₁₃BrFeS₂ requires C, 53.01; H, 2.89%). IR (CH₂Cl₂): 2202 cm^{−1} ($\nu_{\text{C}\equiv\text{C}}$). ¹H NMR (CDCl₃): δ 7.08 (d, *J*_{H–H} = 3.8 Hz, 1H, thienyl), 6.97 (d, *J*_{H–H} = 3.8 Hz, 1H, thienyl), 6.96 (d, *J*_{H–H} = 3.8 Hz, 1H, thienyl),

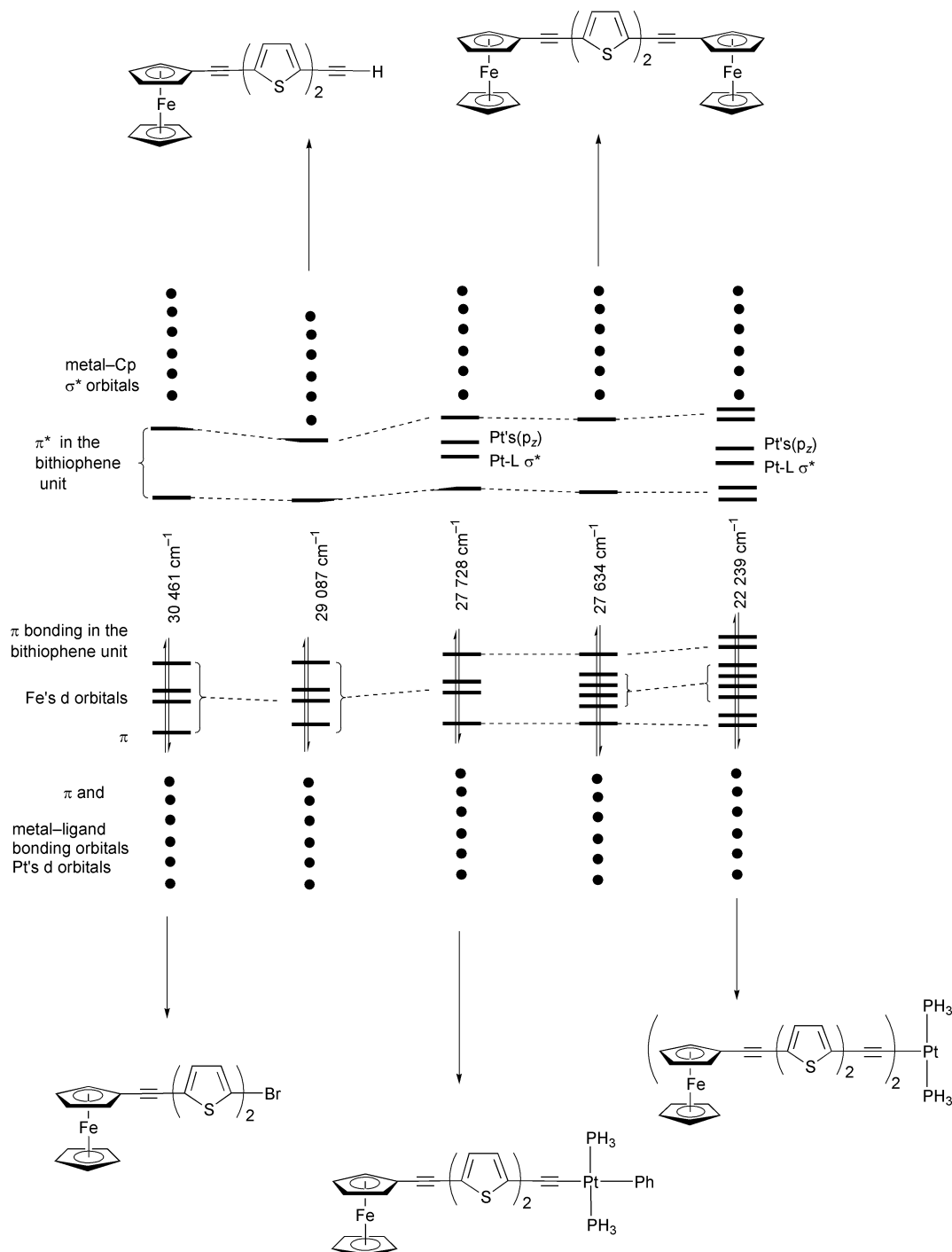


Fig. 10 Bonding characteristics of the frontier molecular orbitals for the bithienyl-linked ferrocenyl compounds.

6.91 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 4.50 (t, $J_{\text{H-H}} = 2.0$ Hz, 2H, C_5H_4), 4.27 (t, $J_{\text{H-H}} = 2.0$ Hz, 2H, C_5H_4) and 4.25 (s, 5H, Cp). MS (FAB): m/z 453 (calc. M^+ 453).

5'-Bromo-5-(2-ferrocenylethynyl)[2,2' : 5',2'']terthiophene 2c. Compound **2c** was synthesized similarly from 5,5'-dibromo[2,2' : 5',2'']terthiophene (406 mg, 1.00 mmol) and ethynylferrocene (105 mg, 0.50 mmol) and isolated as an orange solid in 35% yield (94 mg) by TLC on silica ($R_f = 0.48$) eluting with hexane- CH_2Cl_2 (4 : 1, v/v). The diferrocenyl complex **1c** was also formed as a minor orange band ($R_f = 0.25$, yield 12%). (Found: C, 53.65; H, 2.71. $\text{C}_{24}\text{H}_{15}\text{BrFeS}_3$ requires C, 53.85; H, 2.82%). IR (CH_2Cl_2): 2199 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.10 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 7.06 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 7.02 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 7.00 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 6.97 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 6.91 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 4.50 (t, $J_{\text{H-H}} = 1.9$ Hz, 2H, C_5H_4), 4.26 (t, $J_{\text{H-H}}$

$= 1.9$ Hz, 2H, C_5H_4) and 4.25 (s, 5H, Cp). MS (FAB): m/z 535 (calc. M^+ 535).

2-Trimethylsilylthienyl-5-(2-ferrocenylethynyl)thiophene 3a.

A mixture of **2a** (111 mg, 0.30 mmol), $\text{Me}_3\text{SiC}\equiv\text{CH}$ (0.42 cm^3 , 3.00 mmol) and NHPr^t_2 (10 cm^3) combined with catalytic quantities of $\text{Pd}(\text{OAc})_2$ (1 mg), CuI (1 mg) and PPh_3 (2 mg) were allowed to reflux for 17 h. The red solid obtained by removing the solvent *in vacuo* was redissolved in CH_2Cl_2 . Upon filtration through a short silica pad, the filtrate was concentrated and purified by preparative TLC ($R_f = 0.35$) using hexane- CH_2Cl_2 (24 : 1, v/v) as eluent. An analytically pure sample of **3a** was collected as an orange solid in an isolated yield of 95% (110 mg). (Found: C, 64.78; H, 5.07. $\text{C}_{21}\text{H}_{20}\text{FeSiS}$ requires C, 64.94; H, 5.19%). IR (CH_2Cl_2): 2210 and 2145 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.08 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 7.02 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 4.50 (t, $J_{\text{H-H}} = 1.8$ Hz, 2H, C_5H_4), 4.27 (t,

$J_{\text{H-H}} = 1.8$ Hz, 2H, C_5H_4), 4.25 (s, 5H, Cp) and 0.25 (s, 9H, SiMe_3). MS (FAB): m/z 388 (calc. M^+ 388).

5'-Trimethylsilyl ethynyl-5-(2-ferrocenylethynyl)[2,2']bithiophene 3b. Compound **3b** was prepared in 70% yield (82 mg) by following a procedure similar to that described for **3a** using **2b** (113 mg, 0.25 mmol). (Found: C, 63.75; H, 4.64. $\text{C}_{25}\text{H}_{22}\text{FeSi}_2$ requires C, 63.82; H, 4.71%). IR (CH_2Cl_2): 2200 and 2140 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.11 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 7.08 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 7.02 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 7.00 (d, $J_{\text{H-H}} = 3.8$ Hz, 1H, thienyl), 4.50 (t, $J_{\text{H-H}} = 1.9$ Hz, 2H, C_5H_4), 4.26 (t, $J_{\text{H-H}} = 1.9$ Hz, 2H, C_5H_4), 4.25 (s, 5H, Cp) and 0.25 (s, 9H, SiMe_3). MS (FAB): m/z 470 (calc. M^+ 470).

5''-Trimethylsilyl ethynyl-5-(2-ferrocenylethynyl)[2,2':5',2'']terthiophene 3c. From **2c** (107 mg, 0.20 mmol), this procedure provided the title compound **3c** in moderate yield (46%, 51 mg). (Found: C, 62.85; H, 4.30. $\text{C}_{29}\text{H}_{24}\text{FeSi}_3$ requires C, 63.03; H, 4.38%). IR (CH_2Cl_2): 2229 and 2139 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.14 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 7.11 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 7.08 (m, 2H, thienyl), 7.04 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 7.01 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 4.51 (t, $J_{\text{H-H}} = 2.0$ Hz, 2H, C_5H_4), 4.27 (t, $J_{\text{H-H}} = 2.0$ Hz, 2H, C_5H_4), 4.26 (s, 5H, Cp) and 0.26 (s, 9H, SiMe_3). MS (FAB): m/z 552 (calc. M^+ 552).

2-Ethynyl-5-(2-ferrocenylethynyl)thiophene 4a. To a solution of the silylated complex **3a** (93 mg, 0.24 mmol) in Et_2O (15 cm^3) was added K_2CO_3 (17 mg, 0.12 mmol) in MeOH (20 cm^3). The mixture was stirred for 24 h at room temperature. After evaporation of the solvent the crude material was dissolved in CH_2Cl_2 and purified *via* silica TLC using hexane– CH_2Cl_2 (5 : 1, v/v) as eluent to afford a major orange solid ($R_f = 0.48$) in 93% yield (71 mg). (Found: C, 68.27; H, 3.71. $\text{C}_{18}\text{H}_{12}\text{FeS}$ requires C, 68.37; H, 3.83%). IR (CH_2Cl_2): 3272 ($\nu_{\text{C}\equiv\text{H}}$), 2201 and 2101 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.13 (d, $J_{\text{H-H}} = 3.6$ Hz, 1H, thienyl), 7.04 (d, $J_{\text{H-H}} = 3.6$ Hz, 1H, thienyl), 4.50 (t, $J_{\text{H-H}} = 1.6$ Hz, 2H, C_5H_4), 4.27 (t, $J_{\text{H-H}} = 1.6$ Hz, 2H, C_5H_4), 4.25 (s, 5H, Cp) and 3.36 (s, 1H, $\text{C}\equiv\text{CH}$). MS (FAB): m/z 316 (calc. M^+ 316).

5'-Ethynyl-5-(2-ferrocenylethynyl)[2,2']bithiophene 4b. The same desilylation method was employed to give **4b** from **3b** and the compound was isolated as an orange powdery solid in 84% yield by TLC (hexane– CH_2Cl_2 , 3 : 1, v/v, $R_f = 0.55$). (Found: C, 66.35; H, 3.44. $\text{C}_{22}\text{H}_{14}\text{FeS}_2$ requires C, 66.34; H, 3.54%). IR (CH_2Cl_2): 3274 ($\nu_{\text{C}\equiv\text{H}}$), 2192 and 2098 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.17 (d, $J_{\text{H-H}} = 3.7$ Hz, 1H, thienyl), 7.10 (d, $J_{\text{H-H}} = 3.7$ Hz, 1H, thienyl), 7.05 (d, $J_{\text{H-H}} = 3.7$ Hz, 1H, thienyl), 7.02 (d, $J_{\text{H-H}} = 3.7$ Hz, 1H, thienyl), 4.51 (t, $J_{\text{H-H}} = 1.9$ Hz, 2H, C_5H_4), 4.27 (t, $J_{\text{H-H}} = 1.9$ Hz, 2H, C_5H_4), 4.26 (s, 5H, Cp) and 3.42 (s, 1H, $\text{C}\equiv\text{CH}$). MS (FAB): m/z 398 (calc. M^+ 398).

5''-Ethynyl-5-(2-ferrocenylethynyl)[2,2':5',2'']terthiophene 4c. Compound **4c** was prepared in a similar manner to **3c** and the usual work-up by TLC on silica (hexane– CH_2Cl_2 , 7 : 1, v/v) gave the desired product as an orange solid ($R_f = 0.25$) in 86% yield. (Found: C, 64.85; H, 3.44. $\text{C}_{26}\text{H}_{16}\text{FeS}_3$; C, 65.00; H, 3.36%). IR (CH_2Cl_2): 3272 ($\nu_{\text{C}\equiv\text{H}}$), 2201 and 2098 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.18 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 7.11 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 7.09 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 7.08 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 7.04 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 7.03 (d, $J_{\text{H-H}} = 4.0$ Hz, 1H, thienyl), 4.51 (t, $J_{\text{H-H}} = 1.8$ Hz, 2H, C_5H_4), 4.27 (t, $J_{\text{H-H}} = 1.8$ Hz, 2H, C_5H_4), 4.25 (s, 5H, Cp) and 3.43 (s, 1H, $\text{C}\equiv\text{CH}$). MS (FAB): m/z 480 (calc. M^+ 480).

General procedures for the synthesis of platinum(II) complexes 5a–5c. To a mixture of *trans*-[Pt(PEt_3) $_2$ PhCl] (33 mg, 0.06 mmol) and **4a–4c** (0.06 mmol) in deoxygenated CH_2Cl_2 – NHPr^t_2

mixture (10 cm^3 , 1 : 1, v/v) was added CuI (1 mg). The solution was stirred at room temperature over 18 h. Evaporation of the volatile components left behind a reddish residue, purification of which was accomplished by preparative TLC using hexane– CH_2Cl_2 (6 : 1 (**5a**); 4 : 1, v/v (**5b** and **5c**)) as eluent. Subsequent removal of the solvent and recrystallization of the product from the same solvent system led to pure **5a–5c** as red-orange solids.

5a: Yield 60% (30 mg). (Found: C, 52.30; H, 5.61. $\text{C}_{36}\text{H}_{46}\text{FeP}_2\text{PtS}$ requires C, 52.49; H, 5.63%). IR (CH_2Cl_2): 2201 and 2081 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.31 (d, $J_{\text{H-H}} = 6.8$ Hz, 2H, H_{ortho} of Ph), 6.99–6.95 (m, 3H, thienyl + H_{meta} of Ph), 6.81 (t, $J_{\text{H-H}} = 7.4$, 1H, H_{para} of Ph), 6.70 (d, $J_{\text{H-H}} = 3.6$ Hz, 1H, thienyl), 4.47 (t, $J_{\text{H-H}} = 2.0$ Hz, 2H, C_5H_4), 4.24 (m, 7H, Cp + C_5H_4), 1.78–1.58 (m, 12H, CH_2) and 1.13–1.02 (m, 18H, CH_3). ^{31}P NMR (CDCl_3): δ 11.04 ($^1J_{\text{P-Pt}} = 2624$ Hz). MS (FAB): m/z 824 (calc. M^+ 824).

5b: Yield 74% (40 mg). (Found: C, 52.89; H, 5.21. $\text{C}_{40}\text{H}_{48}\text{FeP}_2\text{PtS}_2$ requires C, 53.04; H, 5.34%). IR (CH_2Cl_2): 2201 and 2080 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.31 (d, $J_{\text{H-H}} = 7.2$ Hz, 2H, H_{ortho} of Ph), 7.06 (d, $J_{\text{H-H}} = 3.6$ Hz, 1H, thienyl), 6.99–6.94 (m, 4H, thienyl + H_{meta} of Ph), 6.81 (t, $J_{\text{H-H}} = 7.4$, 1H, H_{para} of Ph), 6.74 (d, $J_{\text{H-H}} = 3.6$ Hz, 1H, thienyl), 4.49 (t, $J_{\text{H-H}} = 1.8$ Hz, 2H, C_5H_4), 4.26 (t, $J_{\text{H-H}} = 1.8$ Hz, 2H, C_5H_4), 4.25 (s, 5H, Cp), 1.77–1.70 (m, 12H, CH_2) and 1.14–1.06 (m, 18H, CH_3). ^{31}P NMR (CDCl_3): δ 11.10 ($^1J_{\text{P-Pt}} = 2626$ Hz). MS (FAB): m/z 906 (calc. M^+ 906).

5c: Yield 86% (51 mg). (Found: C, 53.25; H, 5.01. $\text{C}_{44}\text{H}_{50}\text{FeP}_2\text{PtS}_2$ requires C, 53.49; H, 5.10%). IR (CH_2Cl_2): 2197 and 2086 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.31 (d, $J_{\text{H-H}} = 6.8$ Hz, 2H, H_{ortho} of Ph), 7.10 (d, $J_{\text{H-H}} = 3.6$ Hz, 1H, thienyl), 7.05 (d, $J_{\text{H-H}} = 3.6$ Hz, 1H, thienyl), 7.01–6.96 (m, 5H, thienyl + H_{meta} of Ph), 6.81 (t, $J_{\text{H-H}} = 7.0$ Hz, 1H, H_{para} of Ph), 6.76 (d, $J_{\text{H-H}} = 3.6$ Hz, 1H, thienyl), 4.51 (t, $J_{\text{H-H}} = 1.8$ Hz, 2H, C_5H_4), 4.27 (t, $J_{\text{H-H}} = 1.8$ Hz, 2H, C_5H_4), 4.26 (s, 5H, Cp), 1.78–1.71 (m, 12H, CH_2) and 1.14–1.00 (m, 18H, CH_3). ^{31}P NMR (CDCl_3): δ 11.09 ($^1J_{\text{P-Pt}} = 2622$ Hz). MS (FAB): m/z 988 (calc. M^+ 988).

General procedures for the synthesis of platinum(II)-bridged diferrocenyl complexes 6a–6c. The compound *trans*-[Pt(PBu_3) $_2$ –Cl] (20 mg, 0.03 mmol) and two molar equivalents of **4a–4c** (0.06 mmol) were charged in a reaction flask containing a CuI– NHPr^t_2 – CH_2Cl_2 mixture under a N_2 atmosphere and stirred for 18 h under ambient conditions. In each case, the solvent was then expelled to result in a deep orange product. It was subsequently purified on preparative TLC plates on silica using a hexane– CH_2Cl_2 mixture (3 : 1 (**6a**); 2 : 1 (**6b**); 4 : 1, v/v (**6c**)) to give good yields of air-stable reddish orange solids after recrystallization from the same solvents.

6a: Yield 63% (23 mg). (Found: C, 58.35; H, 6.12. $\text{C}_{60}\text{H}_{76}\text{Fe}_2\text{P}_2\text{PtS}_2$ requires C, 58.59; H, 6.23%). IR (CH_2Cl_2): 2204 and 2094 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 6.98 (d, $J_{\text{H-H}} = 4.0$ Hz, 2H, thienyl), 6.68 (d, $J_{\text{H-H}} = 4.0$ Hz, 2H, thienyl), 4.48 (t, $J_{\text{H-H}} = 1.8$ Hz, 4H, C_5H_4), 4.24 (m, 14H, Cp + C_5H_4), 2.09 (m, 12H, PCH_2), 1.57 (m, 12H, PCH_2CH_2), 1.48 (m, 12H, CH_2CH_3) and 0.94 (t, $J_{\text{H-H}} = 7.6$ Hz, 18H, CH_3). ^{31}P NMR (CDCl_3): δ 4.51 ($^1J_{\text{P-Pt}} = 2322$ Hz). MS (FAB): m/z 1230 (calc. M^+ 1230).

6b: Yield 90% (38 mg). (Found: C, 58.35; H, 5.82. $\text{C}_{68}\text{H}_{80}\text{Fe}_2\text{P}_2\text{PtS}_4$ requires C, 58.58; H, 5.78%). IR (CH_2Cl_2): 2199 and 2079 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.07 (d, $J_{\text{H-H}} = 3.9$ Hz, 2H, thienyl), 6.96 (d, $J_{\text{H-H}} = 3.9$ Hz, 2H, thienyl), 6.94 (d, $J_{\text{H-H}} = 3.9$ Hz, 2H, thienyl), 6.73 (d, $J_{\text{H-H}} = 3.9$ Hz, 2H, thienyl), 4.50 (t, $J_{\text{H-H}} = 2.0$ Hz, 4H, C_5H_4), 4.25 (m, 14H, Cp + C_5H_4), 2.11 (m, 12H, PCH_2), 1.60 (m, 12H, PCH_2CH_2), 1.49 (m, 12H, CH_2CH_3) and 0.95 (t, $J_{\text{H-H}} = 7.6$ Hz, 18H, CH_3). ^{31}P NMR (CDCl_3): δ 4.49 ($^1J_{\text{P-Pt}} = 2325$ Hz). MS (FAB): m/z 1394 (calc. M^+ 1394).

6c: Yield 70% (33 mg). (Found: C, 58.32; H, 5.22. $\text{C}_{76}\text{H}_{84}\text{Fe}_2\text{P}_2\text{PtS}_6$ requires C, 58.57; H, 5.43%). IR (CH_2Cl_2): 2202 and 2077 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 7.10 (d, $J_{\text{H-H}} = 3.9$ Hz, 2H, thienyl), 7.05 (d, $J_{\text{H-H}} = 3.9$ Hz, 2H, thienyl), 7.01 (d, $J_{\text{H-H}} =$

Table 7 Crystal data for complexes **1b**, **2b**, **4b**, **5b** and **6b**

	1b	2b	4b	5b	6b
Empirical formula	C ₃₃ H ₂₃ Fe ₂ S ₂	C ₂₀ H ₁₃ BrFeS ₂	C ₂₃ H ₁₄ FeS ₂	C ₄₀ H ₄₈ FeP ₂ PtS ₂	C ₆₈ H ₈₀ Fe ₂ P ₂ PtS ₄
<i>M</i>	582.32	453.18	398.30	905.78	1394.29
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)	293(2)
<i>a</i> /Å	5.9211(4)	5.8596(4)	5.8487(4)	10.9280(6)	10.271(1)
<i>b</i> /Å	18.602(1)	27.334(2)	28.156(2)	14.6387(8)	11.198(2)
<i>c</i> /Å	11.2551(8)	10.7396(7)	10.7594(7)	24.620(2)	14.226(2)
<i>a</i> °					95.844(3)
<i>β</i> °	101.799(1)	96.729(1)	97.990(1)	96.225(1)	101.305(2)
<i>γ</i> °					93.949(3)
<i>U</i> /Å ³	1213.5(2)	1708.2(2)	1754.6(2)	3915.2(4)	1589.5(4)
<i>Z</i>	2	4	4	4	1
<i>μ</i> (Mo-Kα)/mm ^{−1}	1.389	3.464	1.098	4.154	2.866
No. reflections collected	7112	9988	10265	22570	9617
Unique reflections (<i>R</i> _{int})	2747 (0.0231)	3852 (0.0220)	3953 (0.0220)	8725 (0.0200)	8227 (0.0312)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	2747	3852	3953	8725	8227
<i>R</i> indices ^a	<i>R</i> 1 = 0.0281	<i>R</i> 1 = 0.0289	<i>R</i> 1 = 0.0283	<i>R</i> 1 = 0.0320	<i>R</i> 1 = 0.0563
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> 2 = 0.0704	<i>wR</i> 2 = 0.0723	<i>wR</i> 2 = 0.0736	<i>wR</i> 2 = 0.0950	<i>wR</i> 2 = 0.1253
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0397	<i>R</i> 1 = 0.0361	<i>R</i> 1 = 0.0371	<i>R</i> 1 = 0.0418	<i>R</i> 1 = 0.1010
	<i>wR</i> 2 = 0.0794	<i>wR</i> 2 = 0.0808	<i>wR</i> 2 = 0.0866	<i>wR</i> 2 = 0.0995	<i>wR</i> 2 = 0.1544

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}.$$

3.9 Hz, 2H, thienyl), 6.99 (d, *J*_{H-H} = 3.9 Hz, 2H, thienyl), 6.96 (d, *J*_{H-H} = 3.9 Hz, 2H, thienyl), 6.74 (d, *J*_{H-H} = 3.9 Hz, 2H, thienyl), 4.51 (t, *J*_{H-H} = 1.8 Hz, 4H, C₅H₄), 4.27 (t, *J*_{H-H} = 1.8 Hz, 4H, C₅H₄), 4.26 (s, 10H, Cp), 2.11 (m, 12H, PCH₂), 1.59 (m, 12H, PCH₂CH₂), 1.49 (m, 12H, CH₂CH₃) and 0.96 (t, *J*_{H-H} = 7.0 Hz, 18H, CH₃). ³¹P NMR (CDCl₃): δ 4.46 (¹*J*_{P-Pt} = 2316 Hz). MS (FAB): *m/z* 1559 (calc. M⁺ 1559).

Crystallography

Yellow crystals of **1b**, **2b**, **4b**, **5b** and **6b** suitable for X-ray diffraction studies were grown by slow evaporation of their respective solutions in hexane–CH₂Cl₂ at room temperature. Geometric and intensity data were collected using graphite-monochromated Mo-Kα radiation (*λ* = 0.71073 Å) on a Bruker AXS SMART 1000 CCD area-detector. Cell parameters and orientation matrices for all crystal samples were obtained from the least-squares refinement of reflections measured in three different sets of 15 frames each. The collected frames were processed with the software SAINT^{37a} and an absorption correction was applied (SADABS)^{37b} to the collected reflections.

The space groups of each crystal were determined from the systematic absences and Laue symmetry check and confirmed by successful refinement of the structure. The structures of these molecules were solved by direct methods (SHELXTL)³⁸ in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on *F*². Except for **5b** and **6b**, all non-hydrogen atoms were assigned with anisotropic displacement parameters. For **6b**, only the heavy atoms were refined anisotropically and constraints were placed on the C–C bond distances of the ferrocenyl moieties. For **5b**, all ethyl groups were refined isotropically and those attached to the P(2) atom showed positional disorder in which a two-sites model with occupancy factors of 0.5 each was applied. The resulting model was refined to convergence and yielded reasonable bond lengths and angles. Hence, no hydrogen atoms were included for these disordered ethyl groups in the *F*_c calculations. In all other cases, the hydrogen atoms were generated in their idealized positions and allowed to ride on the respective carbon atoms. Crystal data and other experimental details are summarized in Table 7.

CCDC reference numbers 165361–165365.

See <http://www.rsc.org/suppdata/doi/10.1039/b105016h/> for crystallographic data in CIF or other electronic format.

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