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Synthesis and characterisation of new platinum ethynyl dimers and polymers with pendant ferrocenyl groups

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Abstract

The square-planar platinum(II) complex *trans*-$[(Ph_2FcP)_2PtCl_2]$ (**1**) (Fc = ferrocenyl), that is a metal-containing polymer precursor, has been synthesised and its single crystal structure determined. Using **1**, new ferrocene-containing platinum ethynyl dimers *trans*-$[(Ph_2FcP)_2Pt(–C{\equiv}C–R)_2]$ {R = $SiMe_3$ (**2**), C_6H_5 (**3**) and C_6H_4-*p*-NO_2 (**4**)} and a polymer $[(Ph_2FcP)_2Pt(–C{\equiv}C–C_6H_2\text{-}p\text{-}(OC_8H_{17})_2–C{\equiv}C–)]_n$ (**5**) have been formed by the reaction of the metal precursor with the appropriate mono- and bis-ethynyl ligands. Single crystal X-ray studies of **4** have shown it to exist as two different polymorphic forms, both having *trans*-geometry with respect to the ferrocenyl phosphines and ethynyl ligands. GPC measurements on the polymer show a high degree of polymerisation with an average molecular weight of ca. 88 000.

Keywords: Ferrocene; Alkyne; Platinum; Polymer

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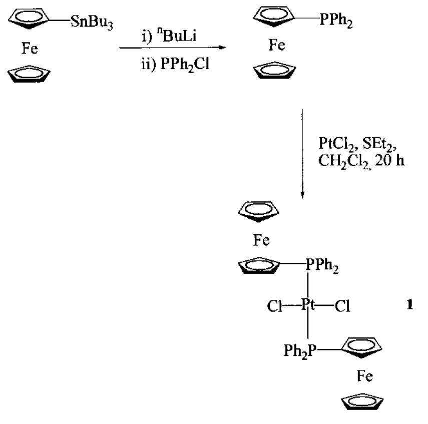
1. Introduction

Interest in the synthesis and characterisation of metal-containing conjugated polymers has grown rapidly in recent years due to their potential in materials science [1]. The introduction of a metallocene or a metal centre into the conjugated polymeric chain may produce a range of characteristics that differ from those of conventional organic polymers, i.e. redox, magnetic, optical and electronic properties. It has been shown that rigid-rod conjugated ethynyl polymers of Group 10 transition metals (Pt, Pd and Ni) possess nonlinear optical properties [2], liquid crystallinity [3], luminescence and photoconductivity [4], and this behaviour has been a driving force in the development of late transition metal alkynyl complexes [5]. The electronic and optical properties of these polymers can be fine-tuned by variation of: (i) the metal; (ii) the aromatic spacers of the organic ligands; and (iii) the auxiliary ligands on the metal [6]. Introduction of ferrocenyl units into the polymer chain increases the donor–acceptor interactions within the poly-alkynes along with the useful incorporation of a redox-active centre [1c,d,i,7]. In a previous paper [7c], we reported the synthesis and characterisation of platinum ethynyl polymers with ferrocenyl units in the main chain and found, at least in these cases, that there was negligible ferrocene–ferrocene interaction through the platinum–alkynyl bridges, largely due to a mismatch of the ligand and metal orbitals. In this paper, we report the preparation



Scheme 1. The synthesis of complex **1**.

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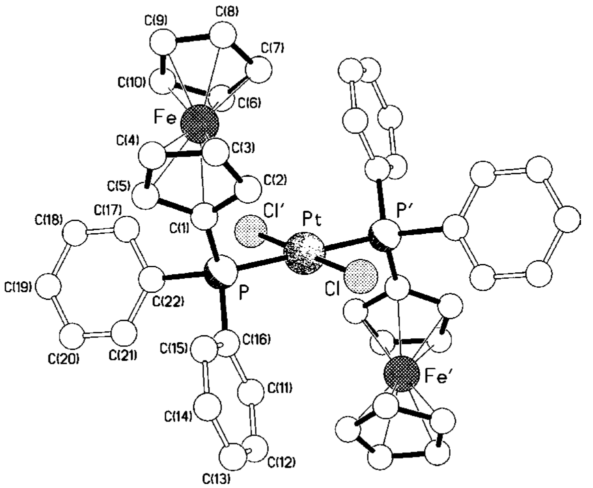
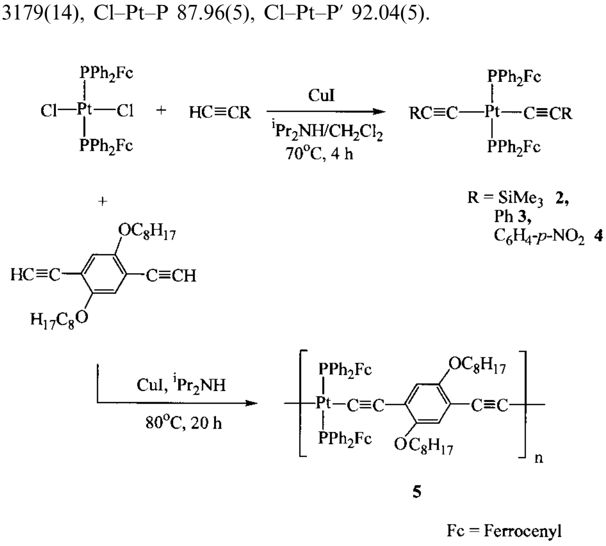


Fig. 1. The molecular structure of the dichloromethane solvate **1**. Selected bond lengths (Å) and angles (°); Pt–Cl 2.3120(14), Pt–P 2.3179(14), Cl–Pt–P 87.96(5), Cl–Pt–P′ 92.04(5).



Scheme 2. The syntheses of complexes **2**–**5**.

and characterisation of platinum ethynyl monomers and polymers with *pendant* ferrocenyl groups.

2. Results and discussion

Ferrocenyl diphenylphosphine was prepared following the literature procedure (Scheme 1) [8] and its reaction with $PtCl_2(SEt_2)_2$ (prepared in situ by the reaction of $PtCl_2$ with SEt_2) in dichloromethane for 20 h afforded the metal precursor **1** as a bright yellow powder in 42% yield (Scheme 1). Compound **1** was characterised by $^{31}P\{^1H\}$- and ^1H-NMR spectroscopy and mass spectrometry and its structure was determined by a single crystal X-ray analysis. The structure of the dichloromethane solvate of **1** (Fig. 1) is seen to have a geometry virtually identical to that of the benzene solvate reported by Otto and Roodt [9]. The pattern of bond lengths in the two structures does not differ significantly. The rotation of the P–C(ferrocenyl) bond out of the platinum coordination plane is ca. 71° cf. 69° in the benzene solvate. The degree of stagger of the five-membered rings in the ferrocenyl unit is greater in **1** (ca. 5°) than that found in the literature structure (ca. 1°). Other ferrocenylphosphine platinum(II) complexes are known, featuring either COOH or $PPh_2\{W(CO)_5\}$ substituents on the ferrocenyl unit [10].

Complexes **2**–**4** were prepared by dehydrohalogenation reactions [11] between **1** and the appropriate ethynyl ligands in diisopropylamine in the presence of CuI (Scheme 2). The crude products were purified via column chromatography (neutral, grade II alumina) and isolated in 62–79% yield. Each complex exhibited a singlet in the $^{31}P\{^1H\}$-NMR and a single sharp IR band at ca. 2000–2100 cm^{-1}, indicating a *trans*-configuration of the ligands. Complex **4** crystallises as two different polymorphic forms; one (**4a**) is triclinic and the other (**4b**) is orthorhombic. Both polymorphs have similar centrosymmetric structures with, in each case, the platinum atom being positioned on a crystallographic inversion centre. In **4a**, the geometry at the metal is distorted square-planar (Fig. 2a) with *cis* angles in the range 84.88(12)–95.12(12)°, whereas in **4b** the *cis* angles do not deviate significantly from 90° (Fig. 2b). The comparable platinum coordination distances in the two polymorphs are essentially identical and unexceptional. The inclinations of the P–C(ferrocenyl) bonds to the platinum coordination plane are ca. 66 and 72° in **4a** and **4b**, respectively, very similar to the value seen in the parent complex **1**. There is a small difference in the degrees of stagger within the ferrocenyl units with departures from eclipsed geometries of ca. 10 and 5° for **4a** and **4b**, respectively. The principal difference between the two forms is in the orientation of the pairs of nitrophenyl rings with respect to the platinum coordination plane. In **4a** the *trans*-bis(ethynyl-*p*-nitrophenyl)platinum unit has a slightly sinusoidal conformation with the two phenyl rings tilted by ca. 11° out of the platinum coordination plane, the distortion being due principally to small non-linearities at C(1) and C(2) of 173.5(4) and 173.2(5)°, respectively. As a consequence the two terminal nitro groups lie ca. 1 Å ‘above’ and ‘below’ the PtP_2C_2 plane, respectively. By contrast, in **4b** this bis(ethynyl) unit, whilst still having similar non-linearities at C(1) and C(2) [174.3(10) and 175.4(11)°, respectively] has its *p*-nitrophenyl ring systems inclined substantially (by ca. 40°) to the platinum coordination plane. In **4a** there are intramolecular C–H···π interactions between ferrocenyl C–H groups and each of the ethynyl C≡C linkages with C(21)–H and C(12)–H lying 2.88 and 2.85 Å, respectively, from the centre of the C(1)≡C(2) bond; the associated C–H···centroid angles are 165 and 136°, respectively. There are no equivalent interactions in **4b**, the ferrocenyl unit being rotated about the P–Fc bond away from the ethynyl linkage. The other important difference between the two structures is in the packing of the molecules. Surprisingly, in **4a** there is not the anticipated stacking of the π-nitrophenyl units, which whilst arranged head-to-tail have a substantial lateral offset. The only intermolecular packing interaction of note in this polymorph is the formation of loosely linked chains held together by C–H···O hydrogen bonds between the C(20) hydrogen atom of one molecule and the O(10) nitrophenyl oxygen atom of a C_i-related counterpart; the H···O distance is 2.50 Å with a C–H···O angle of 153°. In the packing of **4b**, however, the *p*-nitrophenyl ring systems of C_i-related pairs of molecules form head-to-tail *p*-stacks with a mean interplanar separation between the two aromatic rings of 3.44 Å and a centroid···centroid distance of 3.93 Å, thereby again forming an extended chain of molecules.

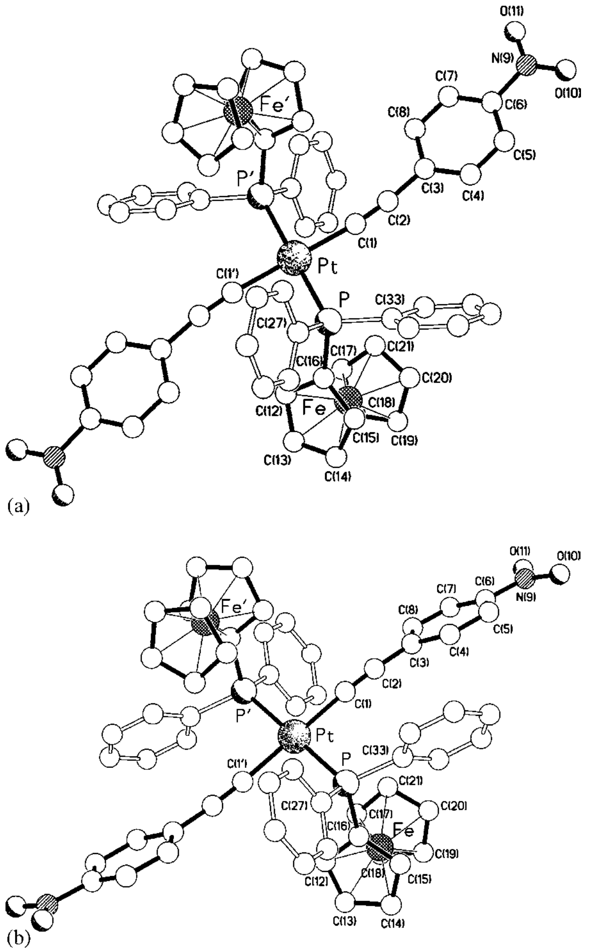


Fig. 2. (a) The molecular structure of the triclinic polymorph **4a**. Selected bond lengths (Å) and angles (°); Pt–C(1) 2.029(5), Pt–P 2.3111(10), C(1)–C(2) 1.167(7), C(1)–Pt–P 95.12(12), C(1)–Pt–P′ 84.88(12). (b) The molecular structure of the orthorhombic polymorph **4b**. Selected bond lengths (Å) and angles (°); Pt–C(1) 2.033(10), Pt–P 2.313(2), C(1)–C(2) 1.156(13), C(1)–Pt–P 90.3(2), C(1)–Pt–P′ 89.7(2).

The poly-condensation reaction of **1** and a diethynyl xylene ligand unfortunately afforded an insoluble polymeric product. Solid-state IR spectra showed the presence of a broad band due to ν(–C≡C–) in the 2100 cm^{-1} region, indicating the formation of a polymeric chain, but the lack of solubility of the polymer in organic solvents precluded other spectroscopic investigations. Instead, an alkoxy substituted ethynyl ligand [12] was prepared via a Cu/Pd catalysed cross-coupling reaction, in order to aid solubility and allow characterisation and exploitation of any useful properties. As the ligand is sensitive to air and moisture it was used for the polymer synthesis within 24 h. The polymer **5** was synthesised by adoption of the literature route pioneered by Hagihara et al. [11,13] with the reaction of the bifunctional ethynyl ligand with **1** in diisopropylamine, in the presence of CuI catalyst, at 70 °C for 20 h. The desired polymer was isolated as a pale yellow coloured powder in 69% yield (Scheme 2) and was purified by column chromatography on neutral-grade II alumina, followed by recrystallisation in dichloromethane–hexane. The reaction was monitored by IR spectroscopy and the disappearance of the band for ν(C≡C–H) of the ethynyl ligands at 3301 cm^{-1} indicated the formation of metal–ethynyl bonds. The new IR band observed at ca. 2100 cm^{-1} is diagnostic for the *trans*-[–C≡C–Pt–C≡C–] monomers and polymers [11]. The IR stretching frequency of the polymer (ν(C≡C) = 2100 cm^{-1}) is very broad compared to that of the dimers, which is consistent with polymer chains of different sizes. Molecular weight estimations of the polymer were carried out using gel permeation chromatography techniques (vs. polystyrene standards). After purification by column chromatography, the GPC spectra showed the presence of high and low molecular weight polymers. Therefore, the polymer was further reprecipitated by dichloromethane and hexane and subjected to GPC analysis again. The GPC analysis of the second run showed the average molecular weight of the sample to be ca. $M_w = 88\,000$. The figures indicate a high degree of polymerisation, and similar molecular weight distributions have been reported for other platinum(II) poly-ynes [1c,d,i]. As with the dimers, the polymer displays a singlet with satellites ($^1J_{(Pt-P)}$ = ca. 2670 Hz) in its $^{31}P\{^1H\}$-NMR spectrum which is consistent with a *trans*-geometry for the P–Pt–P unit [14].

In conclusion, we have established the synthesis of a new class of novel ferrocene-containing platinum ethynyl species, and the synthesis of highly soluble polymers is underway by introducing solubilising alkyl groups on the phosphine ligand, along with detailed electrochemical measurements.

3. Experimental

3.1. General

All preparations were carried out using standard Schlenk techniques [15]. All solvents were distilled over standard drying agents under nitrogen directly before use and all reactions were carried out under an atmosphere of nitrogen. Alumina gel (neutral-grade II) was used for chromatographic separations. All NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 270.1 (^{1}H), 67.9 (^{13}C{^{1}H}) and 101.3 MHz (^{31}P{^{1}H}). Chemical shifts (δ) are reported in ppm using $CDCl_3$ (^{1}H, 7.25 ppm, ^{13}C{^{1}H} 77.0 ppm) as the reference, whilst ^{31}P{^{1}H} spectra were referenced to H_3PO_4. Infrared spectra were recorded using NaCl solution cells (CH_2Cl_2) using a Mattson Polaris Fourier Transform IR spectrometer. Mass spectra were recorded using positive FAB methods, on an Autospec Q mass spectrometer. Microanalyses were carried out at SACS, University of North London. The molecular weights were estimated by gel permeation chromatography using polystyrene standards [16].

3.2. Synthesis

$FcSnBu_3$ [8], $FcPh_2P$ [8] and HC≡C-*p*-(OC_8H_{17}-*p*-C_6H_2-*p*-OC_8H_{17})$_2$-*p*-C≡CH [12] were prepared by following published procedures.

3.2.1. *Trans-[dichlorobis-(diphenylferrocenylphosphine)-platinum(II), trans-[(Ph₂FcP)₂PtCl₂] (**1**)*

Diethylsulfide (0.05 g, 0.55 mmol) was added to a suspension of platinum(II) dichloride (0.08 g, 0.30 mmol) in degassed CH_2Cl_2 (30 ml). The reaction was stirred for 2 h and then filtered and diphenylferrocenylphosphine (0.22 g, 0.60 mmol) was added to the filtrate. The resulting mixture was stirred for another 20 h with the appearance of a precipitate. The mixture was evaporated to dryness and the residue was subjected to column chromatography on alumina using CH_2Cl_2–hexane (1:1) as eluant. The pure product was isolated as a bright yellow crystalline solid (0.13 g, 42% yield). Anal. Calc. for $C_{44}H_{38}Cl_2P_2Fe_2Pt\cdot CH_2Cl_2$: C 49.53; H 3.69. Found: C 49.96; H 4.01%. ^{1}H-NMR ($CDCl_3$): δ 4.41 (t, 4H, C_5H_4), 4.44 (s, 10H, C_5H_5), 4.53 (t, 4H, C_5H_4), 7.37 (m, 12H, C_6H_5), 7.65 (m, 8H, C_6H_5); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 11.20 (s, PPh_2Fc, $^1J_{Pt-P}$ = 2624 Hz); FAB +ve; *m/z*: 1006 [M]$^+$.

3.2.1.1. *Crystal data for **1***

$C_{44}H_{38}P_2Cl_2Fe_2Pt\cdot CH_2Cl_2$, $M = 1091.3$, triclinic, $P\bar{1}$ (no. 2), $a = 9.674(1)$ Å, $b = 11.008(1)$ Å, $c = 11.735(1)$ Å, $\alpha = 111.89(1)°$, $\beta = 104.87(1)°$, $\gamma = 104.97(1)°$, $V = 1029.7(2)$ Å^3, $Z = 1$ (C_i symmetry), $D_{calc} = 1.760$ g cm^{-3}, μ(Mo–K$_\alpha$) = 4.45 mm^{-1}, $T = 293$ K, yellow prisms; 3446 independent measured reflections, F^2 refinement, $R_1 = 0.034$, $wR_2 = 0.077$, 3268 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 236 parameters.

3.2.2. *Trans-[bis-(trimethylsilylethynyl)-bis-(diphenylferrocenylphosphine)platinum(II), trans-[(Ph₂FcP)₂Pt(C≡CSiMe₃)₂] (**2**)*

Compound **1** (0.05 g, 0.05 mmol) was dissolved in diisopropylamine–CH_2Cl_2 (40 ml) and trimethylsilylethyne (0.50 ml, excess) and CuI (2 mg) were added. The reaction was stirred at 70 °C for 4 h then the solvent was removed in vacuo. The residue was redissolved in CH_2Cl_2 (50 ml) and the solution was filtered. The filtrate was then subjected to chromatography on a short alumina column with CH_2Cl_2 as eluant and a pale yellow product was isolated by recrystallisation from CH_2Cl_2–hexane in 62% yield (0.04 g). Anal. Calc. for $C_{54}H_{56}Si_2P_2Fe_2Pt$: C, 57.40; H, 4.96. Found: C, 57.27; H, 4.79%. IR (cm^{-1}, CH_2Cl_2): ν(C≡C) 2036. ^{1}H-NMR ($CDCl_3$): δ 4.36 (t, 4H, C_5H_4), 4.42 (s, 10H, C_5H_5), 4.65 (t, 4H, C_5H_4), 7.34 (m, 12H, C_6H_5), 7.71 (m, 8H, C_6H_5); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 7.71 (PPh_2Fc, $^1J_{(Pt-P)}$ = 2670 Hz). FAB +ve; *m/z*: 1128 [M − 1]$^+$.

3.2.3. *Trans-[bis-(phenylethynyl)-bis-(diphenylferrocenylphosphine)platinum(II), trans-[(Ph₂FcP)₂-Pt(C≡CPh)₂] (**3**)*

Following the procedure adopted for the formation of **2**, but using phenylethyne gives 62% (0.03 g) of a yellow solid **3**. Anal. Calc. for $C_{60}H_{48}P_2Fe_2Pt$: C, 63.33; H, 4.22. Found: C, 63.59; H, 4.31%. IR (cm^{-1}, CH_2Cl_2): ν(C≡C) 2107. ^{1}H-NMR ($CDCl_3$): δ 4.38 (t, 4H, C_5H_4), 4.40 (s, 10H, C_5H_5), 4.63 (t, 4H, C_5H_4), 6.53 (m, 4H, C≡CC_6H_5), 6.98 (m, 6H, C≡CC_6H_5), 7.32 (m, 12H, (C_6H_5)$_2$P), 7.76 (m, 8H, (C_6H_5)$_2$P); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 8.83 (PPh_2Fc, $^1J_{(Pt-P)}$ = 2662 Hz). FAB +ve; *m/z*: 1137 [M]$^+$.

3.2.4. *Trans-[bis-(4-nitrophenylethynyl)-bis-(diphenylferrocenylphosphine)platinum(II), trans-[(Ph₂FcP)₂-Pt(C≡C–C₆H₄-p-NO₂)₂] (**4**)*

As for the formation of **2** but using nitrophenylethyne gives 79% (0.03 g) of a bright yellow solid (**4**). Anal. Calc. for $C_{60}H_{46}N_2O_4P_2Fe_2Pt$: C, 58.68; H, 3.75. Found: C, 58.72; H, 3.87%. IR (cm^{-1}, CH_2Cl_2): ν(C≡C) 2103. ^{1}H-NMR ($CDCl_3$): δ 4.40 (s, 10H, C_5H_5), 4.44 (t, 4H, C_5H_4), 4.57 (t, 4H, C_5H_4), 6.51 (d, 4H, C≡CC_6H_4–NO_2), 7.34 (m, 12H, (C_6H_5)$_2$P), 7.73 (m, 8H, (C_6H_5)$_2$P), 7.88 (d, 4H, C≡CC_6H_4–NO_2); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 9.77 (PPh_2Fc, $^1J_{(Pt-P)}$ = 2562 Hz). FAB +ve; *m/z*: 1226 [M − 1]$^+$.

3.2.4.1. *Crystal data for **4a***

$C_{60}H_{46}N_2O_4P_2Fe_2Pt$, $M = 1227.7$, triclinic, $P\bar{1}$ (no. 2), $a = 10.317(1)$ Å, $b = 10.951(2)$ Å, $c = 11.768(1)$ Å, $\alpha = 87.30(1)°$,

$\beta = 68.32(1)°$, $\gamma = 88.38(1)°$, $V = 1234.0(2)$ Å^3, $Z = 1$ (C_i symmetry), $D_{calc} = 1.652$ g cm^{-3}, μ(Cu–K$_\alpha$) = 10.9 mm^{-1}, $T = 293$ K, yellow prismatic needles; 3675 independent measured reflections, F^2 refinement, $R_1 = 0.030$, $wR_2 = 0.067$, 3483 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 299 parameters.

3.2.4.2. Crystal data for ***4b***. $C_{60}H_{46}N_2O_4P_2Fe_2Pt$, $M = 1227.7$, orthorhombic, *Pbca* (no. 61), $a = 14.322(1)$ Å, $b = 16.424(2)$ Å, $c = 20.627(2)$ Å, $V = 4852.3(9)$ Å^3, $Z = 4$ (C_i symmetry), $D_{calc} = 1.681$ g cm^{-3}, μ(Cu–K$_\alpha$) = 11.1 mm^{-1}, $T = 293$ K, orange/yellow hexagonal prisms; 3608 independent measured reflections, F^2 refinement, $R_1 = 0.045$, $wR_2 = 0.085$, 2205 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$], 299 parameters.

3.3. Poly-*trans*-[1,4-bis(ethynyl)-2,5-dioctyloxy)-benzene]platinum(II), [(Ph$_2$FcP)$_2$Pt(C≡C-*p*-(OC$_8$H$_{17}$)$_2$C$_6$H$_2$–C≡C)$_2$]$_n$ (**5**)

A mixture of HC≡C-*p*-(OC$_8$H$_{17}$)$_2$C$_6$H$_2$–C≡CH (0.38 g, 1.00 mmol), *trans*-[(Ph$_2$FcP)$_2$PtCl$_2$] (0.10 g, 1.00 mmol) and CuI (5 mg) was stirred under nitrogen in diisopropylamine at 80 °C for 20 h. The solvent was evaporated to dryness and the residue was subjected to chromatography using CH_2Cl_2–hexane (2:1) as eluant. A yellow solid **5** was isolated in 69% yield (0.090 g). IR (cm^{-1}, CH_2Cl_2): ν(C≡C) 2100. ^{1}H-NMR ($CDCl_3$); δ 0.86 (t, 6H, CH_3), 1.23 (br m, 28H, CH_2), 3.40 (t, 4H, CH_2), 4.29 (t, 4H, C_5H_4) 4.36 (s, 10H, C_5H_5), 4.70 (t, 4H, C_5H_4), 7.24 (m, 8H, C_6H_5), 7.35 (m, 12H, C_6H_5); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 8.28 (PPh$_2$Fc, $^1J_{(Pt-P)}$2670 Hz).

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 175658, 175659 and 175660 for compounds **1**, **4a** and **4b**, respectively. 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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