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Synthesis and characterisation of new acetylide-functionalised aromatic and hetero-aromatic ligands and their dinuclear platinum complexes

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A new series of rigid rod protected and terminal dialkynes with extended π-conjugation through aromatic and hetero-aromatic linker units in the backbone, 2,5-bis(trimethylsilylethynyl)-1-(2-ethylhexyloxy)-4-methoxybenzene **1a**, 2,5-bis(ethynyl)-1-(2-ethylhexyloxy)-4-methoxybenzene **1b**, 5,8-bis(trimethylsilylethynyl)quinoline **2a**, 5,8-bis(ethynyl)quinoline **2b**, 2,3-diphenyl-5,8-bis(trimethylsilylethynyl)quinoxaline **3a**, 2,3-diphenyl-5,8-bis(ethynyl)quinoxaline **3b**, 4,7-bis(trimethysilylethynyl)-2,1,3-benzothiadiazole **4a** and 4,7-bis(ethynyl)-2,1,3-benzothiadiazole **4b**, has been synthesised. Treatment of the complex *trans*-[Pt(Ph)(Cl)(Et_3P)$_2$] with half an equivalent of the diterminal alkynes **1b**–**4b** in $^{i}Pr_2NH$–CH_2Cl_2, in the presence of CuI, at room temperature, afforded the platinum(II) di-yne complexes *trans*-[(Et_3P)$_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)(Et_3P)$_2$] [R = 1-(2-ethylhexyloxy)-4-methoxybenzene-2,5-diyl **1c**, quninoline-5,8-diyl **2c**, 2,3-diphenylquinoxaline-5,8-diyl **3c**, 2,1,3-benzothiadiazole-4,7-diyl **4c**] in good yields. The new acetylide-functionalised ligands and the platinum(II) σ-acetylide complexes have been characterised by analytical and spectroscopic methods and X-ray single crystal structure determinations for **2c**–**4c**. The absorption spectra of the complexes **2c**–**4c** show substantial donor–acceptor interaction between the platinum(II) centres and the conjugated ligands. The photoluminescence spectra of **1c**–**3c** show characteristic singlet (S_1) and triplet (T_1) emissions. Both the singlet and triplet emissions as well as the absorption decrease in energy with increasing electronegativity of the spacer groups along the series **1c**–**4c**.

Introduction

Conjugated polymers are presently regarded as promising materials for the development of optoelectronic devices such as light-emitting diodes, photovoltaic cells, sensors, and nonlinear optical systems.[1,2] Among the variety of conjugated polymers, rigid-rod organometallic poly-ynes of general formula *trans*-[(L)$_n$M–C≡C–R–C≡C–]$_x$ (M = Group 8 or 10 metals, L = phosphines, n = 4 or 2; R = phenyl, oligopyridyl, oligothienyl, fluorenyl, *etc*.) represent a particularly important class of new materials for basic and applied research, since the various acetylide-functionalised ligands can be easily synthesised and the alkynyl ligands can be readily incorporated into metal-containing polymers. The conjugation of the ligand continues through the metal centres along the polymer chain since there is mixing between the frontier orbitals of the metal and those of the ligand.[3,4] The inclusion of a heavy transition metal such as platinum in the polymer backbone introduces sufficient spin–orbit coupling to allow light emission from the triplet excited state of the conjugated ligand.[5–8] It is conceived that metal poly-ynes are good model systems to study the triplet excited state and provide important information on the photophysical processes that occur in conjugated organic polymers.[4,9,10]

For commercial exploitation of these new materials and for direct application-oriented synthesis, a thorough understanding of the structure–property relationship is necessary such that suitable modifications of the chemical structures may fine-tune the optoelectronic properties of the polymers. It has been demonstrated that the incorporation of electron-deficient or electron-rich spacer units into the polymer backbone provides an important tool for controlling opto-electronic properties in platinum(II) poly-ynes.[5,11–15] We recently investigated a series of platinum(II) poly-ynes where the spacer unit was systematically varied to give optical bandgaps from 1.7–3.0 eV.[7] With decreasing optical gap, the intensity and lifetime of the triplet state emission were seen to reduce in accordance with the energy gap law.[7] Herein we report the synthesis and characterisation of a series of new acetylide-functionalised ligands containing some of these aromatic and hetero-aromatic spacer units and their dinuclear platinum(II) σ-acetylide complexes. The dinuclear complexes can be considered as building blocks for the high molecular weight polymers and valuable information concerning their molecular and electronic properties can be obtained through the studies of these model compounds. Recently, attention has been directed toward linear π-conjugated dimers and oligomers, taken not only as model compounds, but also as efficient molecular wires in electronic applications.[16] There is also considerable interest in the solid-state structures of the polymeric materials because of evidence for inter-chain interactions that influence their optoelectronic properties. In this context an analysis of intermolecular interactions in the crystal structures of model complexes may lead to a better understanding of the interactions in the polymers.[17] The crystal structures of three model complexes are described in this paper, and the electronic properties of the new materials are presented and compared with related organometallic complexes.

Results and discussion

Syntheses

The trimethylsilyl-protected alkynyl ligand precursors **1a**–**4a** were synthesised by a Pd(II)/CuI catalysed cross-coupling reaction of the dibromo/diiodo-substituted arene/hetero-arenes

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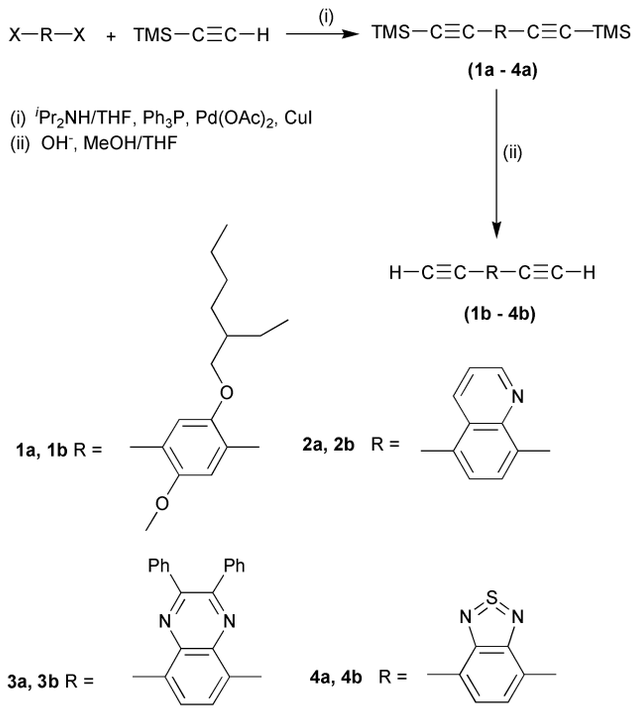


Scheme 1

with trimethysilylethyne[18] (Scheme 1). These ligands were isolated as off-white to yellow solids in yields of 75–90%. The protected diynes are indefinitely stable in air and towards light and were fully characterised by IR, NMR (^{1}H and ^{13}C) spectroscopy, EI mass spectrometry as well as by satisfactory elemental analyses.

Conversion of the protected ligand precursors **1a**–**4a** into their terminal H derivatives HC≡C–R–C≡CH **1b**–**4b** was accomplished by smooth removal of the trimethylsilyl protecting groups with dilute aqueous KOH in MeOH–THF (Scheme 1). The products were purified by silica column chromatography and characterised by elemental analyses and by IR, NMR (^{1}H and ^{13}C) spectroscopy and mass spectrometry. The diterminal alkynes **2b**–**4b** are indefinitely stable in air and under light and could be stored at room temperature while **1b** is somewhat unstable; long storage times at ambient temperature and under aerobic conditions led to the formation of a black tar that was presumed to be a polymerisation product.

The reaction of each of the diynes with two equivalents of the platinum complex *trans*-[Pt(Ph)(PEt$_3$)$_2$Cl], in ^{i}Pr$_2$NH–CH$_2$Cl$_2$, in the presence of CuI, at room temperature, readily affords the dinuclear complexes *trans*-[(Et$_3$P)$_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)(Et$_3$P)$_2$] **1c**–**4c** in good yields (Scheme 2). Purification of the complexes was achieved by preparative TLC as well as by silica column chromatography. The formulae of the complexes were established by positive FAB mass spectrometry and IR, NMR (^{1}H, ^{13}C and ^{31}P) spectroscopy, and they all gave satisfactory analytical data.

All the organic ligands and the platinum complexes exhibit good solubility in common organic solvents.

Spectroscopic properties

The IR spectra of the platinum σ-acetylide complexes exhibit a single strong $\nu_{C\equiv C}$ absorption at around 2095 cm^{-1} consistent with a *trans*-configuration of the acetylenic units around the Pt(II) centre. As expected, the $\nu_{C\equiv C}$ values of the complexes are lower than those of the corresponding terminal or trimethylsilyl-substituted acetylides. This may be attributed to either metal-yne π-backbonding or the $M^{\delta+}$–$C^{\delta-}$ polarity.[19] Furthermore, the $\nu_{C\equiv C}$ values of the terminal acetylenes **1b**–**4b** (2107 cm^{-1}) are much lower than those of the trimethylsilyl-substituted diynes **1a**–**4a** (2159 cm^{-1}). The fact that terminal ethynes (HC≡C–R) have lower $\nu_{C\equiv C}$ frequencies than their protected counterparts RC≡C–R (by 52 cm^{-1} in this case) is well established.[20] The ^{1}H and ^{13}C NMR spectra of all the compounds exhibit the expected signals for the systems including resonances for the acetylenic carbons. The ^{31}P-{^{1}H} NMR spectral data of all the platinum σ-acetylide complexes confirm that the phosphines are mutually *trans* at the platinum(II) giving a square planar geometry. The mass spectrometric results confirm the molecular assignments for the organic ligands and the dinuclear platinum complexes.

The absorption spectra of acetylenes **1b**–**4b**, measured in solution are compared to the absorption spectra of films of the corresponding dinuclear platinum complexes **1c**–**4c** in Fig. 1.

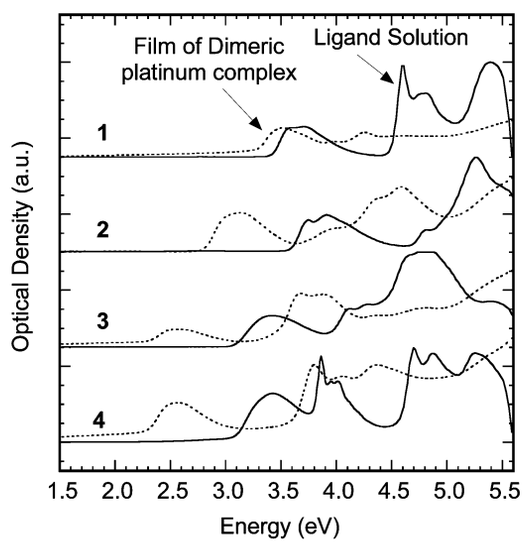
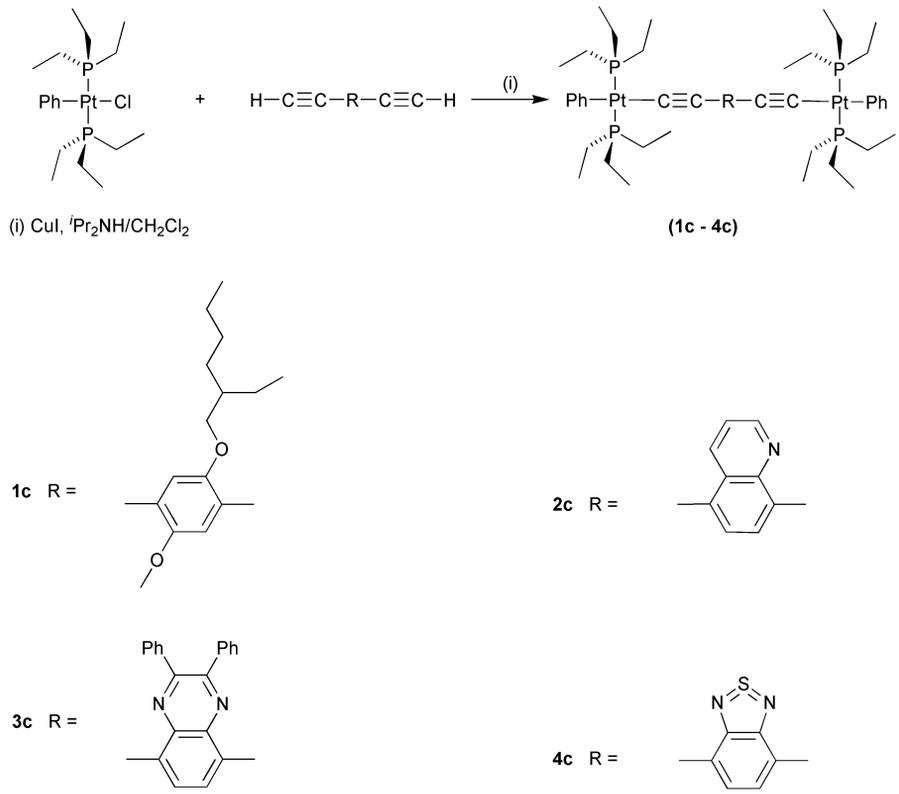


Fig. 1 Comparison of the absorption spectra of films of the dinuclear platinum(II) complexes **1c**–**4c** (dotted lines), and solutions of the corresponding ligands **1b**–**4b** (solid lines) in dichloromethane. The spectra have been displaced on the vertical axis for clarity.

Overall, the optical densities of the ligands and of the metal complexes are comparable across the series. The spectral shape of the first absorption band is similar for the ligands and the dinuclear platinum(II) complexes, suggesting that in the complexes this band is mainly due to the π–π* transition on the ligand, possibly with some admixture of metal d orbitals which may alter the overall energy of the transition.[6] In fact, there is only a small shift of 0.15 eV between the onset of absorption in the ligand and the platinum complex for **1c**, but a large shift of 0.8 eV for complexes **2c**–**4c**. While it is possible to attribute the small shift in complex **1c** to the difference between measurements made for solutions and films, the large shift observed for the other complexes indicates a substantial donor–acceptor interaction between the platinum(II) centres and the conjugated ligand.[5]

The photoluminescence (PL) spectra of the dimeric platinum complexes **1c**–**4c**, measured at room temperature and 10 K, are shown in Fig. 2 along with their absorption spectra. All of the spectra (with the exception of that of **4c**) show two characteristic emissions. The higher energy emission is due to the same singlet excited state as the first band in the absorption spectra, and is denoted by S_1. The lower energy band is attributed to that of a triplet excited state T_1 for the following reasons. The triplet state emission of a similar platinum(II) complex has been well characterised previously[4] by lifetime and photoinduced absorption measurements, and the lower energy emissions from complexes **1c**–**4c** have similar lifetimes, temperature dependencies and energies to this complex. In addition, the emissions do not change in dilute solutions, and show vibronic structure that excludes an excimer origin.

Both the singlet and triplet emissions can be seen to decrease in energy, along with the absorption, as the electronegativity of



Scheme 2

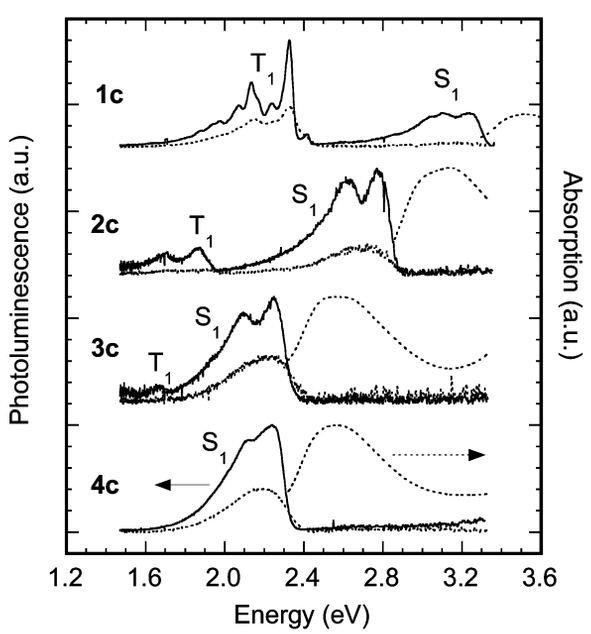


Fig. 2 The photoluminescence and absorption spectra of the dinuclear platinum(II) complexes **1c**–**4c** taken with UV excitation. The first bands of the absorption spectra are the higher energy dotted lines. Measurements of photoluminescence at 10 (solid lines) and 290 K (dotted lies) are compared. All of the photoluminescence spectra give the correct relative intensities for 10 and 290 K. Spectra have been displaced on the vertical axis for clarity.

the spacer group is increased along the series **1c**–**4c**. The decreasing intensity of emission from the T_1 state along the series has been explained in terms of the energy gap law for non-radiative decay, whereby the non-radiative decay rate increases exponentially with decreasing T_1–S_0 energy.[9]

Crystal structure determinations

In order to investigate the structure–property relationship in these systems the crystal structures of three of the diplatinum complexes, *trans*-[$(Et_3P)_2$PhPt–C≡CRC≡C–PtPh$(PEt_3)_2$] (R = quinoline-5,8-diyl **2c**; 2,3-diphenylquinoxaline-5,8-diyl **3c**; 2,1,3-benzothiadiazole-4,7-diyl **4c**), have been determined by single-crystal X-ray diffraction. Two key features that can be obtained from the structures of these complexes are a confirmation of the linearity of the whole species, a linearity that should be retained in polymers prepared from these precursors, and the relative orientations of the square planar ligand sets around the platinum(II) centres and those of the aromatic spacer groups. Significant twisting between these planes may reduce the π-overlap between these units and thus limit the magnitude of the delocalisation along the chain length, although these groups are separated by the almost cylindrical set of orbitals on the linking acetylene units.

The molecular structure of **2c** is shown in Fig. 3 while selected bond parameters are listed in Table 1. The molecular structure is closely related to those reported for the diplatinum thiophenediyl and bithiophenediyl complexes, *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–$(C_4H_2S)_n$–C≡C–Pt$(PEt_3)_2$(Ph)] (n = 1, 2),[13] and to the diplatinum 2,2′-bipyridine-6,6′-diyl complex, *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–$(C_5H_3N)_2$–C≡C–Pt$(PEt_3)_2$(Ph)],[14] with the *trans*-

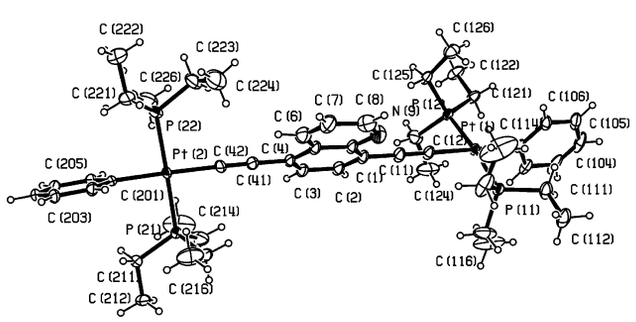


Fig. 3 The molecular structure of *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] **2c** (R = quinoline-5,8-diyl) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and the C(6) and N(9) sites are disordered with each atom type occupying each site in 50% of the molecules. A half molecule of dichloromethane present in the crystal lattice is not shown.

Table 1 Selected bond lengths (Å) and angles (°) for *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] **2c** (R = quinoline-5,8-diyl)

Pt(1)–P(11)	2.2868(12)	Pt(2)–P(21)	2.2936(12)
Pt(1)–P(12)	2.2856(12)	Pt(2)–P(22)	2.2965(14)
Pt(1)–C(12)	2.007(5)	Pt(2)–C(42)	2.019(5)
Pt(1)–C(101)	2.061(4)	Pt(2)–C(201)	2.061(4)
C(11)–C(12)	1.213(7)	C(41)–C(42)	1.209(7)
C(1)–C(11)	1.435(7)	C(4)–C(41)	1.437(6)
C(1)–C(2)	1.374(9)	C(3)–C(4)	1.383(8)
C(1)–C(10)	1.430(9)	C(4)–C(5)	1.422(8)
C(2)–C(3)	1.421(7)	C(5)–C(10)	1.417(6)
P(12)–Pt(1)–P(11)	174.83(5)	P(22)–Pt(2)–P(21)	175.86(6)
C(12)–Pt(1)–P(11)	90.18(14)	C(42)–Pt(2)–P(21)	87.41(14)
C(101)–Pt(1)–P(11)	91.66(13)	C(201)–Pt(2)–P(21)	91.03(12)
C(12)–Pt(1)–P(12)	86.53(14)	C(42)–Pt(2)–P(22)	87.41(14)
C(101)–Pt(1)–P(12)	91.52(13)	C(201)–Pt(2)–P(22)	87.76(12)
C(12)–Pt(1)–C(101)	177.5(2)	C(42)–Pt(2)–C(201)	178.22(18)
Pt(1)–C(12)–C(11)	175.4(5)	Pt(2)–C(42)–C(41)	178.0(5)
C(12)–C(11)–C(1)	175.3(7)	C(42)–C(41)–C(4)	176.8(6)

arrangement of the two '$Pt(PEt_3)_2$' groups separated by the aromatic spacer group. The coordination geometry about Pt(1) and Pt(2) is square planar with *cis*-L–Pt–L angles in the range 86.53(14)–91.66(13)°. As with the related diplatinum complexes the two terminal phenyl rings are essentially perpendicular to the planes of the two square planar platinum(II) centres; the dihedral angle between the ring C(101)–C(106) and the plane defined by Pt(1), P(11), P(12), C(101), C(12) is 86.55° and that between the ring C(201)–C(206) and Pt(2), P(21), P(22), C(201), C(42) is 89.04°. The central quinoline group is effectively planar, with a dihedral angle of only 2.16° between the two six-membered rings. The two alkynyl groups are linear with average C–C≡C angles of 176.05° and average Pt–C≡C angles of 176.7° confirming that the whole molecule is linear. These angular values are within the range of 176(2)–179(2)° found for the equivalent angles in *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–$(C_4H_2S)_n$–C≡C–Pt$(PEt_3)_2$(Ph)] (n = 1, 2).[13] What is of significance are the dihedral angles between the quinoline group and the two square planar platinum centres, the angle between the C(1), C(2), C(3), C(4), C(5), C(10) ring and the Pt(1) coordination plane [Pt(1), P(11), P(12), C(101), C(12)] is 60.47° and that between the same central ring and the Pt(2) coordination plane [Pt(2), P(21), P(22), C(201), C(42)] is 63.83°. The dihedral angle between the two platinum coordination planes is 56.90°. These values compare to dihedral angles of 42.86 and 67.60° between the central thiophene ring and the two platinum(II) square planes in *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–(C_4H_2S)–C≡C–Pt$(PEt_3)_2$(Ph)],[13] and values of 64.40 and 72.42° between the two platinum(II) square planes and the adjacent pyridine rings of the bipyridyl group in *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–$(C_5H_3N)_2$–C≡C–Pt$(PEt_3)_2$(Ph)].[14]

In **2c** the average Pt–P distance of 2.291 Å is similar to the average values of the Pt–P distances of 2.290, 2.303 and 2.289 Å in *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–(C_4H_2S)–C≡C–Pt$(PEt_3)_2$(Ph)], *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–$(C_4H_2S)_2$–C≡C–Pt$(PEt_3)_2$(Ph)][13] and *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–$(C_5H_3N)_2$–C≡C–Pt$(PEt_3)_2$(Ph)],[14] respectively. Also, as with the related thiophene and bipyridine complexes the Pt–C(alkynyl) distance, average 2.013 Å, is significantly shorter than the Pt–C(arene) distance, average 2.061 Å, consistent with the difference in formal hybridisation at the carbon centre. The C≡C bond distances, average 1.211 Å, are also within the expected range. Within the central quinoline group the position of the nitrogen is disordered over two sites, N(9) and C(6), and N(6) and C(9). Each atom type was refined with an occupancy ratio of 68 : 32 on each of the two sites, with the atomic positions of each of the two pairs tied together. The hydrogen atom associated with the carbon was also refined with the 68 : 32 occupancy ratio on each site. The bond parameters within the quinoline group did not deviate significantly from expected values, with some evidence of bond length alternation around the arene ring; the alternate C–C distances can be split into two groups with average distances of 1.391 and 1.424 Å.

In the crystal, molecules of **2c** co-crystallise with dichloromethane solvent molecules, with 0.42 of a CH_2Cl_2 molecule per asymmetric unit. This dichloromethane was involved in C–H ··· Cl hydrogen bond interactions with a C(2)–H(2) ··· Cl(6) distance of 2.83 Å (H ··· Cl) and an angle of 126.1° (with the Cl atom in the same asymmetric unit), and C(226)–H(226) ··· Cl(6) distance of 2.82 Å (H ··· Cl) and angle of 142.0° (with the Cl atom related by the symmetry operation $-x + 2$, $-y$, $-z + 1$). There is also evidence of a C–H ··· N interaction involving the quinoline nitrogen atom and an aromatic C–H unit on an adjacent molecule. The H(7) ··· N(6) distance is 2.65 Å, and the C(7)–H(7) ··· N(6) angle is 126.2°, where N(6) is related by the symmetry operation $-x + 2$, $-y + 1$, $-z + 1$. There is no evidence of graphitic packing between aromatic rings. This type of interaction may be prevented by the presence of the PEt_3 groups.

The molecular structure of *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] (R = 2,3-diphenylquinoxaline-5,8-diyl) **3c** is illustrated in Fig. 4, and selected bond parameters are listed in

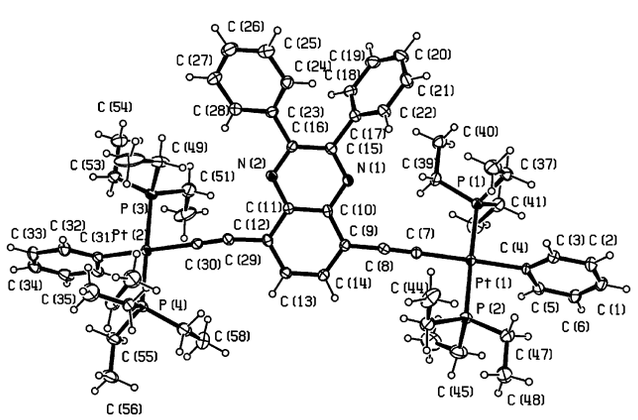


Fig. 4 The molecular structure of *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] **3c** (R = 2,3-diphenylquinoxaline-5,8-diyl) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 2. As with **2c** the coordination geometry around the two independent platinum(II) centres is square planar, with *cis*-L–Pt–L angles in the range 86.36(16)–91.57(16)°. The geometry along the backbone is again linear with average Pt–C≡C and C≡C–C angles of 174.5 and 173.6°, respectively. The two terminal arene rings make dihedral angles of 81.47° [for C(1)–C(6) and Pt(1)] and 88.41° [for C(31)–C(36) and Pt(2)] with the two platinum square planes. The quinoxaline group is essentially planar, with a dihedral angle of only 5.79° between the C(9)–C(14) and the N(1)–C(15) rings. The two substituent arene rings make angles of 59.95° [C(17)–C(22)] and 27.42° [C(23)–

Table 2 Selected bond lengths (Å) and angles (°) for *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] **3c** (R = 2,3-diphenylquinoxaline-5,8-diyl)

Pt(1)–P(1)	2.2873(15)	Pt(2)–P(3)	2.2874(15)
Pt(1)–P(2)	2.2902(15)	Pt(2)–P(4)	2.2899(15)
Pt(1)–C(7)	2.018(5)	Pt(2)–C(30)	2.019(5)
Pt(1)–C(4)	2.075(5)	Pt(2)–C(31)	2.060(5)
C(7)–C(8)	1.202(7)	C(29)–C(30)	1.194(7)
C(8)–C(9)	1.443(7)	C(12)–C(29)	1.453(7)
C(9)–C(14)	1.372(7)	C(12)–C(13)	1.387(8)
C(9)–C(10)	1.425(8)	C(12)–C(11)	1.436(7)
C(13)–C(14)	1.402(7)	C(10)–C(11)	1.435(7)
P(1)–Pt(1)–P(2)	178.46(5)	P(3)–Pt(2)–P(4)	175.01(6)
C(7)–Pt(1)–P(1)	90.62(16)	C(30)–Pt(2)–P(3)	86.36(16)
C(4)–Pt(1)–P(1)	89.38(15)	C(31)–Pt(2)–P(3)	91.41(16)
C(7)–Pt(1)–P(2)	90.63(16)	C(30)–Pt(2)–P(4)	91.57(15)
C(4)–Pt(1)–P(2)	89.41(15)	C(31)–Pt(2)–P(4)	91.08(16)
C(4)–Pt(1)–C(7)	177.2(2)	C(30)–Pt(2)–C(31)	174.0(3)
Pt(1)–C(7)–C(8)	176.0(5)	Pt(2)–C(30)–C(29)	172.6(5)
C(7)–C(8)–C(9)	177.7(6)	C(30)–C(29)–C(12)	169.3(6)

C(28)] with the N(1)–C(15) ring, and an angle of 64.74° with each other. Again, the most significant feature of the structure are the dihedral angles between the central C(9)–C(14) ring and the two platinum square planes, that are 32.51° [with Pt(1), P(1), P(2), C(4), C(7)] and 36.82° [with Pt(2), P(3), P(4), C(30), C(31)]. These values are *ca.* 30° lower than the dihedral angles observed in **2c**, and *ca.* 10° lower than the lower value of 42.86° observed for *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–(C_4H_2S)–C≡C–Pt$(PEt_3)_2$(Ph)].[13] Also, the dihedral angle between the two platinum square planes is only 25.34°, showing that the whole of the central unit, between the two platinum atoms, is significantly closer to planarity than in any of the other reported structures.

The average Pt–P, Pt–C(alkynyl) and Pt–C(arene) distances in **3c** at 2.289, 2.018 and 2.068 Å, respectively, are similar to those observed in **2c**. The average C≡C bond length of 1.198 Å is also within the expected range. Within the quinoxaline ligand the bond parameters adhere to the expected values and, although not statistically significant, the bond length alternation observed in the quinoline ring of **2c** is also observed here. Within the C(9)–C(14) ring the alternate C–C bond lengths can be separated into two groups with averages of 1.421 and 1.398 Å. In the N(1)–C(15) ring the two groups have average values of 1.385 and 1.362 Å.

Within the crystal structure of **3c** there is no significant hydrogen bonding, but one of the substituent phenyl rings, C(23)–C(28), on the quinoxaline ligand is involved in π–π stacking with a parallel, equivalent ring related by the symmetry operation $-x$, $-y$, $1 - z$. The ring centroid–ring centroid distance is 4.074 Å. It is this ring that has the smaller dihedral angle with the N(1)–C(15) ring. The other phenyl substituent, C(17)–C(22), does not show any stacking interactions.

The molecular structure of *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] (R = 2,1,3-benzothiadiazole-4,7-diyl) **4c** is illustrated in Fig. 5, and selected bond parameters are listed in Table 3. Again, the structural diagram confirms the linear nature of the molecular backbone, with average Pt–C≡C and C≡C–C angles of 174.7 and 175.9°, respectively, and the square planar geometry at each of the two platinum(II) centres, with *cis*-L–Pt–L angles in the range 87.7(3)–93.0(3)°. In this structure the two terminal arene rings make dihedral angles of 84.02 and 86.63° with adjacent platinum square planes, these values lying within the range observed for **2c** and **3c**, 81.47–89.04°. The benzothiadiazole ligand is, as expected, planar, with a dihedral angle of only 1.78° between the six- and five-membered rings. The dihedral angles between the central arene ring, C(9)–C(14), and the two platinum square planes are much closer in value to those observed for **2c** than for **3c**, with angles of 60.26° [with the Pt(1) plane] and 69.18° [with the Pt(2) plane]. The dihedral angle between the two platinum square planes is only 23.36°, however.

Table 3 Selected bond lengths (Å) and angles (°) for *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] **4c** (R = 2,1,3-benzothiadiazole-4,7-diyl)

Pt(1)–P(1)	2.286(2)	Pt(2)–P(3)	2.293(3)
Pt(1)–P(2)	2.293(2)	Pt(2)–P(4)	2.292(3)
Pt(1)–C(7)	2.021(8)	Pt(2)–C(16)	2.015(10)
Pt(1)–C(6)	2.077(8)	Pt(2)–C(17)	2.074(9)
C(7)–C(8)	1.207(11)	C(15)–C(16)	1.208(12)
C(8)–C(9)	1.414(12)	C(14)–C(15)	1.414(12)
C(9)–C(10)	1.380(12)	C(12)–C(14)	1.385(13)
C(9)–C(11)	1.431(12)	C(13)–C(14)	1.435(12)
C(10)–C(12)	1.432(13)	C(11)–C(13)	1.458(12)
N(1)–C(11)	1.333(11)	N(2)–C(13)	1.330(11)
N(1)–S(1)	1.608(8)	N(2)–S(1)	1.615(8)
P(1)–Pt(1)–P(2)	178.34(4)	P(3)–Pt(2)–P(4)	177.28(12)
C(7)–Pt(1)–P(1)	93.0(2)	C(16)–Pt(2)–P(3)	88.0(3)
C(6)–Pt(1)–P(1)	88.2(2)	C(17)–Pt(2)–P(3)	92.4(3)
C(7)–Pt(1)–P(2)	88.1(2)	C(16)–Pt(2)–P(4)	89.3(3)
C(6)–Pt(1)–P(2)	90.6(2)	C(17)–Pt(2)–P(4)	90.3(3)
C(6)–Pt(1)–C(7)	175.9(3)	C(16)–Pt(2)–C(17)	178.7(4)
Pt(1)–C(7)–C(8)	175.0(8)	Pt(2)–C(16)–C(15)	174.0(9)
C(7)–C(8)–C(9)	174.5(10)	C(16)–C(15)–C(14)	177.5(11)

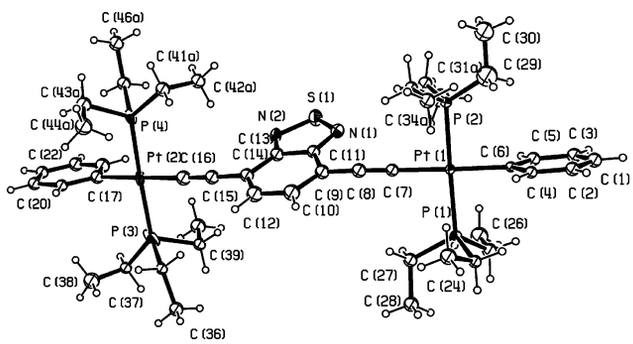


Fig. 5 The molecular structure of *trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] **4c** (R = 2,1,3-benzothiadiazole-4,7-diyl) showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The ethyl groups on the four phosphine ligands exhibited considerable positional disorder, only one orientation of these groups is shown for clarity.

The average Pt–P, Pt–C(alkynyl) and Pt–C(arene) distances in **4c** at 2.292, 2.018 and 2.075 Å, respectively, are similar to those observed in **2c** and **3c**, and the average C≡C bond length of 1.209 Å is also not significantly different. In the benzothiadiazole ligand the bond length alternation observed in the six-membered arene rings in **2c** and **3c** is broken by the relatively long C(11)–C(13) bond, of 1.460(13) Å, that acts as the hinge between the five- and six-membered rings. Otherwise, adjacent C–C bonds within this ring show the same 'longer' and 'shorter' distribution as in **2c** and **3c**, with averages of 1.434 and 1.375 Å. Within the five-membered heterocyclic ring the C–N and N–S bond length are close to the idealised values.

Within the crystal lattice of **4c** the benzothiadiazole ligand is involved in a hydrogen bonding network with only the ethyl protons on the phosphine ligands. The atoms N(1), N(2) and S(1) all act as hydrogen bond acceptors. There is a S(1) ··· H(38a)–C(38) interaction with an S ··· H distance of 2.960 Å, and a S ··· H–C angle of 147.22°, with the H–C group related by the symmetry operator $x + 1$, $-y + 0.5$, $z - 0.5$. N(1) is involved in two interactions: C(30)–H(30b) ··· N(1), 2.930 Å and 117.05°, N(1) related by $x - 1$, y, z and C(40)–H(40a), 2.968 Å and 118.62°, N(1) related by $x + 1$, y, z. In contrast, N(2) is only involved in one interaction: C(36a)–H(36f) ··· N(2), 2.939 Å and 104.58°, N(2) is related by x, $-y + 0.5$, $z - 0.5$.

A potentially interesting feature in the three structures, **2c**, **3c** and **4c**, is the change in dihedral angle between the central six-membered ring and the two platinum square planes. The data is summarised in Table 4, and shows the average dihedral angle

Table 4 Selected dihedral angles (°) for **2c**, **3c** and **4c**

	2c	3c	4c
Central ring/Pt(1) plane	60.47	32.51	60.26
Central ring/Pt(2) plane	63.83	36.82	69.18
Pt(1)/Pt(2) planes	56.90	25.34	23.36
Average central ring/Pt plane	62.15	34.67	64.72
Average angle − 45°	17.15	−10.34	19.72

and the deviation from 45°. The reason for comparing the angular value to 45° is that this is the angle where minimum orbital overlap between the π orbitals on the aromatic ring and the platinum d orbitals (*via* the the acetylenic pπ orbitals) is to be expected. At angles closer to 0 or 90° one or other set of the π-orbitals on the metal alkynyl unit will be available for overlap. In **3c** the dihedral angle is *ca*. 10° below this value, and for **2c** and **4c** the angle is *ca*. 18° above. Since, from the spectroscopic data *vide supra* the shift in the emission spectra follows the electronegativity of the central group, and the value for **3c** lies between those for **2c** and **4c**, there is no correlation between the electronic properties of the spacer group that this dihedral twist of the central ligand to the platinum square planes. This is not surprising because of the almost cylindrical nature of the sets of p orbitals on the intervening acetylene linkers. These orbitals are available for bonding to both groups, almost independent of angle, and negate the importance of orientational differences between the planar groups. The difference in the dihedral angles between **3c** and **2c** and **4c** may, perhaps, be a result of packing effects in the solid state. In **3c** the substituted central quinoxaline ligand is oriented to favour π–π stacking, while in **2c** and **4c** the rings are involved in weak hydrogen bonding.

Conclusion

Four series of diplatinum diyne complexes and their organic ligand precursors containing the central ligand spacer groups, 1-(2-ethylhexyloxy)-4-methoxybenzene **1**, quinoline **2**, quinoxaline **3** and benzothiadiazole **4** have been prepared. The new compounds have been characterised spectroscopically, and the crystal structures of three of the diplatinum complexes, **2c**, **3c** and **4c** have been determined. The structures confirm the linear nature of the molecular backbone, and establish that there is a variation in dihedral angle between the platinum(II) square planes and the central aromatic rings of up to 30° depending on the nature of the central ring system. The absorption spectra of the complexes **2c**–**4c** show substantial donor–acceptor interaction between the platinum and the conjugated ligands. The photoluminescence spectra of **1c**–**3c** show characteristic singlet (S_1) and triplet (T_1) emissions. Both the singlet and triplet emissions as well as the absorption decrease in energy with increasing electronegativity of the spacer groups along the series **1c**–**4c**.

Experimental

General

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk or glove box techniques. Solvents were pre-dried and distilled before use by standard procedures.[21] All chemicals, except where stated otherwise, were obtained from Sigma Aldrich and used as received. The compounds 1-(2-ethylhexyloxy)-4-methoxybenzene,[22] 5,8-diiodoquinoline,[23] 2,3-diphenyl-5,8-diiodoquinoxaline,[24] 4,7-dibromo-2,1,3-benzothiadiazole[25] and *trans*-[(Ph)$(PEt_3)_2$PtCl][26] were prepared *via* literature procedures.

The NMR spectra were recorded on a Bruker WM-250 or AM-400 spectrometer in $CDCl_3$. The ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to solvent resonances and ^{31}P{^{1}H} NMR spectra were referenced to external trimethylphosphite. Infrared spectra were recorded as CH_2Cl_2 solutions, in a NaCl cell, on a Perkin-Elmer 1710 FT-IR spectrometer, mass spectra on a Kratos MS 890 spectrometer by the electron impact (EI) and fast atom bombardment (FAB) techniques. Microanalyses were performed in the University Chemical Laboratory, University of Cambridge. Preparative TLC was carried out on commercial Merck plates with a 0.25 mm layer of silica. Column chromatography was performed on Kieselgel 60 (230–400 mesh) silica gel. Thin films of the ligands and dimeric platinum complexes were produced on quartz substrates using a conventional photoresist spin-coater. Films were typically 100–150 nm in thickness as measured on a Dektak profilometer. The optical absorption was measured with a Hewlett-Packard ultraviolet-visible (UV-VIS) spectrometer. Measurements of photoluminescence (PL) were made with the sample in a continuous-flow helium cryostat. The temperature was controlled with an Oxford-Intelligent temperature controller-4 (ITC-4) and a calibrated silicon diode adjacent to the sample. For PL measurements, excitation was provided by the UV lines (334–365 nm) of a continuous wave (cw) argon ion laser. Typical intensities used were a few mW mm^{-2}. The emission spectra were recorded using a spectrograph with an optical fibre input coupled to a cooled charge coupled device (CCD) array (Oriel Instaspec IV).

X-Ray crystallography

Data for compounds **2c**–**4c** were collected on an Enraf Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream crystal cooling apparatus. Semi-empirical absorption corrections based on interframe scaling were applied. The structures were solved by heavy atom methods and subsequent Fourier difference syntheses (SHELX 86)[27] and refined by full-matrix least-squares on F^2 (SHELXL 97).[28] Hydrogen atoms were placed in geometrically-idealised positions and refined using a riding model. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance. In the structure of **2c** 0.42 of a dichloromethane molecule crystallised in the asymmetric. This molecule was refined without positional disorder but with an occupancy 0.42. Within the quinoline group, the nitrogen was disordered with a carbon over the sites C(6)/N(6) and N(9)/C(9); the SHELXL commands EXYZ and EADP were used to simultaneously refine the two atom types on each of the two sites, with refined occupancies of 0.68 and 0.32%, respectively. In all three structures the ethyl groups display relatively large displacement parameters consistent with positional disorder. Where appropriate this disorder has been modelled by splitting the atom position into two sites and refining the pairs of sites so that the total occupancy was fixed at unity. Crystal data and refinement details are summarised in Table 5.

CCDC reference numbers 192672–192674.

See http://www.rsc.org/suppdata/dt/b2/b208494e/ for crystallographic data in CIF or other electronic format.

Ligand syntheses

All the ligand precursors were synthesised by following a general procedure outlined below for **1a** and **1b**.

2,5-Diiodo-1-(2-ethylhexyl)oxy-4-methoxybenzene 1

Method A. ICl (4.46 g, 27.5 mmol) in acetic acid (10 cm^3) was added to 1-(2-ethylhexyloxy)-4-methoxybenzene (2.95 g, 12.5 mmol) in acetic acid (15 cm^3). The reaction mixture was heated with stirring at 100 °C for 2 h and then cooled to room temperature. Aqueous $Na_2S_2O_4$ (20%) was added until the brown colour of iodine had disappeared, and the reaction mixture was poured into ice water (100 cm^3). The organic layer was collected and the aqueous layer was extracted with hexane (3 × 100 cm^3). The combined organic layers were dried over $MgSO_4$, and the

Table 5 Crystallographic data for compounds **2c**, **3c** and **4c**

Compound	**2c**	**3c**	**4c**
Molecular formula	$C_{49.5}H_{76}ClNP_4Pt_2$	$C_{60}H_{82}N_2P_4Pt_2$	$C_{46}H_{72}N_2P_4Pt_2S$
M	1234.62	1345.34	1199.18
Crystal system	Triclinic	Monoclinic	Monoclinic
a/Å	9.1794(1)	9.3306(1)	9.2450(1)
b/Å	16.7290(2)	35.3016(4)	38.0140(4)
c/Å	18.8959(2)	18.0831(2)	14.6550(2)
α/°	112.396(1)	90	90
β/°	95.200(1)	95.793(1)	105.065(10)
γ/°	94.282(1)	90	90
U/Å^3	2652.93(5)	5925.88(11)	4973.33(10)
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$	$P2_1/c$
Z	2	4	4
D_c/Mg m^{-3}	1.546	1.508	1.602
μ/mm^{-1}	5.470	4.861	5.822
Data collection range/°	$3.53 < \theta < 30.05$	$2.93 < \theta < 27.46$	$3.52 < \theta < 27.49$
Reflections measured	54771	30974	28015
Independent reflections	15461 ($R_{int} = 0.048$)	12537 ($R_{int} = 0.059$)	10244 ($R_{int} = 0.070$)
Parameters, restraints	534, 0	611, 0	612, 0
$wR2$ (all data) [b]	0.1013	0.0893	0.1277
$R1$ [$I > 2\sigma(I)$)] [b]	0.0387	0.0451	0.0538

[a] Data in common: graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 150(2)$ K. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^2$.

solvent was removed *in vacuo* to give a brown oil. After column chromatography (silica gel, hexane) the pure product was obtained as a thick yellow liquid (5.18 g, 85%).

Method B. 1-(2-Ethylhexyloxy)-4-methoxybenzene (2.95 g, 12.5 mmol), KIO_4 (3.45 g, 15 mmol) and iodine (3.8 g, 15 mmol) were added to a stirred solution of acetic acid (22.5 cm^3), water (1.75 cm^3) and H_2SO_4 (0.75 cm^3). The resulting solution was stirred for 20 h at 70 °C and then cooled to room temperature. The product was worked up as in method A to obtain a yellow liquid (5.49 g, 90%) identified as **1**.

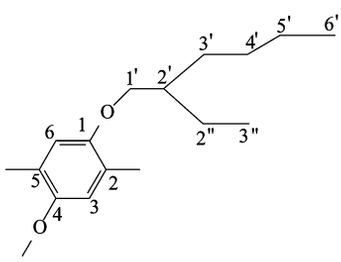


Chart 1 Numbering scheme for 1-(2-ethylhexyloxy)-4-methoxybenzene.

^{1}H NMR (250 MHz, $CDCl_3$, see Chart 1 for atom numbering scheme): δ 7.15 (1H, s, H_6), 7.14 (1H, s, H_3), 3.85 (2H, d, J = 3.08 Hz, $H_{1'}$), 3.80 (3H, s, O–CH_3), 1.72 (1H, m, $H_{2'}$), 1.50 (4H, m, $H_{5',2''}$), 1.31 (4H, m, $H_{3',4'}$), 0.87 (6H, t, $H_{6',3''}$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 153.12 ($C_{1,4}$), 122.44 (C_6), 121.56 (C_3), 86.12 (C_2), 85.41 (C_5), 72.36 ($C_{1'}$), 57.10 (O–CH_3), 39.46 ($C_{2'}$), 30.51 ($C_{3'}$), 29.05 ($C_{4'}$), 23.95 ($C_{2''}$), 23.03 ($C_{5'}$), 14.10 ($C_{6'}$), 11.22 ($C_{3''}$). EI mass spectrum: m/z 488 (M^+). (Found: C, 37.01; H, 4.48. Calc. for $C_{15}H_{22}O_2I_2$: C, 36.91; H, 4.54%).

2,5-Bis(trimethylsilylethynyl)-1-(2-ethylhexyloxy)-4-methoxybenzene 1a

To a solution of 2,5-diiodo-1-(2-ethylhexyloxy)-4-methoxybenzene **1** (2.00 g, 4.10 mmol) in ^{i}Pr$_2$NH–THF (70 cm^3, 1 : 4 v/v) under nitrogen were added catalytic amounts of CuI (10 mg, 0.05 mmol), $Pd(OAc)_2$ (10 mg, 0.04 mmol) and PPh_3 (30 mg, 0.11 mmol). The solution was stirred for 0.5 h at room temperature and then trimethylsilylethyne (1.00 g, 10.18 mmol) was added at room temperature to the vigorously stirred solution; during the addition a white precipitate formed. After the addition was completed, the reaction mixture was stirred at reflux for 2 h. The completion of the reaction was determined by silica TLC and IR spectroscopy. After being cooled to room temperature, the mixture was filtered to eliminate the ammonium salt and the solvent mixture was removed *in vacuo*. The soiled residue was dissolved in dichloromethane and subjected to silica column chromatography eluting with hexane–CH_2Cl_2 (1 : 2 v/v) to afford **1a** as a viscous oil which crystallised as a pale-brown solid (1.32 g, 75%) on standing overnight in a low temperature fridge. IR (CH_2Cl_2): ν/cm^{-1} 2159 (C≡C). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.89 (1H, s, H_6), 6.87 (1H, s, H_3), 3.87 (2H, d, J = 4.95 Hz, $H_{1'}$), 3.83 (3H, s, O–CH_3), 1.71 (1H, m, $H_{2'}$), 1.48 (4H, m, $H_{5',2''}$), 1.28 (4H, m, $H_{3',4'}$), 0.86 (6H, t, $H_{6',3''}$), 0.065 (18H, s, $SiMe_3$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 154.40 (C_4), 154.08 (C_1), 116.01 (C_6), 114.91 (C_3), 113.39 (C_2), 112.93 (C_5), 101.06 (C≡C), 100.19 (C≡C), 71.72 ($C_{1'}$), 56.66 (O–CH_3), 39.63 ($C_{2'}$), 30.57 ($C_{3'}$), 29.19 ($C_{4'}$), 23.97 ($C_{2''}$), 23.13 ($C_{5'}$), 14.16 ($H_{6'}$), 11.35 ($C_{3''}$), −0.002 ($SiMe_3$). EI mass spectrum: m/z 428 (M^+). (Found: C, 70.12; H, 9.34. Calc. for $C_{25}H_{40}O_2Si_2$: C, 70.03; H, 9.40%).

2,5-Bis(ethynyl)-1-(2-ethylhexyloxy)-4-methoxybenzene 1b

Compound **1a** (1.00 g, 2.33 mmol) was proto-desilylated in THF–methanol (50 cm^3, 4 : 1, v/v) using aqueous KOH (0.287 g, 5.12 mmol in 1 cm^3 water). The reaction mixture was stirred at room temperature for 2 h during which period IR and TLC showed that all protected compound had been converted to the terminal alkyne ligand. The solvent mixture was then removed and the residue was dissolved in CH_2Cl_2 and subjected to column chromatography on silica using hexane–CH_2Cl_2 (1 : 2 v/v) as eluant. The solvent mixture was removed to give **1b** (0.50 g, 75%) as yellow oil. This compound was somewhat unstable; storage overnight under nitrogen at 4 °C resulted in the oil darkening its colour. Long storage times led to the formation of a black tarry liquid that was presumed to be a polymerisation product. This ligand was therefore freshly prepared for use in further synthesis. IR (CH_2Cl_2): ν/cm^{-1} 2107 (C≡C), 3299 (C≡C–H). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.95 (1H, s, H_6), 6.93 (1H, s, H_3), 3.88 (2H, d, J = 5.74 Hz, $H_{1'}$), 3.82 (3H, s, O–CH_3), 3.37–3.31 (2H, s, C≡C–H), 1.72 (1H, m, $H_{2'}$), 1.51–1.25 (8H, m, $H_{3',4',5',2''}$), 0.86 (6H, t, $H_{6',3''}$). ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 154.38 (C_4), 154.24 (C_1), 117.73 (d, C_6), 115.91 (C_3), 113.37 (C_2), 112.48 (C_5), 82.53 (C≡C), 79.74 (C≡C), 72.09 ($C_{1'}$), 56.35 (O–CH_3), 39.34 ($C_{2'}$), 30.46 ($C_{3'}$), 29.02 ($C_{4'}$), 23.86 ($C_{2''}$), 23.01 ($C_{5'}$), 14.04 ($H_{6'}$), 11.12 ($C_{3''}$). EI mass spectrum: m/z 284 (M^+). Satisfactory microanalytical data could not be obtained due to the instability of the compound.

5,8-Bis(trimethysilylethynyl)quinoline 2a

5,8-Diiodoquinoline (2.00 g, 5.24 mmol), trimethylsilylethyne (1.28 g, 13.03 mmol) and $^{i}Pr_2NH$–THF (70 cm^3, 1 : 4 v/v) were mixed with catalytic amounts of CuI (12 mg), $Pd(OAc)_2$ (12 mg) and PPh_3 (36 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 and eluted with the same solvent. The desired compound **2a** was obtained as an off-white solid in 80% isolated yield. IR (CH_2Cl_2): ν/cm^{-1} 2159 (C≡C). ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.02 (1H, dd, J= 4.21, 1.77 Hz, H_2), 8.59 (1H, dd, J = 8.41, 1.77 Hz, H_4), 7.85 (1H, d, J = 7.57 Hz, H_7), 7.65 (1H, d, J = 7.57 Hz, H_6), 7.49 (1H, dd, J = 8.44, 4.21 Hz, H_3), 0.32 (18H, t, $SiMe_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 151.49 (C_2), 147.85 (C_9), 134.97 (C_3), 134.23 (C_4), 130.34 (C_7), 128.67 (C_{10}), 124.06 (C_8), 122.17 (C_6), 121.63 (C_5), 102.52 (C≡C), 101.43 (C≡C), 0.53 ($SiMe_3$). EI mass spectrum: m/z 321 (M^+). (Found: C, 70.87; H, 7.19. Calc. for $C_{19}H_{23}NSi_2$: C, 70.97; H, 7.21%).

5,8-Bis(ethynyl)quinoline 2b

Compound **2a** was proto-desilylated as in**1a** and the crude product was worked up, as before, to yield a dark-yellow solid. Silica column chromatography with hexane–CH_2Cl_2 (1 : 1 v/v) gave a pale yellow solid identified as **2b**. Yield: 85%. IR (CH_2Cl_2): ν/cm^{-1} 2107 (C≡C), 3299 (C≡C–H). ^{1}H NMR (250 MHz, $CDCl_3$): δ 9.01 (1H, dd, J = 4.20, 1.66 Hz, H_2), 8.57 (1H, dd, J = 8.44, 1.61 Hz, H_4), 7.84 (1H, d, J = 7.54 Hz, H_7), 7.65 (1H, d, J = 7.52 Hz, H_6), 7.47 (1H, dd, J = 8.47, 4.22 Hz, H_3), 3.65–3.54 (2H, s, C≡C–H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 151.57 (C_2), 148.00 (C_9), 134.83 (C_3), 133.82 (C_4), 130.69 (C_7), 128.67 (C_{10}), 123.31 (C_8), 122.08 (C_6), 121.00 (C_5), 84.58 (C≡C), 80.57 (C≡C). EI mass spectrum: m/z 177 (M^+). (Found: C, 88.09; H, 4.02. Calc. for $C_{13}H_7N$: C, 88.11; H, 3.98%).

2,3-Diphenyl-5,8-bis(trimethylsilylethynyl)quinoxaline 3a

This compound was prepared as described above for **1a** from 2,3-diphenyl-5,8-diiodoquinoxaline (2.00 g, 3.74 mmol), trimethylsilylethyne (0.92 g, 9.36 mmol), CuI (10 mg), $Pd(OAc)_2$ (10 mg), PPh_3 (30 mg) in $^{i}Pr_2NH$–THF (50 cm^3, 1 : 4 v/v). After the usual work-up, the soiled residue was purified by silica column chromatography eluting with dichloromethane–hexane (2 : 1 v/v) to yield off-white solid identified as **3a**. Recrystallisation from hexane–dichloromethane led to snow-white crystals of **3a** in 78% yield (1.39 g). IR (CH_2Cl_2): ν/cm^{-1} 2159 (C≡C). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.83 (2H, s, $H_{6,7}$), 7.74 (4H, dd, J = 5.78, 1.49 Hz, H_{ortho} of Ph), 7.37–7.25 (6H, m, $H_{meta,para}$ of Ph), 0.35 (18H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 152.95 ($C_{9,10}$), 141.02 ($C_{2,3}$), 138.71–123.46 (C_{5-8} and Ph Cs), 103.71 (C≡C), 101.29 (C≡C), 0.002 ($SiMe_3$). EI mass spectrum: m/z 474 (M^+). (Found: C, 75.84; H, 6.28. Calc. for $C_{30}H_{30}N_2Si_2$: C, 75.90; H, 6.37%).

2,3-Diphenyl-5,8-bis(ethynyl)quinoxaline 3b

This compound was synthesised as described above for **1b** from **3a** (1.00 g, 2.1 mmol) and KOH (0.26 g, 4.6 mmol) in THF–methanol (50 cm^3, 4 : 1, v/v). The residue dissolved in CH_2Cl_2 was subjected to a silica column and the desired colourless band was collected with the aid of hexane–dichloromethane (1 : 1 v/v) to afford **3b** (0.63 g, 90%) as a colourless microcrystalline solid. IR (CH_2Cl_2): ν/cm^{-1} 2107 (C≡C), 3299 (C≡C–H). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.89 (2H, s, $H_{6,7}$), 7.58 (4H, dd, J = 8.37, 2.82 Hz, H_{ortho} of Ph), 7.36–7.25 (6H, m, $H_{meta,para}$ of Ph), 3.62 (2H, s, C≡C–H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 153.83 ($C_{9,10}$), 141.22 ($H_{2,3}$), 138.55–123.07 (C_{5-8} and Ph), 85.35 (C≡C), 79.98 (C≡C). EI mass spectrum: m/z 330 (M^+). (Found: C, 87.17; H, 4.31. Calc. for $C_{24}H_{14}N_2$: C, 87.25; H, 4.27%).

4,7-Bis(trimethylsilylethynyl)-2,1,3-benzothiadiazole 4a

This compound was prepared as described above for **1a** from 4,7-dibromo-2,1,3-benzothiadiazole (1.52 g, 5.17 mmol), trimethylsilylethyne ((1.27 g, 12.93 mmol), CuI (10 mg), $Pd(OAc)_2$ (10 mg) and PPh_3 (30 mg) in $NHPr^{i}_2$–THF (50 cm^3, 1 : 4 v/v). After the usual work-up, the soiled residue was purified by silica column chromatography eluting with hexane–CH_2Cl_2 (1 : 2 v/v) to yield light yellow solid identified as **4a** in 78% yield (1.32 g). IR (CH_2Cl_2): ν/cm^{-1} 2159 (C≡C). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.68 (2H, s, $H_{5,6}$), 0.30 (18H, s, $SiMe_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 154.20 ($C_{8,9}$), 133.09 ($C_{5,6}$), 117.25 ($C_{4,7}$), 103.60 (C≡C), 99.98 (C≡C), −0.14 ($SiMe_3$). EI mass spectrum: m/z 328.39 (M^+). (Found: C, 58.56; H, 6.16. Calc. for $C_{16}H_{20}N_2Si_2S$: C, 58.49; H, 6.14%).

4,7-Bis(ethynyl)-2,1,3-benzothiadiazole 4b

This compound was synthesised from **4a** (1.00 g, 3.04 mmol) and KOH (0.375 g, 6.70 mmol). The residue dissolved in CH_2Cl_2 was applied to a silica column and the desired light yellow band was collected with the aid of hexane–CH_2Cl_2 (1 : 1 v/v) to afford **4b** (0.51 g, 90%) as an off-white solid. IR (CH_2Cl_2): ν/cm^{-1} 2107 (C≡C), 3300 (C≡C–H). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.64 (2H, s, $H_{5,6}$), 3.60 (2H, s, C≡C–H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 154.28 ($C_{8,9}$), 133.17 ($C_{5,6}$), 116.68 ($H_{4,7}$), 102.35 (C≡C), 99.53 (C≡C). EI mass spectrum: m/z 184 (M^+). (Found: C, 65.34; H, 2,22. Calc. for $C_{10}H_4N_2S$: C, 65.20; H, 2.19%).

Metal complex preparations

***Trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] 1c [R = 1-(2-ethylhexyloxy)-4-methoxybenzene-2,5-diyl].** To a stirred solution of *trans*-[$(PEt_3)_2$(Ph)PtCl] (0.598 g, 1.10 mmol) and **1b** (0.142 g, 0.50 mmol, freshly prepared from **1a**) in $^{i}Pr_2NH$–CH_2Cl_2 (50 cm^3, 1 : 1 v/v) under nitrogen was added CuI (5 mg). The yellow solution was stirred at room temperature for 15 h, after which all volatile components were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and passed through a silica column eluting with hexane–CH_2Cl_2 (1 : 1 v/v). Removal of the solvents *in vacuo* gave the title complex as a light yellow solid in 75% yield (0.49 g). IR (CH_2Cl_2): ν/cm^{-1} 2096 (C≡C). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.33 (1H, s, H_6), 7.32 (1H, s, H_3), 6.94 (4H, dd, J = 14.87, 7.37 Hz, H_{ortho} of Ph), 6.78 (4H, dd, J = 18.97, 7.03 Hz, H_{meta} of Ph), 6.73 (2H, s, H_{para} of Ph), 3.88 (2H, d, J = 1.71 Hz, $H_{1'}$), 3.75 (3H, s, O–CH_3), 1.80–1.76 (24H, m, P–CH_2), 1.72 (1H, m, $H_{2'}$), 1.51–1.09 (8H, m, $H_{3',4',5',2''}$), 1.07 (36H, m, P–CH_2CH_3), 0.89 (6H, t, $H_{6',3''}$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 153.79 (C_4), 153.15 (C_1), 139.32–120.99 (Ph), 117.42 (C_6), 116.84 (C_3), 116.41 (C_2), 115.96 (C_5), 106.57, 106.29 (C≡C), 72.05 ($C_{1'}$), 56.53 (O–CH_3), 39.18 ($C_{2'}$), 30.19 ($C_{3'}$), 29.00 ($C_{4'}$), 23.47 ($C_{2''}$), 23.19 ($C_{5'}$), 15.10 (P–CH_2), 14.14 ($C_{6'}$), 10.88 ($C_{3''}$), 8.02 (P–CH_2CH_3). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ −131.25 ($^1J_{Pt-P}$ = 2620 Hz). FAB-MS: 1299 (M^+). (Found: C, 50.75; H, 7.17. Calc. for $C_{55}H_{92}O_2P_4Pt_2$: C, 50.84; H, 7.13%).

***Trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] 2c (R = quinoline-5,8-diyl).** Treatment of the terminal di-yne **2b** (0.088 g, 0.50 mmol) with *trans*-[$(PEt_3)_2$(Ph)PtCl] (0.598 g, 1.10 mmol) for 15 h at room temperature, in the presence of a catalytic amount of CuI (5 mg), in $^{i}Pr_2NH$–CH_2Cl_2 (50 cm^3, 1 : 1 v/v) gave the required complex as a brownish–yellow solid in 65% isolated yield (0.386 g) after purification on a silica column using hexane–CH_2Cl_2 (1 : 1) as eluant. IR (CH_2Cl_2): ν/cm^{-1} 2095 (C≡C). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.83 (1H, dd, J = 4.06, 1.68 Hz, H_2), 8.76 (1H, dd, J = 8.34, 1.84 Hz, H_4), 7.55 (1H, d, J = 7.58 Hz, H_7), 7.36 (1H, d, J = 13.13, 7.46 Hz, H_6), 7.32 (1H, dd, J = 8.37, 4.06 Hz, H_3), 6.96 (4H, dd,

J = 13.42, 7.33 Hz, H_{meta} of Ph), 6.89 (4H, dd, J = 13.90, 7.15 Hz, H_{ortho} of Ph), 6.81 (2H, dd, J = 13.74, 6.56 Hz, H_{para} of Ph), 1.76 (24H, q, P–CH_2), 1.09 (36H, t, P–CH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.62 (C_2), 147.97 (d, C_9), 139.37–120.08 (C_3, C_4, C_7, C_{10}, C_8, C_6, C_5, and Ph), 103.47, 103.19 (C≡C), 15.19 (t, P–CH_2), 7.89 (q, CH_3). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ −131.17 ($^1J_{Pt-P}$ = 2618 Hz). FAB-MS: 1192 (M^+). (Found: C, 49.52; H, 6.28. Calc. for $C_{49}H_{75}NP_4Pt_2$: C, 49.37; H 6.34%).

***Trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] 3c (R = 2,3-diphenylquinoxaline-5,8-diyl).** This complex was synthesised employing similar reaction conditions to those described for **2c** but **3b** was used instead of **2b**. The product was purified on preparative TLC plates with hexane–CH_2Cl_2 (1 : 1 v/v) as eluant giving compound **3c** as pale yellow micro-crystals in an isolated yield of 56%. IR (CH_2Cl_2): ν/cm^{-1} 2095 (C≡C). ^1H NMR (250 MHz, $CDCl_3$): δ 7.60 (2H, s, $H_{6,7}$), 7.47 [4H, dd, J = 6.34, 1.40 Hz, H_{ortho} of Ph (quinoxaline)], 7.33 [4H, dd, J = 6.32, 1.42 Hz, H_{ortho} of Ph (Pt)], 7.26–7.25 [6H, m, $H_{meta,para}$ of Ph (quinoxaline)], 6.95 [4H, dd, J = 15.5, 8.12 Hz, H_{meta} of Ph (Pt)], 6.79 [2H, dd, 14.50, 7.20 Hz, H_{para} of Ph (Pt)], 1.78 (24H, m, P–CH_2), 1.02 (36H, q, P–CH_2CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 156.92 ($C_{9,10}$), 151.72 ($C_{2,3}$), 142.42–121.87 (C_{5-8} and Ph), 107.88 (C≡C), 15.10 (P–CH_2), 121.87 (P–CH_2CH_3). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ −131.00 ($^1J_{Pt-P}$ = 2621 Hz). FAB-MS: 1345.3 (M^+). (Found: C, 52.68; H, 6.19. Calc. for $C_{60}H_{82}N_2P_4Pt_2$: C, 53.57; H, 6.14%).

***Trans*-[$(Et_3P)_2$(Ph)Pt–C≡C–R–C≡C–Pt(Ph)$(PEt_3)_2$] 4c (R = 2,1,3-benzothiadiazole-4,7-diyl).** Similar procedures as for complex **3c** were adopted using **4b** (0.092 g, 0.50 mmol), *trans*-[$(PEt_3)_2$(Ph)PtCl] (0.598 g, 1.10 mmol) and CuI (5 mg) to produce bright yellow solid in 56% yield (341 mg) after TLC purification and recrystallisation. IR (CH_2Cl_2): ν/cm^{-1} 2095 (C≡C). ^1H NMR (250 MHz, $CDCl_3$): δ 7.32 (4H, s, H_{ortho} of Ph), 7.25 (2H, s, $H_{5,6}$), 6.96 (4H, t, J = 7.47 Hz, H_{meta} of Ph), 6.79 (2H, t, J = 7.20 Hz, H_{para} of Ph), 1.87–1.80 (24H, m, P–CH_2), 1.10 (36H, m, P–CH_2CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 156.46 ($C_{8,9}$), 139.18 ($C_{5,6}$), 130.30–121.18 (Ph), 119.09 ($C_{4,7}$), 107.48 (C≡C), 15.14 (P–CH_2), 8.07 (P–CH_2CH_3). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ −131.30 ($^1J_{Pt-P}$ = 2619 Hz). FAB-MS: 1199 (M^+). (Found: C, 46.07; H, 6.12. Calc. for $C_{46}H_{72}N_2P_4SPt_2$: C, 46.07; H, 6.05%).

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