Synthesis, characterisation and properties of platinum(II) acetylide complexes of ferrocenylfluorene: novel soluble donor–acceptor heterometallic materials ‡

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Two new bis(acetylide)-functionalised ferrocenylfluorene complexes, 9-ferrocenylmethylene-2,7-bis-(trimethylsilylethynyl)fluorene 1 and -2,7-bis(ethynyl)fluorene 2, have been prepared in good yield by condensation of ferrocenecarbaldehyde with 2,7-bis(trimethylsilylethynyl)fluorene and the subsequent desilylation of 1. Treatment of trans-[PtPh(Cl)(PEt$_3$)$_2$] with half an equivalent of 2 in CH$_2$Cl$_2$–NHPr$^i_2$, in the presence of CuI, at room temperature, gives the dimeric platinum(II) complex trans-[Ph(Et$_3$P)$_2$-Pt−C≡CRC≡C−Pt(PEt$_3$)$_2$Ph] 3 (R = 9-ferrocenylmethylenefluorene-2,7-diyl) in 56% yield. Soluble polymeric trans-[{-Pt(PBu$^n_3$)$_2$-C≡CRC≡C-}$_n$] 4 has been obtained in good yield by the CuI-catalysed dehydrohalogenation of trans-[Pt(PBu$^n_3$)$_2$Cl$_2$] with 2 (1 : 1 molar ratio) in an amine solvent. Optical measurements on the thin films indicated that there is a significant reduction in the bandgap value for polymer 4 (2.1 eV) as compared to that of trans-[{-Pt(PBu$^n_3$)$_2$-C≡CRC≡C-}$_n$] 5 (R = fluorene-2,7-diyl) (2.9 eV) without the ferrocenyl moiety, featuring the importance of donor–acceptor interaction in such conjugated systems. All the new compounds have been characterised by analytical, spectroscopic and electrochemical methods, and the single-crystal structures of 2, 3 and 5 have been established.

There has been considerable interest in the chemistry of soluble conjugated organometallic materials in view of their potential applications in photocells, field-effect transistors, light-emitting diodes or molecules for non-linear optics (NLO).[1] Research into ferrocene-containing complexes and polymers is undergoing something of a 'renaissance' since ferrocene has long been recognised as being able to stabilise α-carbocations and can act as a good donor for an NLO-phore.[2] On the other hand, fluorene electron acceptors are widely used as electron transport materials.[3] Based on the recent development in organic polymers in which their bandgaps can be reduced by the copolymerisation of donor and acceptor units,[4] it was envisaged that fluorenylferrocenes would constitute an interesting new class of spacer units in the novel organometallic polyyne systems and their electronic properties might reduce the energy difference of the HOMO − LUMO bandgap.

Bearing these concepts in mind we set out to synthesize new ferrocenylfluorenes acetylide-substituted at the 2 and 7 positions which can afford trimetallic (M−Fe−M) or polymeric materials. Here, we report results on the synthesis of the first examples of platinum(II) acetylide-functionalised fluorene complexes and polymers bearing a pendant ferrocene group in the side chain. The crystal structures of related dimeric model complexes are also reported.

Results and Discussion

Syntheses

The synthesis of all new compounds are outlined in Scheme 1. The new ferrocenylfluorene complex 1 was prepared in 80% yield by condensing 2,7-bis(trimethylsilylethynyl)fluorene[5] with ferrocenecarbaldehyde in dry thf using lithium diisopropylamide. Upon deprotection with K$_2$CO$_3$ in Et$_2$O–MeOH, 1 was

converted readily into 2 in 68% yield. Complex 3 and the polymer 4 were synthesized by the dehydrohalogenation reaction between trans-[PtPh(Cl)(PEt$_3$)$_2$] or trans-[Pt(PBu$^n_3$)$_2$-Cl$_2$] with 2 in NHPr$^i_2$, with a catalytic amount of CuI, following a procedure reported for related platinum(II) acetylide complexes.[6] Compound 3 was purified by silica TLC and recrystallisation from CH$_2$Cl$_2$–hexane gave air-stable red crystals in moderate yield (56%). Complexes 1–3 have been characterised by satisfactory elemental analyses, mass spectrometry (EI or FAB), IR and NMR spectroscopies. Purification of the polymer 4 was achieved by alumina column chromatography using CH$_2$Cl$_2$ as eluent, and it was isolated in high purity and good yield (60%). It is soluble in common organic solvents and readily casts tough free-standing red films. The weight-average molecular weight (M_w) value of 34 540 (polydispersity = 1.922) for 2 determined by gel permeation chromatography shows a high degree of polymerisation. The number-average molecular weight (M_n) corresponds to 18 repeat units per polymer chain.

Optical, electrochemical and thermal properties

The trans geometry of the Pt(PR$_3$)$_2$ (R = Et or Bu^n) unit in the dimer 3 and polymer 4 was clearly revealed by the simple singlet pattern of their $\nu_{C≡C}$ IR and ^{31}P-{^{1}H} NMR spectra. For all the new compounds, proton signals stemming from the ferrocenyl group were observed. The $^1J_{Pt-P}$ coupling constant for 3 is larger than that for 4 by about 280 Hz.

The electronic absorption spectra of compounds 3 and 4 both display strong absorptions in the UV range at ca. 355–382 nm in CH$_2$Cl$_2$, tentatively assigned as ligand-localised transitions. Longer wavelength transitions due to metal-to-ligand charge transfer (MLCT) appear as shoulders at 434 (for 3) and 437 nm (for 4). It is found that the bandgap (onset of absorption) value E_g of the thin film of 4 is 2.1 eV, lower than those found in the corresponding non-ferrocenyl substituted polymer 5[5] (E_g = 2.9 eV) and other platinum(II) polyynes with phenyl,[7]
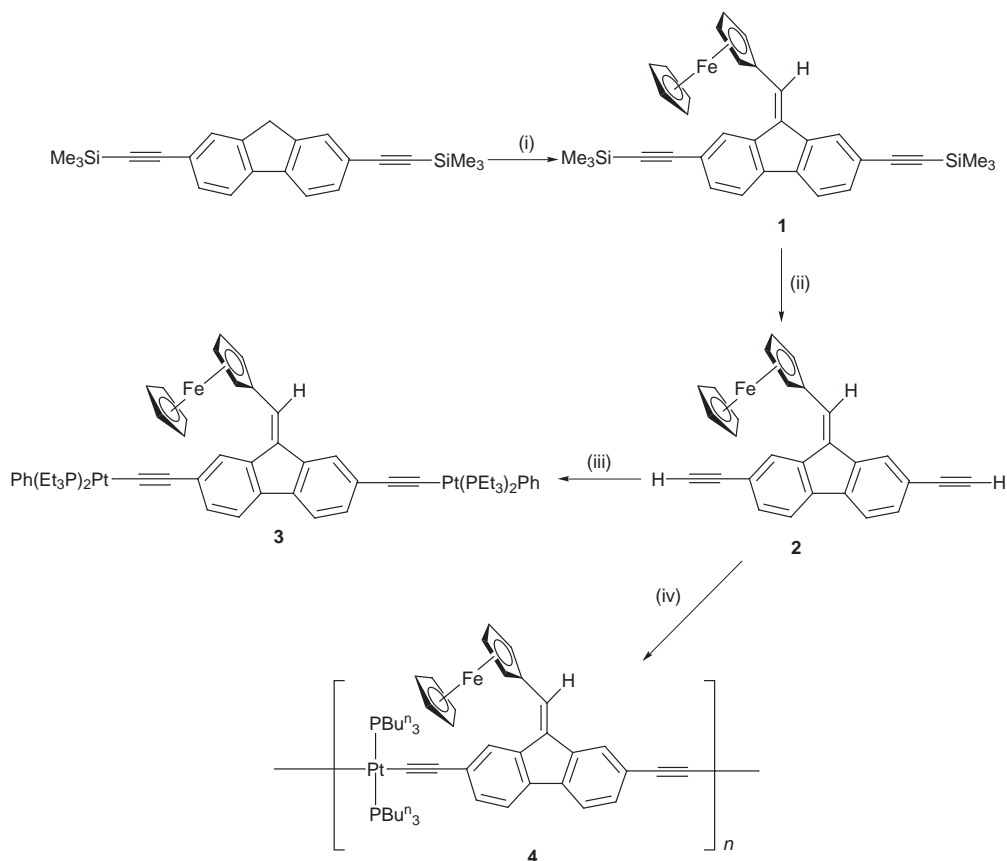
Scheme 1 (i) LiNPr$^i_2$, −78 °C, ferrocenecarbaldehyde; (ii) K$_2$CO$_3$, MeOH; (iii) *trans*-[PtPh(Cl)(PEt$_3$)$_2$], NHPr$^i_2$, CuI; (iv) *trans*-[Pt(PBu$^n_3$)$_2$Cl$_2$], NHPr$^i_2$, CuI

Table 1 Electrochemical data for the ferrocenylfluorenes and their platinum(II) complexes

| Compound	Oxidation, $E_{\frac{1}{2}}$/V*
1	+0.60
2	+0.59
3	+0.67 (+1.16)
4	+0.71 (+1.34)

* 0.1 mol dm^{-3} NBu$^n_4$BF$_4$ in CH$_2$Cl$_2$, platinum electrode, scan rate 100 mV s^{-1}, reference silver wire, irreversible waves are shown in parentheses.

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pyridyl,[8] oligothienyl[9] or alkynyl[10] units. It is envisioned that the presence of a pendant ferrocenyl donor unit in the side chain of these soluble organometallic polyynes is particularly attractive as a new approach for controlling the energy gap of this kind of polymeric materials. A reduction in the HOMO − LUMO energy separation in such donor–acceptor based polymers provides us with valuable information in the design of more useful materials for device applications.

Cyclic voltammetry of the new materials, in CH$_2$Cl$_2$, shows a reversible oxidation in each case, attributable to the ferrocene–ferrocenium couple (Table 1). The platinum σ-acetylides **3** and **4** also show an irreversible oxidation wave at greater potentials, assigned to the oxidation of the platinum residue. As expected, the half-wave potential of the ferrocene moiety is slightly more anodic in complexes **3** and **4** than in **1** and **2** because of the loss of electron density from the ferrocenyl donor unit to the net electron-accepting platinum centre through the acetylide bridge.

The thermal behaviour of the Pt–Fe mixed polymer **4** was studied and it showed a relatively good thermal stability as confirmed by thermogravimetry (10 °C min^{-1} under N$_2$), which indicated that no decomposition occurred up to *ca.* 250 °C.
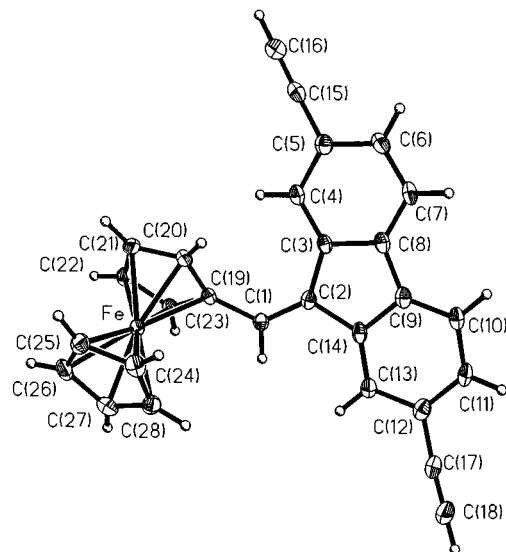
Fig. 1 Molecular structure of complex **2** showing the atomic numbering. Ellipsoids are drawn at the 50% probability level

Mass loss of 30% was, however, detected when it was heated to 500 °C.

Crystal structure analyses

The molecular structure of the precursor complex **2**, as determined crystallographically, is shown in Fig. 1, which includes the atom numbering scheme. Selected bond distances and angles are listed in Table 2. In the solid state the molecule consists of a ferrocene unit appended to the fluorenyl moiety at the 9 position *via* C(1) atom [C(1)–C(2) 1.348(3) and C(1)–C(19) 1.465(3) Å]. The two cyclopentadienyl rings of the ferrocene group are planar and exhibit a staggered conformation. The

C≡C bond distance [average 1.176(5) Å] is typical of terminal acetylides reported previously.[5,6]

The solid-state structures of complexes **3** and **5** have also been determined by X-ray crystallography. The molecular structures are depicted in Figs. 2 and 3, respectively, and selected bond parameters are in Tables 3 and 4. From a fundamental viewpoint, the π-conjugated diyne-bridged diplatinum(II) complex **3** is investigated as a model for the electronic, electrochemical and structural properties of the parent polymer **4**. In each case, the co-ordination geometry at each platinum atom is square planar with the two PEt₃ groups in a *trans* arrangement. The C≡C bond length is characteristic of metal–

acetylide σ bonding and the Pt−C≡C(fluorenyl)C≡C−Pt fragment is essentially planar. In **3** the fluorenyl ring system makes a dihedral angle of 39(±1)° with the η⁵-C₅H₄ ring, which is different from that observed in the vinyl ferrocene systems, where the nature of the substituent tends to control the planarity.[11] The *exo* double bond C(1)–C(14) is distorted from planarity by 5° [defined by C(13)–C(1)–C(14)–C(15)]. As in **2** there is a shortening of the C(14)–C(15) bond and lengthening of the C(1)–C(14) bond in **3** [C(1)–C(14) 1.37(2) and C(14)–C(15) 1.44(2) Å]. The two cyclopentadienyl rings are essentially parallel, with a ring tilt angle of 3.1°, and the ferrocenyl group is nearly eclipsed in the solid state. For **5·0.33C₆H₁₄** there are one and a half molecules in the asymmetric unit, and only the complete unique molecule is shown in Fig. 3; the half molecule is disordered about a centre of inversion. The Pt–P bond lengths lie in the range of 2.274(4)–2.292(4) (**3**) and 2.267(5)–2.284(4) Å (**5**), which are similar to those observed in other Pt–PR₃ acetylide complexes. The average bond angle of 176(1)° for the fragment Pt–C≡C in both **3** and **5** conforms to the linear geometry of the bis(acetylide) complexes.

Experimental

General

Solvents were predried and distilled from appropriate drying

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

Fe–C(19)	2.069(2)	Fe–C(20)	2.046(3)
Fe–C(21)	2.042(3)	Fe–C(22)	2.045(3)
Fe–C(23)	2.037(2)	Fe–C(24)	2.048(2)
Fe–C(25)	2.047(3)	Fe–C(26)	2.046(3)
Fe–C(27)	2.050(3)	Fe–C(28)	2.055(3)
C(1)–C(19)	1.465(3)	C(1)–C(2)	1.348(3)
C(15)–C(16)	1.180(4)	C(17)–C(18)	1.171(5)
C(2)–C(1)–C(19)	128.3(2)	C(1)–C(2)–C(3)	131.6(2)
C(5)–C(15)–C(16)	177.8(3)	C(12)–C(17)–C(18)	176.7(3)
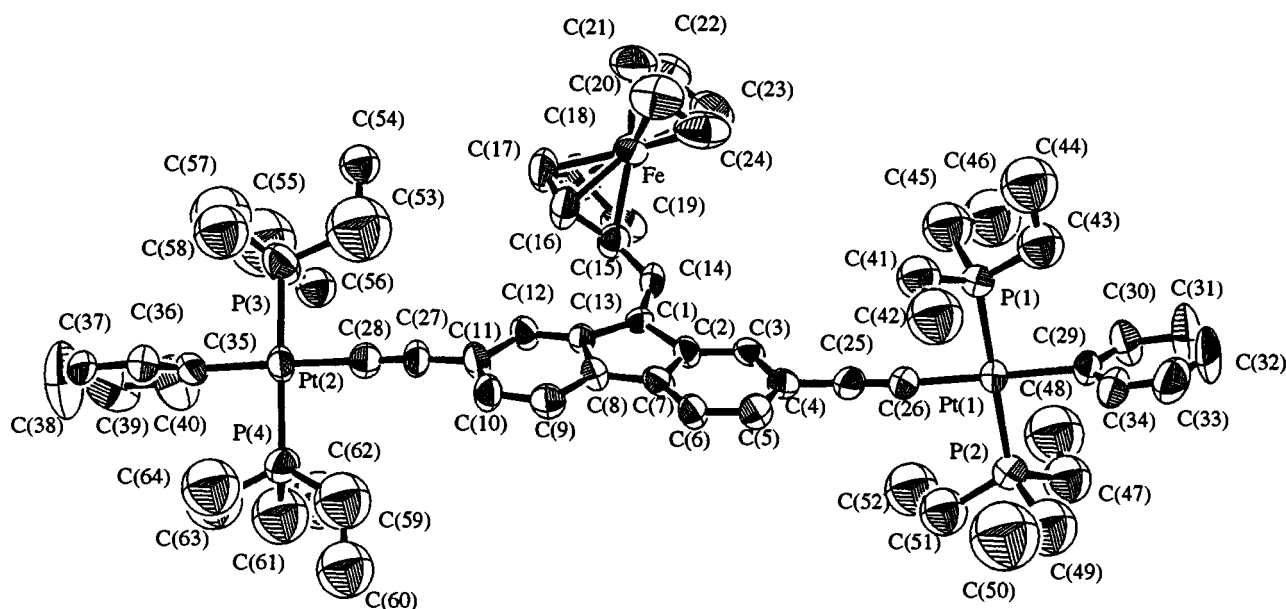
Fig. 2 Molecular structure of complex **3** showing the numbering scheme. Hydrogen atoms and disorder of the ethyl groups attached to P(4) have been omitted for clarity. Ellipsoids are shown at the 50% probability level
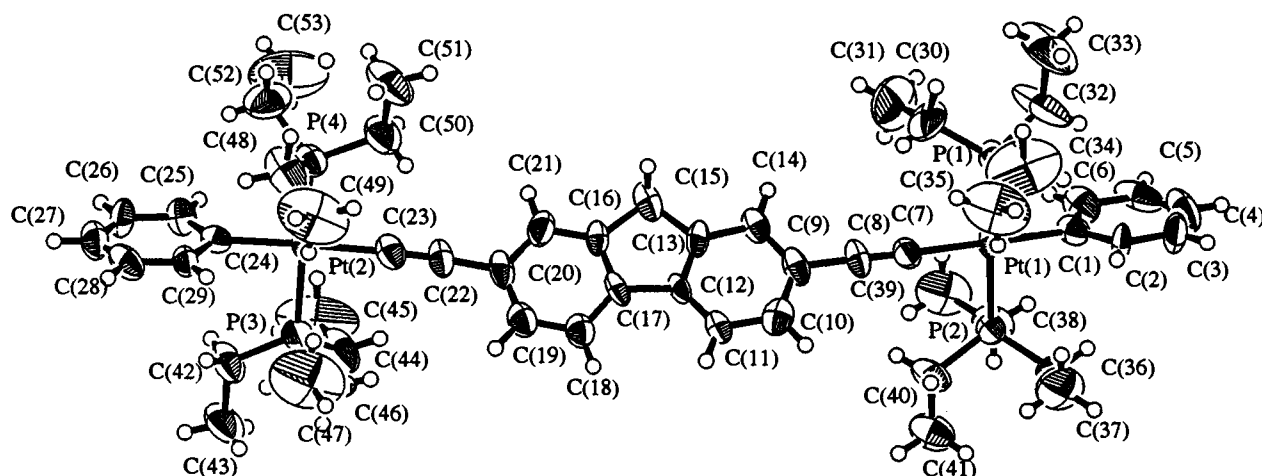
Fig. 3 Molecular structure of complex **5** with the atomic numbering. Ellipsoids are at the 50% probability level

Table 3 Selected bond lengths (Å) and angles (°) for compound **3**

Pt(1)–P(1)	2.290(4)	Pt(1)–P(2)	2.292(4)
Pt(1)–C(29)	2.09(1)	Pt(1)–C(26)	2.00(1)
Pt(2)–P(3)	2.274(4)	Pt(2)–P(4)	2.287(4)
Pt(2)–C(35)	2.07(1)	Pt(2)–C(28)	2.00(1)
C(25)–C(26)	1.22(2)	C(4)–C(25)	1.47(2)
C(27)–C(28)	1.21(2)	C(11)–C(27)	1.45(2)
C(1)–C(14)	1.37(2)	C(14)–C(15)	1.44(2)
Fe–C(15)	2.05(1)	Fe–C(16)	2.05(1)
Fe–C(17)	2.04(2)	Fe–C(18)	1.96(2)
Fe–C(19)	2.04(2)	Fe–C(20)	2.06(2)
Fe–C(21)	2.03(2)	Fe–C(22)	1.97(2)
Fe–C(23)	2.01(2)	Fe–C(24)	1.96(2)
P(1)–Pt(1)–P(2)	179.1(2)	P(1)–Pt(1)–C(26)	86.8(4)
P(2)–Pt(1)–C(26)	93.0(4)	Pt(1)–C(26)–C(25)	173(1)
P(3)–Pt(2)–P(4)	177.6(2)	P(3)–Pt(2)–C(28)	92.2(4)
P(4)–Pt(2)–C(28)	88.1(4)	Pt(2)–C(28)–C(27)	178(1)
C(4)–C(25)–C(26)	176(1)	C(11)–C(27)–C(28)	175(1)
C(13)–C(1)–C(14)	130(1)	C(1)–C(14)–C(15)	130(1)

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

Molecule 1

Pt(1)–P(1)	2.273(5)	Pt(1)–P(2)	2.284(4)
Pt(1)–C(1)	2.06(2)	Pt(1)–C(7)	2.02(2)
Pt(2)–P(3)	2.269(5)	Pt(2)–P(4)	2.273(5)
Pt(2)–C(24)	2.03(2)	Pt(2)–C(23)	2.03(2)
C(7)–C(8)	1.17(2)	C(8)–C(9)	1.45(2)
C(20)–C(22)	1.43(2)	C(22)–C(23)	1.18(2)
P(1)–Pt(1)–P(2)	177.0(2)	P(1)–Pt(1)–C(7)	90.1(5)
P(2)–Pt(1)–C(7)	91.7(5)	Pt(1)–C(7)–C(8)	174(1)
P(3)–Pt(2)–P(4)	171.6(2)	P(3)–Pt(2)–C(23)	87.5(5)
P(4)–Pt(2)–C(23)	91.8(5)	Pt(2)–C(23)–C(22)	177(1)
C(7)–C(8)–C(9)	176(1)	C(20)–C(22)–C(23)	173(2)

Molecule 2

Pt(3)–P(5)	2.276(6)	Pt(3)–P(6)	2.267(5)
Pt(3)–C(54)	2.05(2)	Pt(3)–C(72)	2.01(2)
C(72)–C(73)	1.20(2)	C(73)–C(74)	1.42(2)
P(5)–Pt(3)–P(6)	175.6(2)	P(5)–Pt(3)–C(72)	90.8(6)
P(6)–Pt(3)–C(72)	88.9(5)	Pt(3)–C(72)–C(73)	176(1)
C(72)–C(73)–C(74)	174(1)		

agents.[12] All chemicals, except where stated, were from commercial sources and used without further purification. The compounds *trans*-[PtPh(Cl)(PEt$_3$)$_2$][13] and *trans*-[Pt(PBu$^n_3$)$_2$Cl$_2$][14] were prepared *via* literature methods. The synthesis of the fluorene derivative Me$_3$SiC≡CRC≡CSiMe$_3$ (R = fluorene-2,7-diyl) has been reported recently.[5] The NMR spectra were recorded on a Bruker WM-250 or AM-400 and JEOL EX270 spectrometers in appropriate solvents, ^{31}P-{^{1}H} referenced to external trimethyl phosphite and the ^{1}H and ^{13}C-{^{1}H} to solvent resonances. Infrared spectra were recorded as CH$_2$Cl$_2$ solutions, in a NaCl cell, on a Perkin-Elmer 1000 or 1710 FT-IR spectrometer, mass spectra on a Kratos MS890 or Finnigan MAT SSQ710 spectrometer by either the electron impact (EI) or fast atom bombardment (FAB) technique. Cyclic voltammetric measurements were made with a Princeton Applied Research (PAR) model 273A potentiostat. The supporting electrolyte was 0.1 mol dm^{-3} NBu$_4$BF$_4$ in CH$_2$Cl$_2$. Microanalyses were performed in the University Chemical Laboratory, University of Cambridge. Electronic absorption spectra were obtained with a Perkin-Elmer Lambda UV/NIR or Hewlett-Packard UV/VIS spectrometer. The TGA studies were performed using a Shimadzu DT-40 thermal analyser. Preparative thin-layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica, or on 1 mm silica plates prepared in our laboratories. Column chromatography was performed either on Kieselgel 60 (230–400 mesh) silica gel or alumina (Brockman Grade II-III).

Preparations of fluorene derivatives

Compound 1. A chilled ($-78\,°C$) thf (30 cm^3) solution containing diisopropylamine (0.24 g, 2.3 mmol) was treated with LiBu^n (1.8 cm^3, 2.9 mmol) and then warmed to 0 °C over a period of 30 min to give a pale yellow solution. The reaction mixture was cooled to $-78\,°C$ again and 2,7-bis(trimethylsilylethynyl)fluorene (0.82 g, 2.3 mmol) added in one portion. The orange mixture was stirred for 5 min and then ferrocenecarbaldehyde (0.50 g, 2.3 mmol) added. The cooling bath was removed and stirring continued for 2 h. The deep red solution was diluted with Et$_2$O (100 cm^3) and then washed with water (2 × 100 cm^3) and finally with brine (100 cm^3). The organic layer was dried over MgSO$_4$ and the solvents removed under reduced pressure. The crude product was recrystallised from CHCl$_3$ to afford 1.02 g of pure compound **1** (80%). IR (CH$_2$Cl$_2$): 2152 ($v_{C≡C}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.25 (s, 9 H, SiMe$_3$), 0.30 (s, 9 H, SiMe$_3$), 4.22 (s, 5 H, C$_5$H$_5$), 4.53 (t, 2 H, J_{H-H} = 1.8, C$_5$H$_4$), 4.74 (t, 2 H, J_{H-H} = 1.8, C$_5$H$_4$), 7.42–7.49 (m, 3 H, arene and vinyl CH), 7.54, 7.62 (2d, 2 H, J_{H-H} = 4.0 Hz, arene CH) and 8.39 (s, 1 H, arene CH). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 0.07, 0.12 (SiMe$_3$), 69.66 (C$_5$H$_5$ CH), 70.37, 71.09 (C$_5$H$_4$ CH), 80.57 (*ipso*-C of C$_5$H$_4$), 94.20, 94.29 (C≡C), 106.01, 106.05 (C≡C), 119.69, 119.80, 123.17, 127.74, 128.62, 131.18, 131.59 (arene or vinyl CH), 121.39, 121.56, 131.76, 137.08, 137.51, 139.89 and 140.32 (arene C). EI mass spectrum: *m/z* 554 (Found: C, 73.01; H, 6.30. Calc. for C$_{34}$H$_{34}$FeSi$_2$: C, 73.63; H, 6.18%).

Compound 2. The compound **1** (0.20 g, 0.36 mmol) and K$_2$CO$_3$ (0.05 g, 0.36 mmol) were combined in MeOH–Et$_2$O (40 cm^3, 1:1 v/v) and the mixture was stirred at room temperature for 20 h. Infrared spectroscopy showed that all the starting material had been consumed. Upon removal of solvent under reduced pressure, the deep red residue was purified by column chromatography on silica using hexane–CH$_2$Cl$_2$ (1:1 v/v) as eluent to afford a major deep red powder identified as **2** (0.10 g, 68%). IR (CH$_2$Cl$_2$): 2106 ($v_{C≡C}$), 3298 ($v_{≡CH}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.08 (s, 1 H, C≡CH), 3.16 (s, 1 H, C≡CH), 4.23 (s, 5 H, C$_5$H$_5$), 4.54 (t, 2 H, J_{H-H} = 1.83, C$_5$H$_4$), 4.73 (t, 2 H, J_{H-H} = 1.83, C$_5$H$_4$), 7.46–7.52 (m, 3 H, arene and vinyl CH), 7.65, 7.69 (2d, 2 H, J_{H-H} = 4.0 Hz, arene CH), 7.91 (s, 1 H, arene CH) and 8.40 (s, 1 H, arene CH). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 69.69 (C$_5$H$_5$ CH), 70.48, 71.03 (C$_5$H$_4$ CH), 77.18 (C≡C), 80.46 (*ipso*-C of C$_5$H$_4$), 84.45 (C≡C), 119.84, 119.94, 123.45, 127.91, 128.95, 131.21, 131.67 (arene or vinyl CH), 120.40, 120.61, 131.58, 137.15, 137.68, 140.05 and 140.33 (arene C). EI mass spectrum: *m/z* 410 (Found: C, 81.56; H, 4.60. Calc. for C$_{28}$H$_{18}$Fe: C, 81.97; H, 4.42%).

Dimer and polymer preparations

Compound 3. To a mixture of compound **2** (82 mg, 0.2 mmol) and 2 equivalents of *trans*-[PtPh(Cl)(PEt$_3$)$_2$] (0.22 g, 0.4 mmol) in CH$_2$Cl$_2$–NHPr$^i_2$ (50 cm^3, 1:1 v/v) was added CuI (3 mg). The solution was stirred at room temperature over 15 h, after which all volatile components were removed. The product was purified on preparative TLC plates with hexane–CH$_2$Cl$_2$ (1:1 v/v) as eluent, giving compound **3** as a red crystalline solid in an isolated yield of 56% (0.16 g) after recrystallisation from CH$_2$Cl$_2$–hexane. IR (CH$_2$Cl$_2$): 2088 ($v_{C≡C}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.09 (m, 36 H, Me), 1.76 (m, 24 H, PCH$_2$), 4.20 (s, 5 H, C$_5$H$_5$), 4.38 (t, 2 H, C$_5$H$_4$), 4.72 (t, 2 H, C$_5$H$_4$), 6.79 (m, 2 H, H$_{para}$ of Ph), 6.95 (m, 4 H, H$_{meta}$ of Ph), 7.28 (m, 7 H, H$_{ortho}$ of Ph + arene and vinyl CH), 7.45, 7.48 (2d, 2 H, J_{H-H} = 1.9 Hz, arene CH), 7.65 (s, 1 H, arene CH) and 8.11 (s, 1 H, arene CH). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ −131.73 ($^1J_{Pt-P}$ = 2634 Hz). FAB

Table 5 Summary of crystallographic data for compounds **2**, **3** and **5·0.33C$_6$H$_{14}$**

	2	**3**	**5·0.33C$_6$H$_{14}$**
Empirical formula	C$_{28}$H$_{18}$Fe	C$_{64}$H$_{86}$FeP$_4$Pt$_2$	C$_{53}$H$_{78}$P$_4$Pt$_2$·0.33C$_6$H$_{14}$
M	410.27	1425.31	1256.85
Crystal colour, habit	Red block	Red needle	Off-white plate
Crystal dimensions/mm	$0.30 \times 0.20 \times 0.20$	$0.32 \times 0.08 \times 0.07$	$0.23 \times 0.18 \times 0.07$
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a/Å	24.488(3)	12.298(1)	9.220(1)
b/Å	10.467(2)	13.810(1)	19.960(1)
c/Å	14.773(2)	18.768(1)	22.910(2)
α/°		90.42(1)	102.76(2)
β/°	97.06(3)	94.56(1)	93.83(2)
γ/°		91.92(1)	93.69(2)
U/Å^3	3758(1)	3175.4(4)	4089.3(8)
Z	8	2	3
D_c/g cm^{-3}	1.450	1.491	1.534
$F(000)$	1696	1424	1890
μ(Mo-Kα)/mm^{-1}	0.814	4.739	5.256
T/K	150	298	298
$2\theta_{max}$/°	50.5	50.9	52.1
No. reflections collected	15 770	25 398	34 086
No. independent reflections	3322	10 132	12 311
R_{int}	0.0719	0.044	0.056
Observed reflections [$I > n\sigma(I)$]	3311 ($n = 2$)	6008 ($n = 3$)	6006 ($n = 3$)
No. refined parameters	263	472	767
Residuals	$R1 = 0.048$ [a]	$R = 0.053$ [a]	$R = 0.054$
	$wR2 = 0.090$ [b]	$R' = 0.068$ [c]	$R' = 0.061$
Goodness of fit	1.188 (on F^2) [d]	1.96 (on F) [e]	1.34 (on F) [e]
Residual electron density/e Å^{-3}	$+0.35, -0.57$	$+0.52, -2.48$	$+2.54, -2.04$

[a] $R = R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$. [d] Goodness of fit $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{\frac{1}{2}}$, based on all data. [e] Goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{\frac{1}{2}}$, based on all data.

mass spectrum: m/z 1425. UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm 434 (ϵ 5.1×10^3 dm^3 mol^{-1} cm^{-1}) (Found: C, 53.58; H, 5.93. Calc. for C$_{64}$H$_{86}$FeP$_4$Pt$_2$: C, 53.93; H, 6.04%).

Compound 4. A mixture of *trans*-[Pt(PBu$^n_3$)$_2$Cl$_2$] (0.1 g, 0.15 mmol) and 1 equivalent of the diterminal alkyne **2** (61.5 mg, 0.15 mmol) was dissolved in CH$_2$Cl$_2$–NHPr$^i_2$ (50 cm^3, 1:1 v/v) and CuI (3 mg) subsequently added. After stirring for 15 h the mixture was evaporated to dryness. The residue was redissolved in CH$_2$Cl$_2$ and filtered through a short alumina column using the same eluent to give a red solution of compound **4**. After removal of solvent by a rotary evaporator, a deep red polymer film of **4** was obtained and it was then washed with MeOH to give **4** in 60% yield (0.09 g). IR (CH$_2$Cl$_2$): 2095 ($\nu_{C \equiv C}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.93 (m, 18 H, Me), 1.50 (m, 24 H, CH$_2$), 2.18 (m, 12 H, PCH$_2$), 4.18 (s, 5 H, C$_5$H$_5$), 4.39 (s, 2 H, C$_5$H$_4$), 4.70 (s, 2 H, C$_5$H$_4$), 7.31 (m, 3 H, arene and vinyl CH), 7.48 (2d, 2 H, arene CH), 7.63 (s, 1 H, arene CH) and 8.09 (s, 1 H, arene CH). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ -138.39 ($^1J_{Pt-P} = 2358$ Hz). UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm 437 (ϵ 7.9×10^3 dm^3 mol^{-1} cm^{-1}). $M_w = 34\,540$, $M_n = 17\,970$ ($n = 1.922$) (Found: C, 61.29; H, 7.24. Calc. for C$_{52}$H$_{70}$FeP$_2$Pt: C, 61.96; H, 7.00%).

Crystallography

Red crystals of compounds **2** and **3** suitable for X-ray diffraction studies were grown by slow evaporation of their respective solutions in hexane–CH$_2$Cl$_2$. Off-white crystals of **5·0.33C$_6$H$_{14}$** were obtained from its hexane solution by evaporation at room temperature. Geometric and intensity data were collected using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71\,073$ Å) on Rigaku R-Axis IIc image plate (for **2**) and MAR Research image plate scanners (for **3** and **5·0.33C$_6$H$_{14}$**). All pertinent crystallographic data and other experimental details are summarised in Table 5. For **2** two data sets were collected; one of them involved 60 × 3° oscillation frames with an exposure

time of 10 min, and then the crystal was rotated through 90° about an axis 45° to the vertical and 40 × 3° frames with 10 min exposure were employed for data acquisition. For **3** and **5·0.33C$_6$H$_{14}$** 60 × 3° frames with an exposure time of 5 min per frame were used. The intensity data were corrected for Lorentz-polarisation effects and interframe scaling was applied.

The structure of compound **2** was solved by direct methods (SHELXTL PLUS)[15] and subsequent Fourier-difference syntheses, and refined by full-matrix least squares on F^2 (SHELXL 93)[16] with anisotropic displacement parameters for all non-H atoms. The structures of **3** and **5·0.33C$_6$H$_{14}$** were solved by Patterson methods (DIRDIF 92 PATTY)[17] and refined on F by least squares. For **3** the ethyl groups attached to the P(4) atom showed positional disorder and they were refined with a two-sites model with occupancy factors of 0.5 each. For **5·0.33C$_6$H$_{14}$** the crystal structure contains one and a half molecules in the asymmetric unit, the half molecule being related to its symmetry equivalent through a centre of inversion which sits at the centre of the fluorene ring. This model assumed that the fluorene ring exhibited twofold disorder in the crystal and therefore a pseudo-inversion centre was generated. The fluorene atom positions were then assigned with isotropic displacement parameters and refined in two sites with 50% occupancy. In each case, hydrogen atoms were generated in their idealised positions.

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