Synthesis and characterisation of new acetylide-functionalised oligothiophenes and their dinuclear platinum complexes

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A series of rigid-rod alkynes with extended π conjugation through oligothiophene linkage units in the backbone, 2,5-bis(trimethylsilylethynyl)thiophene **Ia**, 2,5-diethynylthiophene **Ib**, 5,5′-bis(trimethylsilylethynyl)-2,2′-bithiophene **IIa**, 5,5′-diethynyl-2,2′-bithiophene **IIb**, 5,5″-bis(trimethylsilylethynyl)-2,2′ : 5′,2″-terthiophene **IIIa** and 5,5″-diethynyl-2,2′ : 5′,2″-terthiophene **IIIb**, has been prepared. Treatment of the complex *trans*-[PtPh(Cl)(PR$_3$)$_2$] (R = Et or Bu^n) with half an equivalent of the diterminal alkynyl oligothiophene chromophores **Ib–IIIb** in CH$_2$Cl$_2$–NHPr$^i_2$, in the presence of CuI, at room temperature, afforded the platinum dimers *trans*-[(Et$_3$P)$_2$PhPt–C≡CR′C≡C–PtPh(PEt$_3$)$_2$] (R′ = thiophenediyl **1a**, bithiophenediyl **2** or terthiophenediyl **3**) and *trans*-[(Bu$^n_3$P)$_2$PhPt–C≡CR′C≡C–PtPh(PBu$^n_3$)$_2$] **1b** (R′ = thiophenediyl) in good yields. All the new compounds have been characterised by analytical and spectroscopic methods, and the single-crystal structures of **IIa**, **1a** and **2** have been established.

The preparation and physical studies of conjugated organo-metallic complexes and polymers have been the subject of significant research interest during the past two decades because of their possible applications in the materials industry.[1,2] In this respect, α-coupled oligothiophenes are currently attracting a great deal of attention in the field of electronic and optoelectronic devices such as field-effect transistors (FETs)[3–6] and light-emitting diodes (LEDs),[7–9] and even in biological research.[10] Moreover, highly organised molecular assemblies based on the end substitution of thiophene oligomers by the use of trimethylsilyl,[11] alkyl[12] or 4,5,6,7-tetrahydrobenzo[13] groups have recently been studied extensively.

With these ideas in mind we set out to prepare a new range of alkyne-functionalised α-coupled oligothiophenes at their end positions which can then provide direct access to some bimetallic materials bearing these π-conjugated systems. The introduction of transition-metal centres, with their large variety of ligand environments and oxidation states, is usually expected to impart interesting physical properties, particularly non-linear optical properties on the oligothiophene systems.[14] Here, we report the synthesis and characterisation of a series of straight-chain alkynes with extended π conjugation through thiophene, bithiophene or terthiophene units in the backbone and their complexes containing PtPh(PR$_3$)$_2$ groups. The crystal structures of a selected organic precursor and two diplatinum complexes are also described.

Results and Discussion

Syntheses

2,5-Bis(trimethylsilylethynyl)thiophene **Ia**, 5,5′-bis(trimethylsilylethynyl)-2,2′-bithiophene **IIa** and 5,5″-bis(trimethylsilylethynyl)-2,2′ : 5′,2″-terthiophene **IIIa** were prepared by a Pd^{II}/CuI-catalysed cross-coupling reaction of the dibromides with trimethylsilylacetylene[15] (Scheme 1). These ligands were isolated as off-white (**Ia**) and yellow (**IIa** and **IIIa**) solids in yields of 70–85% and have been characterised by elemental analyses and by IR, NMR (^{1}H and ^{13}C), UV/VIS spectroscopy and mass spectrometry. They are all stable in air and towards light.

Conversion of **Ia–IIIa** into their terminal H derivatives

HC≡CR′C≡CH **Ib–IIIb** was accomplished by the desilylation of **Ia–IIIa** with K$_2$CO$_3$ in MeOH[16] (Scheme 1). The products were purified by silica column chromatography and characterised spectroscopically. All the diterminal acetylenes are quite unstable in air and under light and give insoluble brown precipitates on standing.

The reaction of the platinum(II) complex *trans*-[PtPh(Cl)(PEt$_3$)$_2$] with half an equivalent of **Ib** or **IIb** in CH$_2$Cl$_2$–NHPr$^i_2$, in the presence of CuI, at room temperature, readily affords the pure platinum dimers *trans*-[(Et$_3$P)$_2$PhPt–C≡CR′C≡C–PtPh(PEt$_3$)$_2$] (R′ = thiophenediyl **1a**, bithiophenediyl **2** or terthiophenediyl **3**), in good yields (Scheme 2). The corresponding PBu$^n_3$ derivative *trans*-[(Bu$^n_3$P)$_2$PhPt–C≡CR′C≡C–PtPh(PBu$^n_3$)$_2$] (R′ = thiophenediyl) was also prepared in a similar way. The formulae of these complexes were first established by positive FAB mass spectrometry and IR and NMR (^{1}H and ^{31}P) spectroscopies, and they all gave satisfactory analytical data.

All the organic ligands and the platinum complexes exhibit good solubilities in common organic solvents and the solubility of the complexes increased by changing the auxiliary ligands from PEt$_3$ to PBu$^n_3$.

Spectroscopic properties

The IR spectra of the platinum–σ-acetylide complexes display a single strong ν(C≡C) absorption consistent with a *trans* configuration of the acetylenic units around the Pt^{II}. As expected, the ν(C≡C) values of the complexes are lower than those of the corresponding terminal or Me$_3$Si-substituted acetylide ligands. This may be attributed to either (i) the metal-to-alkyne π back bonding or (ii) the M$^{δ+}$–C$^{δ−}$ polarity.[17] There was no significant effect of the different phosphine ligands (PEt$_3$ *vs.* PBu$^n_3$) on the C≡C stretching frequencies of the bimetallic bis(acetylide) complexes. The ^{31}P-{^{1}H} NMR spectral data of all the platinum bis(acetylide) complexes confirm that the phosphines are mutually *trans* around the Pt^{II} giving a square-planar geometry.

The electronic absorption spectra of the ligands show a strong, relatively low-energy π–π* transition. A notable feature is that an increase of the number of thienyl units in the molecule shifts the position of this band toward longer wavelengths. Presumably, a higher degree of conjugation with the
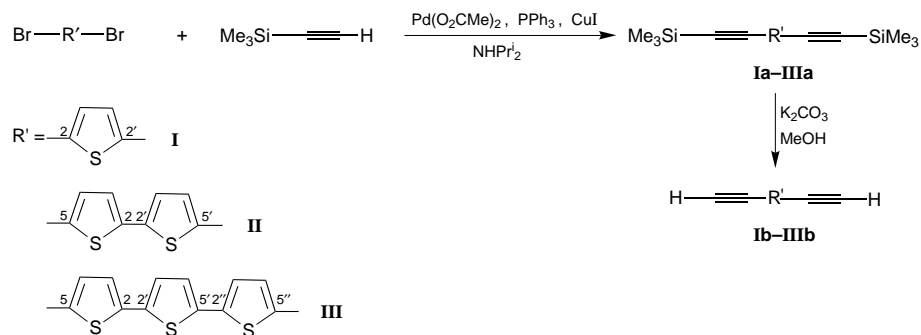
Scheme 1
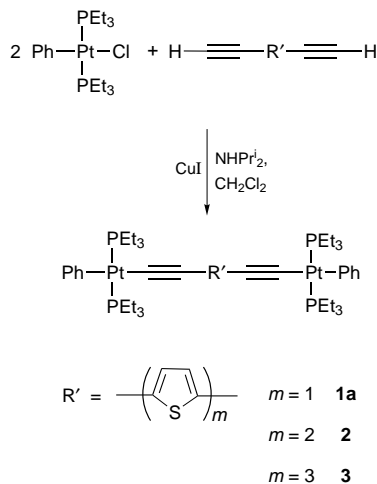
Scheme 2

additional thienyl units reduces the energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). This is consistent with the π–π* transitions observed for the parent oligothiophenes, which vary from 231 nm for thiophene to 350 nm for terthiophene.[18] For Me_3Si-substituted acetylides, this transition red-shifts steadily from 331 to 410 nm. The electronic spectra of the diplatinum(II) complexes **1**–**3** are also dominated by the π–π* transitions of the corresponding bridging ligands (see Experimental section). The effect of attachment of two platinum fragments is found to lower the energies of these transitions. It was clearly shown that the 371 and 353 nm absorptions of free **IIa** and **IIb** respectively move to 406 nm for complex **2**, indicating that the platinum moieties act as net electron acceptors.[19] Again, increasing conjugation through more thienyl units from complexes **1** to **3** leads to a decreased transition energy, with λ_{max} for **3** being the largest. It is also noteworthy that no significant difference between PEt_3 and PBu^n_3 as auxiliary ligands in the absorption spectra of the platinum complexes is observed.

Molecular structures

The molecular structure of compound **IIa** is shown in Fig. 1, which includes the atom numbering scheme. Selected bond distances and angles are listed in Table 1. In the solid state two halves of the molecule are related by a centre of symmetry at the midpoint of C(1)–C(1A) bond. Each molecule is essentially planar and adopts a *trans* configuration with respect to the two thiophene rings. The mean sulfur–carbon bond length is 1.730(6) Å, which is similar to those found in α-terthiophene and α-sexithiophene.[20] The C–C bond distances of the thiophene ring vary from 1.358(8) to 1.406(8) Å with the average being 1.375(8) Å. This average is somewhat shorter than that observed in unsubstituted α-oligothiophenes (range 1.36–1.46 Å).[20] The bond C(5)–C(6) is longer than that of a typical C≡C bond. Moreover, slight shortenings of the bonds C(1)–C(1A) and C(4)–C(5) are observed [1.44(1) and 1.436(8) Å, respect-
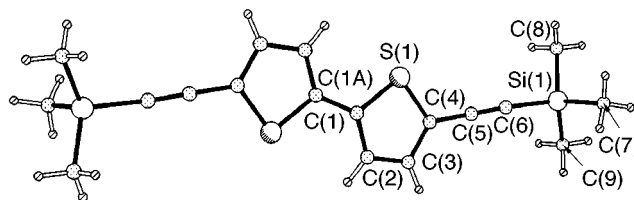

Fig. 1 Molecular structure of Me_3Si–C≡CR′C≡C–$SiMe_3$ **IIa** (R′ = bithiophenediyl)

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

S(1)–C(1)	1.728(5)	C(3)–C(4)	1.358(8)
S(1)–C(4)	1.732(6)	C(4)–C(5)	1.436(8)
Si(1)–C(6)	1.825(7)	C(5)–C(6)	1.204(8)
C(1)–C(2)	1.361(8)	C(1)–C(1A)	1.44(1)
C(2)–C(3)	1.406(8)		
C(1)–S(1)–C(4)	91.9(3)	S(1)–C(1)–C(2)	109.8(4)
S(1)–C(4)–C(3)	111.5(4)	C(1)–C(2)–C(3)	114.9(5)
C(2)–C(3)–C(4)	111.9(5)	C(4)–C(5)–C(6)	179.2(6)
C(5)–C(6)–Si(1)	176.8(6)		

Atoms denoted A are related by the symmetry operation $2 - x$, $-y$, $2 - z$ to the unique atom with the same numbering.

ively], which is consistent with the partial conjugation effect along the molecule. Common to most planar molecules such as α-terthienyl and α-hexathienyl, the unit cell of crystals **IIa** presents the herringbone packing in space group $P2_1/a$.[20,21] No significant interheteroatom contacts are observed and the distances between atoms of nearest molecules are all longer than the sum of the van der Waals radii.

The solid-state structures of complexes **1a** and **2** have also been established by X-ray crystallography. The molecular structures are illustrated in Figs. 2 and 3, respectively, and selected bond parameters are collected in Tables 2 and 3. In each case, the crystal structure consists of discrete dimeric molecules in which the platinum atoms are surrounded by four ligands in a square-planar geometry with the two phosphines in a *trans* arrangement. For **1a** there are one and a half molecules in the asymmetric unit, and only the complete unique molecule is shown in Fig. 2; the half molecule is disordered about a centre of symmetry. For **2** there are two independent half molecules each possessing crystallographic C_i symmetry with the centre of symmetry at the midpoint of the C(6)–C(6A) bond; only one molecule is shown in Fig. 3. The metal-to-phosphorus bond lengths lie in the range of 2.274(5)–2.303(5) (**1a**) and 2.291(6)–2.316(6) Å (**2**). The two PtPh(PEt₃)₂ units are bridged by a thiophenediyl- or bithiophenediyl-spaced bis(acetylide) ligand for **1a** and **2**, respectively. Like free **IIa**, the two thiophene groups in **2** display a *trans* arrangement in order to minimise the steric repulsions between the lone pairs on both sulfur atoms. In both cases, the fragment Pt–C≡CR′C≡C–Pt is nearly planar. The mean metal-to-carbon (acetylide) bond length is 2.03(2) Å for **1a** and 2.01(2) Å for **2**, while the average acetylide C≡C bond
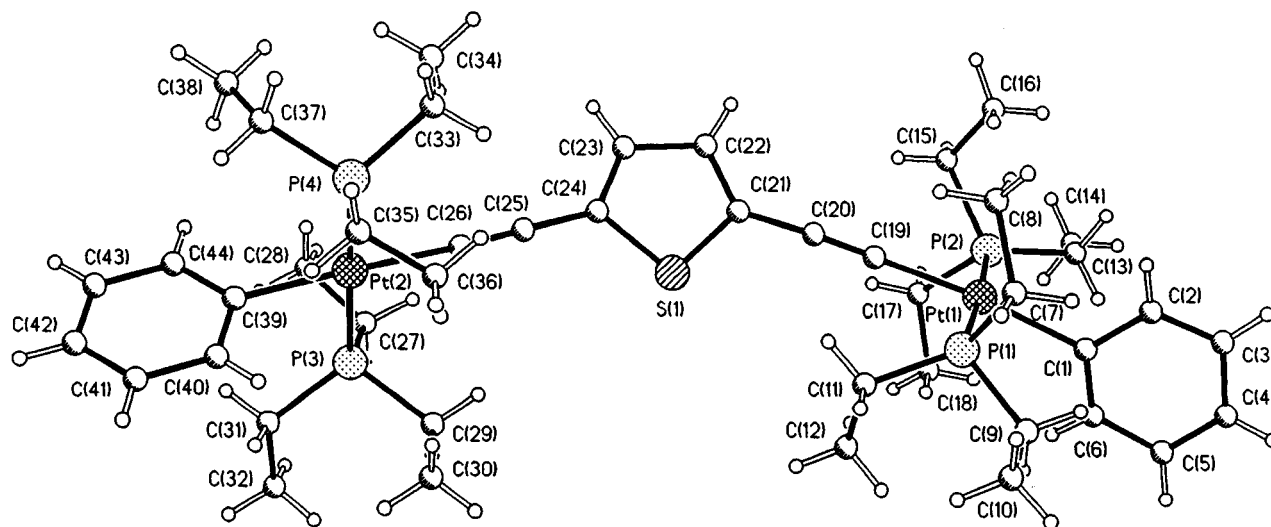
Fig. 2 Molecular structure of *trans*-[(Et$_3$P)$_2$PhPt–C≡CR′C≡C–PtPh(PEt$_3$)$_2$] **1a** (R′ = thiophenediyl)
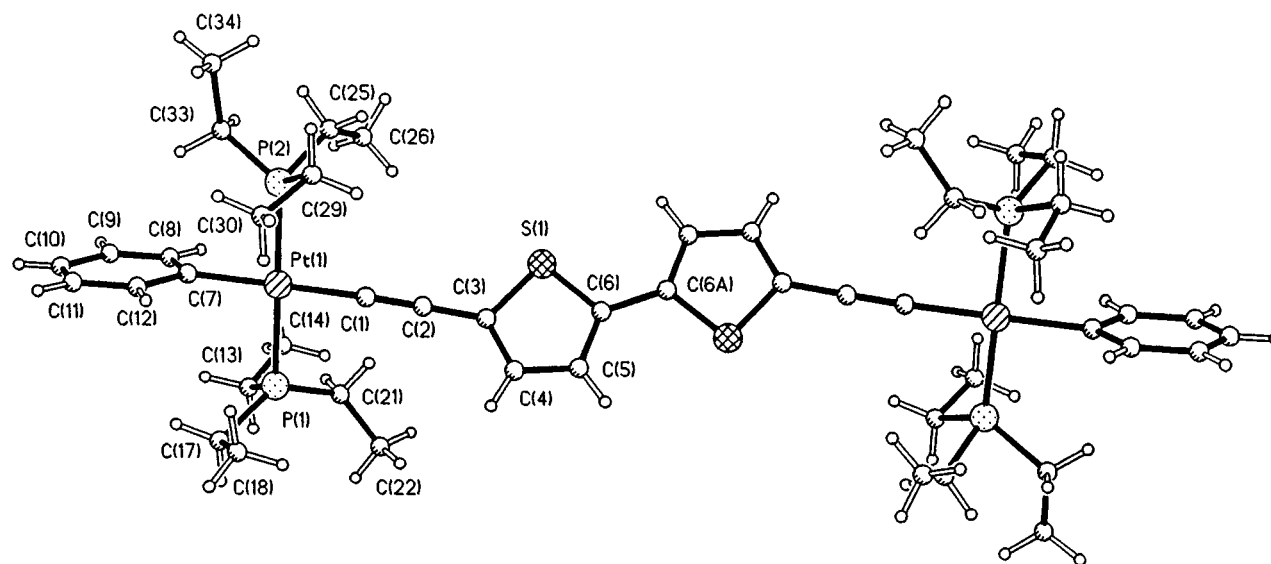

Fig. 3 Molecular structure of *trans*-[(Et$_3$P)$_2$PhPt–C≡CR′C≡C–PtPh(PEt$_3$)$_2$] **2** (R′ = bithiophenediyl)

length is 1.20(3) (**1a**) and 1.25(3) Å (**2**). The S–C bonds of the bithienyl group in **2** show comparable distances to those in **IIa** but the C–C distances of the rings are slightly longer in **2** [1.37(3)–1.42(3) Å]. The mean angles of 178(2) (**1a**) and 177(2)° (**2**) for the fragment Pt–C≡C confirm the linear geometry of the bis(acetylide) complexes.

Experimental

General

Solvents were predried and distilled from appropriate drying agents.[22] All chemicals, except where stated, were from commercial sources and used as received; Me$_3$SiC≡CH was prepared in this laboratory. The compounds *trans*-[PtPh(Cl)(PR$_3$)$_2$] (R = Et or Bu^n),[23] 5,5′-dibromo-2,2′-bithiophene[24] and 5,5″-dibromo-2,2′:5′,2″-terthiophene[24] were prepared *via* literature procedures. The NMR spectra were recorded on a Bruker WM-250 or AM-400 spectrometer 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 1710 Fourier-transform spectrometer and mass spectra on a Kratos MS890 spectrometer by either the electron impact (EI) or fast atom bombardment (FAB) technique. Microanalyses were performed in this department. Electronic absorption spectra were obtained with a Perkin-Elmer Lambda UV/NIR spectrometer. 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 at the University Chemical Laboratory, Cambridge. Column chromatography was performed on Kieselgel 60 (230–400 mesh) silica gel.

Ligand syntheses

All the ligand precursors were made by following a general procedure outlined below for **IIa** and **IIb**.

5,5′-Bis(trimethylsilylethynyl)-2,2′-bithiophene IIa. To an ice-cooled mixture of 5,5′-dibromo-2,2′-bithiophene (3.89 g, 12 mmol) in freshly distilled diisopropylamine (70 cm^3) under nitrogen were added CuI (30 mg, 0.16 mmol), Pd(O$_2$CMe)$_2$ (30 mg, 0.13 mmol) and PPh$_3$ (90 mg, 0.34 mmol). The solution was stirred for 20 min, Me$_3$SiC≡CH (2.95 g, 30 mmol) was then added and the suspension was stirred for 30 min in an ice-bath before being warmed to room temperature. After reacting for 30 min at room temperature the mixture was heated to 75 °C for 20 h. The completion of the reaction was verified by IR spectroscopy and silica TLC. The solution was allowed to cool to room temperature, Et$_2$O (100 cm^3) was added and the precipitate was filtered off. The brown-yellow filtrate was evaporated to dryness. The residue was redissolved in Et$_2$O (100 cm^3) and washed sequen-

Table 2 Selected bond lengths (Å) and angles (°) for complex **1a**

Molecule 1

Pt(1)–P(1)	2.290(5)	C(20)–C(21)	1.42(3)
Pt(1)–P(2)	2.274(5)	C(21)–C(22)	1.34(3)
Pt(1)–C(1)	2.10(1)	C(22)–C(23)	1.50(3)
Pt(2)–P(3)	2.292(6)	C(23)–C(24)	1.33(3)
Pt(2)–P(4)	2.288(6)	S(1)–C(21)	1.74(2)
Pt(1)–C(19)	2.03(2)	S(1)–C(24)	1.74(2)
Pt(2)–C(26)	2.02(2)	C(24)–C(25)	1.40(3)
Pt(2)–C(39)	2.08(1)	C(25)–C(26)	1.20(2)
C(19)–C(20)	1.18(3)		
P(1)–Pt(1)–P(2)	175.7(2)	P(1)–Pt(1)–C(19)	86.7(6)
P(2)–Pt(1)–C(19)	89.5(6)	Pt(1)–C(19)–C(20)	178(2)
C(1)–Pt(1)–C(19)	174(2)	Pt(2)–C(26)–C(25)	177(2)
P(3)–Pt(2)–P(4)	177.1(2)	P(3)–Pt(2)–C(26)	88.7(6)
P(4)–Pt(2)–C(26)	91.5(6)	C(26)–Pt(2)–C(39)	178.3(6)
C(19)–C(20)–C(21)	176(2)	C(21)–S(1)–C(24)	95(1)
S(1)–C(21)–C(22)	110(2)	S(1)–C(24)–C(23)	109(2)
C(21)–C(22)–C(23)	112(2)	C(22)–C(23)–C(24)	115(2)
C(24)–C(25)–C(26)	176(2)		

Molecule 2

Pt(3)–P(5)	2.293(5)	C(65)–C(66)	1.30(4)
Pt(3)–P(6)	2.303(5)	C(66)–C(67)	1.44(7)
Pt(3)–C(45)	2.09(2)	C(67)–C(68)	1.30(4)
Pt(3)–C(63)	2.03(2)	S(2)–C(65)	1.73(2)
C(63)–C(64)	1.22(2)	S(2)–C(68)	1.74(2)
C(64)–C(65)	1.38(2)		
P(5)–Pt(3)–P(6)	176.1(2)	P(5)–Pt(3)–C(63)	87.2(5)
P(6)–Pt(3)–C(63)	91.4(5)	Pt(3)–C(63)–C(64)	179(2)
C(45)–Pt(3)–C(63)	179.0(7)	C(63)–C(64)–C(65)	163(2)
C(65)–S(2)–C(68)	95(2)	S(2)–C(65)–C(66)	108(2)
S(2)–C(68)–C(67)	106(2)	C(65)–C(66)–C(67)	114(2)
C(66)–C(67)–C(68)	116(2)		

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

Molecule 1

Pt(1)–P(1)	2.316(6)	S(1)–C(3)	1.74(2)
Pt(1)–P(2)	2.307(6)	S(1)–C(6)	1.74(2)
Pt(1)–C(1)	1.96(2)	C(3)–C(4)	1.38(3)
Pt(1)–C(7)	2.03(2)	C(4)–C(5)	1.37(3)
C(1)–C(2)	1.25(3)	C(5)–C(6)	1.37(3)
C(2)–C(3)	1.42(3)	C(6)–C(6A)	1.50(4)
P(1)–Pt(1)–P(2)	178.2(2)	P(1)–Pt(1)–C(1)	90.4(6)
P(2)–Pt(1)–C(1)	90.0(6)	C(1)–Pt(1)–C(7)	179.0(8)
P(1)–Pt(1)–C(7)	178(2)	C(1)–C(2)–C(3)	179(2)
C(3)–S(1)–C(6)	90.7(9)	S(1)–C(3)–C(4)	110(1)
S(1)–C(6)–C(5)	112(1)	C(3)–C(4)–C(5)	115(2)
C(4)–C(5)–C(6)	113(2)		

Molecule 2

Pt(2)–P(3)	2.291(6)	S(2)–C(39)	1.73(2)
Pt(2)–P(4)	2.296(6)	S(2)–C(42)	1.74(2)
Pt(2)–C(37)	2.05(2)	C(39)–C(40)	1.42(3)
Pt(2)–C(43)	2.06(2)	C(40)–C(41)	1.42(3)
C(37)–C(38)	1.24(3)	C(41)–C(42)	1.40(3)
C(38)–C(39)	1.35(3)	C(42)–C(42A)	1.44(4)
P(3)–Pt(2)–P(4)	174.5(2)	P(3)–Pt(2)–C(43)	87.5(5)
P(4)–Pt(2)–C(43)	92.3(2)	C(37)–Pt(2)–C(43)	176.8(7)
Pt(2)–C(37)–C(38)	176(2)	C(37)–C(38)–C(39)	167(3)
C(39)–S(2)–C(42)	94(1)	S(2)–C(39)–C(40)	110(1)
S(2)–C(42)–C(41)	109(2)	C(39)–C(40)–C(41)	112(2)
C(40)–C(41)–C(42)	115(2)		

The atoms denoted A are generated from the unique atom with the same number by the symmetry operation $-x$, $1 - y$, $-z$.

tially with 10% HCl (3×100 cm³), water (3×100 cm³), NaHCO₃ (3×100 cm³) and water (3×100 cm³). The resulting organic solution was then dried (MgSO₄), the solvent removed, and the brown-yellow residue chromatographed over a silica gel column by eluting with hexane–CH₂Cl₂ (9 : 1 v/v). The product was eluted as a yellow-orange band and the pure fraction evaporated to dryness and recrystallised from hexane–CH₂Cl₂ to give **IIa** as a yellow crystalline solid in 77% yield (3.31 g). IR (CH₂Cl₂): $\tilde{v}$/cm⁻¹ 2143 (C≡C). ¹H NMR (250 MHz, CDCl₃): δ 0.24 (s, 18 H, SiMe₃), 6.99 [d, 2 H, ³J(H³H⁴) or ³J(H³'H⁴') = 3.9, H³,³'] and 7.10 [d, 2 H, ³J(H⁴H³) or ³J(H⁴'H³') = 3.9 Hz, H⁴,⁴']. ¹³C-{¹H} NMR (100.6 MHz, CDCl₃): δ −0.16 (SiMe₃), 97.18 (C≡C), 100.54 (C≡C), 122.41 (C²,²' or C⁵,⁵'), 123.78 (C³,³' or C⁴,⁴'), 133.51 (C³,³' or C⁴,⁴') and 138.13 (C²,²' or C⁵,⁵'). EI mass spectrum: m/z 358 (M^+). UV/VIS (CH₂Cl₂): λ_{max}/nm 371 (Found: C, 60.10; H, 6.28. Calc. for C₁₈H₂₂S₂Si₂: C, 60.28; H, 6.18%).

5,5′-Diethynyl-2,2′-bithiophene IIb. A mixture of compound **IIa** (0.50 g, 1.4 mmol) and K₂CO₃ (0.19 g, 1.4 mmol) in MeOH (50 cm³) was stirred at room temperature for 20 h. Infrared spectroscopy showed that all the starting material had been consumed. Solvent was removed under reduced pressure to leave a yellow residue. This residue was dissolved in the minimum amount of CH₂Cl₂ and subjected to column chromatography on silica using hexane–CH₂Cl₂ (3 : 2 v/v) as eluent to afford a major brown-yellow product identified as **IIb** (0.21 g, 70%). IR (CH₂Cl₂): $\tilde{v}$/cm⁻¹ 2102 (C≡C) and 3300 (C≡CH). ¹H NMR (250 MHz, CDCl₃): δ 3.41 (s, 2 H, C≡CH), 7.02 [d, 2 H, ³J(H³H⁴) or ³J(H³'H⁴') = 3.8 H³,³'] and 7.16 [d, 2 H, ³J(H⁴H³') or ³J(H⁴'H³') = 3.8 Hz, H⁴,⁴']. ¹³C-{¹H} NMR (100.6 MHz, CDCl₃): δ 76.66 (C≡C), 82.68 (C≡C), 121.44 (C²,²' or C⁵,⁵'), 123.93 (C³,³' or C⁴,⁴'), 133.99 (C³,³' or C⁴,⁴') and 138.10 (C²,²' or C⁵,⁵'). EI mass spectrum: m/z 214 (M^+). UV/VIS (CH₂Cl₂): λ_{max}/nm 353 (Found: C, 67.02; H, 3.08. Calc. for C₁₂H₆S₂: C, 67.26; H, 2.82%).

2,5-Bis(trimethylsilylethynyl)thiophene Ia.[25] 2,5-Dibromothiophene (3.00 g, 12.0 mmol), Me₃SiC≡CH (4.50 g, 45.0 mmol) and NHPr$^i_2$ (100 cm³) were mixed with catalytic amounts of CuI (30 mg), Pd(O₂CMe)₂ (30 mg) and PPh₃ (90 mg). The crude product was worked-up, as before, to yield a pale-brown residue which was then applied to a silica column in hexane (5 cm³) and eluted with the same solvent. The desired compound **Ia** was isolated as an off-white solid (2.80 g, 85%). IR (CH₂Cl₂): $\tilde{v}$/cm⁻¹ 2146 (C≡C). ¹H NMR (250 MHz, CDCl₃): δ 0.24 (s, 18 H, SiMe₃) and 7.04 (s, 2 H, H³,⁴). ¹³C NMR (100.6 MHz, CDCl₃): δ −0.20 (SiMe₃), 96.89 (C≡C), 99.93 (C≡C), 124.50 (C²,⁵) and 132.32 (C³,⁴). EI mass spectrum: m/z 276 (M^+). UV/VIS (CH₂Cl₂): λ_{max}/nm 331 (Found: C, 60.93; H, 7.64. Calc. for C₁₄H₂₀SSi₂: C, 60.81; H, 7.29%).

2,5-Diethynylthiophene Ib.[25] Compound **Ia** (1.00 g, 3.6 mmol) was desilylated using K₂CO₃ (0.55 g, 4.0 mmol) in MeOH (50 cm³). The reaction mixture was covered with aluminium foil and left stirring overnight. The solvent was removed slowly at room temperature using a water pump to afford a yellow oil which was dissolved in Et₂O and washed with water. The organic layer was dried quickly over MgSO₄ and filtered. The solvent was removed to give **Ib** (0.23 g, 50%) as a yellow oil which was unstable. Storage overnight under nitrogen at 4 °C resulted in the oil darkening. Long storage times led to the formation of a black rubber-like insoluble material which was presumed to be a polymerisation product. This ligand was therefore freshly prepared for use in any further synthesis. IR (CH₂Cl₂): $\tilde{v}$/cm⁻¹ 2108 (C≡C) and 3300 (C≡CH). ¹H NMR (250 MHz, CDCl₃): δ 3.20 (s, 2 H, C≡CH) and 7.10 (s, 2 H, H³,⁴). ¹³C-{¹H} NMR (100.6 MHz, CDCl₃): δ 79.04 (C≡C), 81.02 (C≡C), 124.05 (C²,⁵) and 132.40 (C³,⁴). EI mass spectrum: m/z 132 (M^+). Microanalytical data are not available due to the instability.

5,5″-Bis(trimethylsilylethynyl)-2,2′ : 5′2″-terthiophene IIIa. This compound was prepared as described above for **IIa** from 5,5″-dibromo-2,2′ : 5′,2″-terthiophene (0.97 g, 2.4 mmol), Me₃SiC≡CH (0.59 g, 6.0 mmol), CuI (6 mg, 0.03 mmol),

Table 4 Summary of crystal structure data for compounds **IIa**, **1a** and **2**

	IIa	1a	2
Empirical formula	$C_{18}H_{22}S_2Si_2$	$C_{44}H_{72}P_4Pt_2S$	$C_{48}H_{74}P_4Pt_2S_2$
M	358.66	1147.14	1229.25
Crystal colour, habit	Pale yellow	Pale yellow	Yellow
Crystal dimensions/mm	$0.42 \times 0.28 \times 0.13$	$0.40 \times 0.25 \times 0.09$	$0.22 \times 0.15 \times 0.11$
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$	$P\bar{1}$
a/Å	11.534(2)	16.804(3)	15.870(6)
b/Å	5.821(1)	25.107(5)	17.460(8)
c/Å	16.146(2)	9.221(2)	9.525(4)
α/°		98.40(3)	97.28(3)
β/°	110.16(2)	99.67(3)	90.80(3)
γ/°		83.24(3)	82.06(3)
U/Å³	1017.6(3)	3777(1)	2593(2)
Z	2	3	2
D_c/g cm^{-3}	1.171	1.513	1.574
$F(000)$	380	1704	1220
μ(Mo-Kα)/mm^{-1}	0.374	5.745	5.623
T/K	293	293	153
θ Range/°	1.34–25.49	2.50–22.50	1.19–22.35
No. reflections collected	1251	10 226	17 693
No. independent reflections	1251	9823	5732
Observed reflections [$I > 2\sigma(I)$]	845	6321	5309
R_{int}	0	0.0583	0.0948
x, y	0.1262, 0	0.1364, 8.55	0.0944, 37.71
No. refined parameters	103	376	502
$R1,^a wR2^b$ [$I > 2\sigma(I)$]	0.057, 0.189	0.070, 0.185	0.087, 0.199
(all data)	0.084, 0.212	0.138, 0.249	0.097, 0.207
Goodness of fit on F^2	1.121	1.014	1.231
Residual electron density/e Å^{-3}	$+0.28, -0.36$	$+2.24, -1.98$	$+1.93, -3.11$

^{a} $R1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. Goodness of fit $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{observns} - N_{params})]^{\frac{1}{2}}$, based on all data.

Pd(O$_2$CMe)$_2$ (6 mg, 0.03 mmol) and PPh$_3$ (18 mg, 0.07 mmol) in NHPr$^i_2$ (20 cm^3). After the usual work-up, the residue was purified by column chromatography on silica using hexane–CH$_2$Cl$_2$ (4 : 1 v/v) to yield crude yellow product **IIIa**. Recrystallisation from hexane–CH$_2$Cl$_2$ led to bright yellow crystals of **IIIa** in 71% yield (0.75 g). IR (CH$_2$Cl$_2$): $\tilde{v}$/cm^{-1} 2142 (C≡C). ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.24 (s, 18 H, SiMe$_3$), 6.99 [d, 2 H, ^3J(H^{3}H^4) or ^3J(H$^{3''}$H$^{4''}$) = 3.9, H$^{3,3''}$], 7.05 (s, 2 H, H$^{3',4'}$) and 7.12 [d, 2 H, ^3J(H^{4}H^3) or ^3J(H$^{4''}$H$^{3''}$) = 3.9 Hz, H$^{4,4''}$]. ^{13}C-{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ −0.15 (SiMe$_3$), 97.28 (C≡C), 100.48 (C≡C), 122.18 (quaternary C, terthienyl), 123.43 (CH, terthienyl), 124.94 (CH, terthienyl), 133.56 (CH, terthienyl), 136.07 (quaternary C, terthienyl) and 138.25 (quaternary C, terthienyl). EI mass spectrum: m/z 440 (M^+). UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm 410 (Found: C, 59.82; H, 5.50. Calc. for C$_{22}$H$_{24}$S$_3$Si$_2$: C, 59.95; H, 5.49%).

5,5″-Diethynyl-2,2′ : 5′,2″-terthiophene IIIb. This compound was synthesized as described above for **IIb** from **IIIa** (0.50 g, 1.1 mmol) and K$_2$CO$_3$ (0.15 g, 1.1 mmol) in MeOH (50 cm^3). The residue dissolved in CH$_2$Cl$_2$ was applied to a silica column and the desired yellow band was collected with the aid of hexane–CH$_2$Cl$_2$ (7 : 3 v/v) to afford **IIIb** (0.25 g, 74%) as a brownish yellow crystalline solid. IR (CH$_2$Cl$_2$): $\tilde{v}$/cm^{-1} 2102 (C≡C) and 3300 (C≡CH). ^{1}H NMR (250 MHz, CDCl$_3$): δ 3.41 (s, 2 H, C≡CH), 7.01 [d, 2 H, ^3J(H^{3}H^4) or ^3J(H$^{3''}$H$^{4''}$) = 3.9, H$^{3,3''}$], 7.17 [d, 2 H, ^3J(H^{4}H^3) or ^3J(H$^{4''}$H$^{3''}$) = 3.9 Hz, H$^{4,4''}$] and 7.25 (s, 2 H, H$^{3',4'}$). ^{13}C-{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 76.78 (C≡C), 82.59 (C≡C), 121.00 (quaternary C, terthienyl), 123.44 (CH, terthienyl), 124.83 (CH, terthienyl), 134.03 (CH, terthienyl), 136.01 (quaternary C, terthienyl) and 138.54 (quaternary C, terthienyl). EI mass spectrum: m/z 296 (M^+). UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm 395 (Found: C, 64.94; H, 2.94. Calc. for C$_{16}$H$_8$S$_3$: C, 64.83; H, 2.72%).

Complex preparations

trans-[(Et$_3$P)$_2$PhPt−C≡CR′C≡C−PtPh(PEt$_3$)$_2$] **1a** (R′ = thiophenediyl). Treatment of the diterminal alkyne **Ib** (26 mg, 0.2

mmol, freshly prepared by the reaction of **Ia** with NBu$^n_4$F) with 2 equivalents of *trans*-[PtPh(Cl)(PEt$_3$)$_2$] (0.22 g, 0.4 mmol) for 15 h at room temperature, in the presence of CuI (3 mg), in CH$_2$Cl$_2$–NHPr$^i_2$ (50 cm^3, 1 : 1 v/v) gave the required complex as a light yellow solid in 65% yield (0.15 g) after purification on a silica column using hexane–CH$_2$Cl$_2$ (1 : 1) as eluent. IR (CH$_2$Cl$_2$): $\tilde{v}$/cm^{-1} 2083 (C≡C). ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.16 (m, 36 H, CH$_3$), 1.71 (m, 24 H, CH$_2$), 6.60 (s, 2 H, H^{3,4}), 6.78 (t, 2 H, H$_{para}$ of Ph), 6.94 (t, 4 H, H$_{meta}$ of Ph) and 7.31 (br, 4 H, H$_{ortho}$ of Ph). ^{31}P-{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ −131.10 [^1J(Pt−P) = 2677 Hz]. FAB mass spectrum: m/z 1146 (M^+). UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm 378 (Found: C, 45.71; H, 6.28. Calc. for C$_{44}$H$_{72}$P$_4$Pt$_2$S: C, 46.07; H, 6.33%).

trans-[(Bu$^n_3$P)$_2$PhPt−C≡CR′C≡C−PtPh(PBu$^n_3$)$_2$] **1b** (R′ = thiophenediyl). This complex was synthesized using the conditions described for **1a** but *trans*-[PtPh(Cl)(PBu$^n_3$)$_2$] (0.28 g, 0.4 mmol) was used instead of *trans*-[PtPh(Cl)(PEt$_3$)$_2$]. Yield: 0.22 g (74%). IR (CH$_2$Cl$_2$): $\tilde{v}$/cm^{-1} 2084 (C≡C). ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.97 (m, 36 H, CH$_3$), 1.30 (m, 24 H, CH$_2$), 1.41 (m, 24 H, CH$_2$), 1.66 (m, 24 H, CH$_2$), 6.57 (s, 2 H, H^{3,4}), 6.76 (t, 2 H, H$_{para}$ of Ph), 6.92 (t, 4 H, H$_{meta}$ of Ph) and 7.27 [dd, 4 H, ^3J(Pt−H) = 38 Hz, H$_{ortho}$ of Ph]. ^{31}P-{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ −139.28 [^1J(Pt−P) = 2659 Hz]. FAB mass spectrum: m/z 1484 (M^+). UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm 379 (Found: C, 55.58; H, 8.22. Calc. for C$_{68}$H$_{120}$P$_4$Pt$_2$S: C, 55.04; H, 8.15%).

trans-[(Et$_3$P)$_2$PhPt−C≡CR′C≡C−PtPh(PEt$_3$)$_2$] **2** (R′ = bithiophenediyl). To a mixture of compound **IIb** (15 mg, 0.07 mmol) and 2 equivalents of *trans*-[PtPh(Cl)(PEt$_3$)$_2$] (80 mg, 0.14 mmol) in CH$_2$Cl$_2$–NHPr$^i_2$ (30 cm^3, 1 : 1 v/v) was added CuI (2 mg). The solution was stirred at room temperature over 15 h, after which all volatile components were removed under reduced pressure. The product was purified on preparative TLC plates with hexane–CH$_2$Cl$_2$ (3 : 2 v/v) as eluent, giving compound **2** as a pale yellow solid in an isolated yield of 55% (47 mg). IR (CH$_2$Cl$_2$): $\tilde{v}$/cm^{-1} 2082 (C≡C). ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.08 (m, 36 H, CH$_3$), 1.72 (m, 24 H, CH$_2$), 6.70 [d, 2 H,

$^3J(H^3H^4)$ or $^3J(H^{3'}H^{4'})$ = 3.7, $H^{3,3'}$], 6.80 (t, 2 H, H_{para} of Ph), 6.84 [d, 2 H, $^3J(H^4H^3)$ or $^3J(H^{4'}H^{3'})$ = 3.7 Hz, $H^{4,4'}$], 6.96 (t, 4 H, H_{meta} of Ph) and 7.30 (br, 4 H, H_{ortho} of Ph). ^{31}P-$\{^1H\}$ NMR (101.3 MHz, CDCl$_3$): δ -131.10 [$^1J(Pt-P)$ = 2628 Hz]. FAB mass spectrum: m/z 1229 (M^+). UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm 406 (Found: C, 46.20; H, 6.09. Calc. for $C_{48}H_{74}P_4Pt_2S_2$: C, 46.90; H, 6.07%).

trans-[(Et$_3$P)$_2$PhPt−C≡CR′C≡C−PtPh(PEt$_3$)$_2$] 3 (R′ = terthiophenediyl). Similar procedures as for complex **2** were employed using **IIIb** (21 mg, 0.07 mmol) to produce bright yellow **3** in 52% yield (48 mg) after TLC purification and recrystallisation. IR (CH$_2$Cl$_2$): $\tilde{v}$/cm^{-1} 2081 (C≡C). ^1H NMR (250 MHz, CDCl$_3$): δ 1.09 (m, 36 H, CH$_3$), 1.73 (m, 24 H, CH$_2$), 6.73 [d, 2 H, $^3J(H^3H^4)$ or $^3J(H^{3''}H^{4''})$ = 3.7, $H^{3,3''}$], 6.82 (m, 2 H, H_{para} of Ph), 6.91 [d, 2 H, $^3J(H^4H^3)$ or $^3J(H^{4''}H^{3''})$ = 3.7 Hz, $H^{4,4''}$], 6.94 (s, 2 H, $H^{3',4'}$), 6.96 (t, 4 H, H_{meta} of Ph) and 7.30 (m, 4 H, H_{ortho} of Ph). ^{31}P-$\{^1H\}$ NMR (101.3 MHz, CDCl$_3$): δ -131.08 [$^1J(Pt-P)$ = 2629 Hz]. FAB mass spectrum: m/z 1311 (M^+). UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm 433 (Found: C, 47.83; H, 5.97. Calc. for $C_{52}H_{76}P_4Pt_2S_2$: C, 47.63; H, 5.84%).

Crystallography

Pale yellow to yellow crystals of compounds **IIa**, **1a** and **2** suitable for X-ray diffraction experiments were grown by slow evaporation of their respective solutions in hexane–CH$_2$Cl$_2$. Geometric and intensity data were collected using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) on the following diffractometers: MAR Research image plate scanner (**IIa**), Rigaku AFC7R (**1a**) and Rigaku R-Axis IIc image plate (**2**). All pertinent crystallographic data and other experimental details are summarised in Table 4. For **1a** data were collected using the ω–2θ scan technique with a scan rate of 16.00° min^{-1} (in ω). 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 **IIa** 65 × 3° frames with an exposure time of 5 min per frame were used. The intensity data were corrected for Lorentz-polarisation effects. Semi-empirical absorption corrections based upon ψ scans were applied (TEXSAN)[26] for **1a**, interframe scaling for **2**, however no absorption correction was made for **IIa**.

The structures were solved by direct methods (SHELXTL PLUS)[27] and subsequent Fourier-difference syntheses, and refined by full-matrix least squares on F^2 (SHELXL 93)[28] with anisotropic displacement parameters for the non-H atoms. The crystal structure of complex **1a** contains one and a half molecules in the asymmetric unit, the half molecule being related to its symmetry equivalent through a centre of symmetry which sits at the centre of the thiophene ring, and so the thiophene atom positions were refined in two sites with 50% occupancy. Hydrogen atoms were included using a riding model. In the final cycles of refinement, weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = (F_o^2 + 2F_c^2)/3$, was introduced which produced a flat analysis of variance. For **1a** and **2** some of the ethyl groups and the phenyl ring showed positional disorder, and these were refined with partial occupancies, summed to unity and constraints placed on some of the C−C distances.

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