FULL PAPER

A new series of luminescent phosphine stabilised platinum ethynyl complexes[†]

Ramkrishna Saha,^a Md. Abdul Qaium,^a Dipen Debnath,^a Muhammad Younus,^{*a} Nazia Chawdhury,^b Nasim Sultana,^c Gabriele Kociok-Köhn,^d Li-ling Ooi,^d Paul R. Raithby^{*d} and Masashi Kijima^e

- ^a Department of Chemistry, Shahjalal University of Science & Technology, Sylhet, 3114, Bangladesh. E-mail: myounus-che@sust.edu
- ^b Department of Physics, Shahjalal University of Science & Technology, Sylhet, 3114, Bangladesh
- ^c Bangladesh Council for Scientific and Industrial Research, Dhaka, 1205, Bangladesh
- ^d Department of Chemistry, University of Bath, Bath, UK BA2 7AY.
- E-mail: p.r.raithby@bath.ac.uk
- ^e Institute of Material Science, University of Tsukuba, Tsukuba, Ibaraki, 305-8573, Japan

Received 19th April 2005, Accepted 30th June 2005 First published as an Advance Article on the web 12th July 2005

A series of *cis*-platinum ethynyl complexes with the general formula *cis*-[Pt(dppe)(C=CR)₂] (dppe = 1,2-bis(diphenylphosphino)ethane; $R = C_6H_4$ -*p*-NO₂ 1, C_6H_4 -*p*-CH₃ 2, C_6H_4 -*p*-C=CH 3 and C_6H_4 -*p*-C=CH 4) have been prepared by the coupling reaction of *cis*-[Pt(dppe)Cl₂] with two equivalents of the appropriate alkyne. The new complexes have been fully characterized by spectroscopic techniques, and the *cis* square planar arrangement at the platinum centre has been confirmed by single-crystal X-ray diffraction studies of complexes 1, 2 and 4. The absorption spectra of the complexes 1–4 are dominated by a $\pi \to \pi^*$ band that contains some platinum (n + 1) p orbital character. The position of the band is dependent on the electron donating or withdrawing properties of the ethynyl substituents, R. Complex 1 displays a triplet emission in the green, at room temperature, while complexes 2–4, display singlet emissions in the blue. Again, the difference can be attributed to the nature of the R substituents.

Introduction

There is considerable current interest in transition metal σ bonded ethynyl complexes and polymers because of their material and opto-electronic properties.^{1,2} Platinum σ -bonded ethynyl complexes were first prepared by Hagihara and coworkers in 1977,³ and since then a plethora of new materials that contain Group 8,4 Group 9,5 Group 106 and other transition metals⁷ have been prepared and their physical and electronic properties investigated. For the Group 10 systems the majority of the investigations have been centred on transplatinum phosphine complexes. For example, trans-[PtL2Cl2] (L = monoalkyl phosphine) with two equivalents of monoterminal alkynes (HC \equiv CR) gives *trans*-[PtL₂(C \equiv CR)₂] (R = H, Me, Bu, etc.),⁸ while with one equivalent of diterminal alkynes and poly-ynes (HC=CRC=CH) gives linear rigid rod polymers $[-PtL_2-C \equiv CRC \equiv C-]_n$ (R = aromatic or heteroaromatic group).³ We, and others, have prepared and investigated the electronic properties of a wide range of these rigid rod polymers and their molecular precursors, and have shown that the more electron withdrawing is the aromatic or heteroaromatic spacer group, R, the lower is the band gap between the valence and conductance bands in the polymers.9 Until recently cis-platinum ethynyl complexes have been less well studied, partly because the *cis* isomer is thermodynamically unstable with respect to the trans isomer in solution, particularly when monophosphine groups are present as the auxiliary ligands.8 For example, the reaction of cis-[Pt(PBu₃)₂Cl₂] with PhC=CH below -20 °C gives the cis-[Pt(PBu₃)₂(C=CPh)₂] product, while above this temperature a 50 : 50 mixture of the cis and trans isomers are obtained.8 The thermodynamic instability has been overcome by using chelating phosphine¹⁰⁻¹² or diimine groups,^{13,14} and

the diimine-stabilised platinum ethynyl complexes have shown considerable promise as white¹⁵ and red¹⁶ OLED materials. The opto-electronic properties of these materials stimulated our interest in investigating the electronic properties of the chelating phosphine-stabilised *cis*-platinum bis-ethynyl and dienyl complexes. In this paper, for the first time, we describe the synthesis and systematic study of the electronic properties of a series of complexes with the general formula *cis*-[Pt(dppe)(C≡CR)₂] (dppe = 1,2-bis(diphenylphosphino)ethane; R = C₆H₄-*p*-NO₂ 1, C₆H₄-*p*-CH₃ 2, C₆H₄-*p*-C≡CH 3 and C₆H₄-*p*-C=CH 4). We have been able to correlate the electronic properties of the substituent groups on the alkyne with the solution absorption and emission spectra of the complexes.

Results and discussion

Synthesis and characterisation

The synthesis of the *cis*-[Pt(dppe)(C \equiv CR)₂] (dppe = 1,2bis(diphenylphosphino)ethane; R = C₆H₄-*p*-NO₂ **1**, C₆H₄*p*-CH₃ **2**, C₆H₄-*p*-C \equiv CH **3** and C₆H₄-*p*-C₆H₄-*p*-C \equiv CH **4**) complexes were initially carried out by an adaptation of the Sonogashira coupling route (Scheme 1)⁸ using *cis*-[Pt(dppe)Cl₂] with two equivalents of HC \equiv CR, in diethylamine,



 $R = NO_2$, CH_3 , $C = CH_4$ Scheme 1

DOI: 10.1039/b505484b

[†] This paper is dedicated to the memory of Ian Rothwell, an outstanding organometallic chemist.

 Table 1
 Spectroscopic characterisations of the new complexes 1–4

		*			
	$\frac{IR}{(CH_2Cl_2)/cm^{-1}}$	δ ¹ H NMR (CDCl ₃)	δ ¹³ C NMR (CDCl ₃)	δ^{31} P NMR (CDCl ₃)	FAB +ve; m/z
$[Pt(dppe)(C \equiv C-C_6H_4-NO_2)_2] 1$	2116(s), 2096(w).	2.4 (m, 4H, P(CH ₂) ₂ P), 7.15 and 7.96 (dd, 8H, \equiv C-C ₆ H ₄ -NO ₂), 7.37–7.90 (m, 20H, PPh)	28.77 (P(CH_2) ₂ P), 111.72 ($C\equiv C$), 123–145 (PPh and $\equiv CPh$)	43.69 ($J_{Pt-P} =$ 2275 Hz)	$886[\mathrm{M^{*}}+\mathrm{H}]$
[Pt(dppe)(C≡C- C ₆ H ₄ -CH ₃) ₂] 2	2115(m)	2.2 (s, 6H, $-C_6H_4-CH_3$), 2.4 (m, 4H, P(CH_{2}) ₂ P), 6.8 and 7.00 (dd, 8H, $p-C_6H_4-p$), 7.35–7.90 (m, 20H, PPh).	21.69 (- C_6H_4 -CH ₃), 125.74–135.14 (PPh and \equiv CPh)	42.16 ($J_{Pt-P} =$ 2280 Hz)	823 [M] ⁺
[Pt(dppe)(C≡C- C ₆ H ₄ - <i>p</i> -C≡CH) ₂] 3	2104(s), 2115(w), 3295(s), 3299(w)	2.4 (m, 4H, P(C H_2) ₂ P), 2.95 (s, 2H, C=C-H), 7.0 and 7.2 (dd, 8H, =C-C ₆ H ₄ -CCH), 7.35–7.95 (m, 20H, PPh)	84.6 (C=CH), 107,112.1,112.6 (C=C), 129–134 (PPh and = CPh)	42.6 ($J_{Pt-P} =$ 2283 Hz)	843 [M]+
$[Pt(dppe)(C \equiv C-C_6H_4-p-C_6H_4-p-C_6H_4-p-C_6H_4-p-C_6H_4-p-C_6H_4-p-C_6H_4-p-C_6H_2]$	2105(s)	2.45 (m, 4H, P(CH_{2}) ₂ P), 3.1 (s, 2H, C \equiv C- <i>H</i>), 7.2 and 7.35 (dd, 16H, Pt-C \equiv C-C ₆ H ₄ -C ₆ H ₄ -CCH), 7.4–8.0 (m, 28H, PPh and -C ₆ H ₄ -CCH)	77.61, 84.14 (C=CH), 121–142 (PPh and =C- C_6H_4 - C_6H_4 -C=)	42.5 (<i>J</i> _{Pt-P} = 2282 Hz)	996 [M ⁺ + H]

with CuI catalyst. The reaction of *cis*-[Pt(dppe)Cl₂] with *p*-nitrophenyleneacetylene, O_2N -*p*- C_6H_4 - $C\equiv$ CH, afforded *cis*-[Pt(dppe)(C \equiv C- C_6H_4 -*p*-NO₂)₂], **1**, in 70% yield. However, a similar reaction where *p*-tolylacetylene, H_3C -*p*- C_6H_4 - $C\equiv$ CH, was used instead of O_2N -*p*- C_6H_4 - $C\equiv$ CH, gave only a 26% yield. An improved synthesis using a mixture of the more solublizing diisopropylamine and dichloromethane (1 : 3), instead of diethylamine, gave a high yield (86%). Complexes **3** and **4** were synthesized similarly by using a mixture of diisopropylamine and dichloromethane, and dichloromethane. All the reactions were carried out under nitrogen atmosphere, at room temperature, for 24 h.

The complexes 1–4 were characterized by the IR, ${}^{1}H$, ${}^{13}C{H}$, ${}^{31}P{H}NMR$, positive ion FAB-MS, and elemental analysis (Table 1). The molecular and crystal structures of complex 1, 2 and 4 were determined by single crystal X-ray crystallography.

In the IR spectra the $v(C\equiv C)$ stretching frequency is diagnostic of the characterization of the metal ethynyl complexes and is useful in following the course of reactions. In the case of mono alkynes, the absence of terminal C=CH confirms the completion of the reaction. For the *cis*-alkynyl complexes two $v(C\equiv C)$ stretches are expected and this is observed for complexes 1 and 3 with pairs of signals at 2116, 2096 cm⁻¹ and 2115, 2104 cm⁻¹, respectively. In addition, for complex 3 the expected pair of signals for the v(C-H) stretches are observed at 3299 and 3295 cm⁻¹. However, only one broad signal was observed for the v(C=C) stretches in complexes 2 and 4, and only one signal for the v(C-H) stretch is observed for 4. Similar spectral features of single absorption peak for both $v(C\equiv C)$ and v(C-H) have been observed for the complex *cis*-[PtL₂(C=C-C=CH)₂] (L = PEt₃, dppe and dppp).¹⁰

In the ¹H NMR spectra of the complexes **3** and **4** singlet signals at δ 2.95 and 3.1 confirmed the presence of the C=C-*H* groups. For all the complexes, the expected peaks at δ 2.4–2.5 were observed for the methylenic protons of the dppe group, P(CH₂)₂P. The complex multiplets in the range of δ 7.3–8 indicate the presence of diphosphine aromatic protons. All the complexes showed the expected (AA'BB') pattern for the *p*-disubstituted aromatic protons.

In the ¹³C NMR spectrum of complex **3** the signals at δ 84.6, 107, 112.1 and 112.6 indicate the presence of a C=C unit. However, it was not possible to detect all the signals for the C=C group for complexes **1**, **2** and **4** because of the expected weak resonance and because of the relatively low solubility of these complexes. The P(CH₂)₂P carbon signal is observed at δ 28.77 only for **1**. The signals for the aromatic carbons appear at δ 120–145. For complex **2**, two triplets at δ 133.98 and 129.08 with $J \sim 5$ Hz were observed because of the coupling of *ortho* and *meta* carbons, respectively, of the phenyl rings with phosphorus nuclei. Similar spectral features were observed for all the other complexes in the expected region. Similar coupling of the *ortho* and *meta* phenyl ring carbons bonded to phosphorus have been reported for the complex *trans*-[Pt(PPh₃)₂(C \equiv C–*p*-C₆H₄-C₆H₄-*p*-C \equiv CH)(C \equiv CC₆H₄-*p*-NO₂)].¹⁷

For all four complexes the ³¹P NMR spectra contained signals with the expected satellites due to coupling with the ¹⁹⁵Pt nuclei at δ 43.6 [$J_{(P_{1}-P)}$ = 2275 Hz] for complex **1**, δ 42.16 [$J_{(P_{1}-P)}$ = 2280 Hz] for complex **2**, δ 42.6 [$J_{(P_{1}-P)}$ = 2283 Hz] for complex **3**, δ 42.5 [$J_{(P_{1}-P)}$ = 2282 Hz] for complex **4**. The chemical shift in the ³¹P NMR spectrum of *cis*-[Pt(dppe)Cl₂] is δ 42.64 ppm with a coupling constant of 3627 Hz. The coupling constants for the complexes **1**, **2**, **3** and **4** are much lower than for [Pt(dppe)Cl₂]. These lower values are consistent with a *cis*-square planar complex but reflect the greater *trans* influence of the alkynyl ligands compared to the chlorides.^{10,11,18,19}

The molecular formula for the complexes were also established by the intense molecular ion peaks in the positive ion FAB mass spectra observed at m/z 886 [M⁺ + H] for 1, at m/z 823 [M]⁺ for 2, at m/z 843 [M]⁺ for 3, and at m/z 996 [M⁺ + H] for 4. Fragmentation patterns showing the loss of the ethynyl fragments were also observed.

Crystallography

Suitable single crystals of complexes *cis*-[Pt(dppe)($C \equiv CC_6H_4$ *p*-NO₂)₂] **1**, *cis*-[Pt(dppe)($C \equiv CC_6H_4$ -*p*-CG₁)₂] **2** and *cis*-[Pt(dppe)($C \equiv CC_6H_4$ -*p*-C₆H₄-*p*-C $\equiv CH$)₂] **4** were grown from CH₂Cl₂/hexane solutions and the crystal and molecular structures obtained in order to confirm the molecular geometries and to investigate any correlation of structural trends with the electronic properties of the materials. The molecular structure of complexes **1**, **2** and **4** are shown in Figs. 1–3, respectively,



Fig. 1 The molecular structure of *cis*-[Pt(dppe)($C \equiv CC_6H_4$ -*p*-NO₂)₂] **1** showing the atom numbering scheme.

	1	2	4
Pt(1)–C(1)	2.022(8)	2.011(3)	2.027(5)
Pt(1)-C(9)	2.024(8)	2.015(4)	2.020(5)*
C(1) - C(2)	1.197(12)	1.203(5)	1.175(7)
C(2) - C(3)	1.433(12)	1.451(5)	1.424(7)
C(9) - C(10)	1.190(12)	1.214(5)	1.193(7)*
C(10) - C(11)	1.433(11)	1.445(5)	1.435(7)*
Pt(1) - P(1)	2.274(2)	2.2644(9)	2.2716(13)
Pt(1) - P(2)	2.269(2)	2.2645(9)	2.2675(12)*
P(1) - C(17)	1.838(8)	1.846(4)	1.842(5)
P(2)-C(18)	1.848(8)	1.835(4)	1.842(5)*
C(17)–C(18)	1.522(11)	1.529(5	1.514(10)¥
C(1) P _t (1) $C(0)$	06.7(2)	05.01(15)	04.0(3)
C(1) = I(1) = C(3) C(1) = Pt(1) = P(1)	90.7(3)	87 29(10)	94.0(3) 90.81(14)
C(1) - P(1) - P(1)	172.6(2)	175.86(11)	174.89(14)
C(1) = Pt(1) = P(2)	172.0(2) 175.1(2)	172.38(11) 172.78(10)	$174.89(14) \pm 174.89(14) \pm 174$
C(1) - I(1) - I(2) C(0) - Pt(1) - P(2)	86 9(3)	91.00(11)	90.81(14)
P(1) = P(1) = P(2)	85 89(8)	85 72(3)	84 47(7)
$P_{t(1)-C(1)-C(2)}$	169.9(7)	168.0(3)	171.9(4)
C(1) = C(2) = C(3)	1703(9)	179 1(4)	175.8(5)
$P_{t(1)} = C(2) = C(3)$	166 6(8)	167.4(3)	170 9(4)*
C(9)-C(10)-C(11)	179.1(9)	173.7(4)	175.3(6)*
	(.)		

* Structure 4 contains two independent half molecules, the "*" values are quoted for the independent bond parameters in the second molecule. ¥ The final atom in the sequence is related to the others by the symmetry operation 0.5 - x, y, 1.5 - z.

and selected structural parameters are presented in Table 2. Complexes 1 and 2 both crystallise in the monoclinic space group $P2_1/n$ with one independent molecule in the asymmetric unit. Since the cell dimensions for 1 and 2 are also similar it appears that the replacement of the *para*-NO₂ group in 1 by the *para*-CH₃ group in 2 has little influence on the crystal packing in the two materials. In 2 there are no intermolecular interactions that are less than the sum of the van der Waals radii and in 1 there is only a weak contact of 2.466 Å between O(1) of one of the nitro groups and a phenyl proton, H(23), related by the symmetry operation 1 - x, 1 - y, -z. Complex 4 crystallises in the monoclinic space group P2/n with two independent but structurally similar half molecules in the asymmetric unit together with half a molecule of hexane solvent. Again, there are no significant intermolecular interactions. The shortest contact in the crystal structure involving the alkyne H-atoms is a weak C=C-H $\cdots \pi$ (arene ring) interaction between the alkynylic hydrogen, H(26') in the second independent half molecule and a carbon, C(35'), in a adjacent ring, related by the symmetry operation 1 - x, 3 - y, 1 - z, at a distance of 2.875 Å.

The crystal structure of 1 confirms that the platinum(II) centre adopts the square planar cis-configuration (Fig. 1), with the greatest deviation from the PtP_2C_2 plane being 0.038 Å for Pt(1). The two alkyne units show slight deviation from linearity with an average Pt–C=C angle of 168.3° and an average C=C–C angle of 174.7°. The two phenyl rings of the two alkyne ligands make dihedral angles of 86.2° {C(3)–C(8)} and 60.4° {C(11)–C(16)}, respectively, with the PtP_2C_2 square plane. The two NO_2 groups are planar and almost coplanar with the phenyl rings to which they are bonded; the N(1)O(1)O(2) plane makes a dihedral angle of 2.4° with the C(3)–C(8) ring plane, and the N(2)O(3)O(4) plane makes an angle of 12.4° with the C(11)-C(16) ring plane. The chelating phosphine adopts a gauche configuration with a P(1)-C(17)-C(18)-P(2) torsion angle of -49.9° . The molecular parameters are similar to those found in related cis-phosphine substituted platinum alkynes.10,20

The molecular structure of **2** (Fig. 2) is closely related to that of **1**. The platinum(II) centre is again square planar with a maximum deviation from the PtP_2C_2 plane of 0.034 Å for Pt(1). The two alkyne groups again show some deviation from



Fig. 2 The molecular structure of cis-[Pt(dppe)(C=CC₆H₄-p-CH₃)₂] **2** showing the atom numbering scheme.

linearity with the two alkyne units showing slight deviation from linearity with an average Pt–C=C angle of 167.7° and an average C=C–C angle of 176.4°. The two phenyl rings on the alkyne ligands make angles of 62.7° and 58.2° with the PtP₂C₂ square plane. These angles are more similar to each other compared to the values found in 1. The chelating dppe ligand again adopts the *gauche* conformation with a P–CH₂–CH₂–P torsion angle of 50.7°. Despite the difference in the electron donating properties of NO₂, in 1, and CH₃, in 2, the bond parameters in 2 (Table 2) are very similar to those in 1. The trend is that the Pt–C(alkynyl) distances in 2 are *ca*. 0.004 Å shorter than in 1, and the Pt–P distances in 2 are also *ca*. 0.004 Å shorter than those in 1, however, these distances are barely significant at the 3σ significance level.

In the crystal structure of 4 each of the two independent half molecules of the platinum complex sit on crystallographic two-fold axes which, in each case, pass through the platinum atom and the mid point of the C-C bond of the P-CH2-CH2-P unit. One of the independent molecules is shown in Fig. 3 while selected bond parameters are presented in Table 2. As in 1 and 2 the platinum atoms adopt a square planar coordination geometry and the alkyne groups show some deviation from linearity with average Pt–C=C and C=C–C angles of 171.4° and 175.6°, respectively. The arene ring of the biphenyl group, in each half molecule, makes an angle of 63.26° (molecule 1) and 53.49° (molecule 2) with the PtP_2C_2 square plane. The two arene rings in the biphenyl groups make angles of 37.38° (molecule 1) and 30.55° (molecule 2) with each other as is expected to minimise $H \cdots H$ short contacts between the adjacent rings. As in 1 and 2 the P-CH₂-CH₂-P unit of the chelating phosphine adopts the gauche conformation with torsion angles of -53.7° (molecule 1) and -50.5° (molecule 2). The bond parameters around the platinum centres in 4 are in closer agreement with those observed in 1 than those in 2 but at the 3σ level of significance these



Fig. 3 The molecular structure of one of the two independent molecules in the asymmetric unit of *cis*-[Pt(dppe)($C \equiv CC_6H_4$ -*p*- C_6H_4 -*p*- $C \equiv CH_{2}$] **4**. The molecule lies on a crystallographic two-fold axis and the two halves of the molecule are related by the symmetry operation 0.5 - x, *y*, 1.5 - z.

Table 3 Spectral absorption data for complexes 1–4 recorded in $\rm CH_2Cl_2$ at room temperature

Complex	$\lambda_{\rm max}/{\rm nm}$	Extinction coefficient (ϵ)/dm ³ mol ⁻¹ cm ⁻¹
1	365	63,333
2	321	28,340
3	328	69,632
4	334	102,509

differences are hardly meaningful, and all are within the range reported for related square planar complexes of platinum(II) that contain a chelating phosphine group.¹⁰

Absorption and emission spectroscopy

For all four complexes the lowest energy absorption bands in the UV/visible spectra, in dichloromethane solution, at room temperature, occurred in the range 318-360 nm (Fig. 4 and Table 3). The lowest energy band, in each case, was assigned to a predominantly $\pi(C \equiv C) \rightarrow \pi^*(C \equiv C)$ transition by comparison with related systems.^{14,21} but can be considered to have some LMCT character because of the mixing of the π^* orbital of the ligand with the platinum (n + 1) p orbitals.²² A comparison of the spectra (Fig. 4) shows that there is a red shift in the energy of the lowest energy band in the order $2 \rightarrow 3 \rightarrow 4 \rightarrow 1$ as the electron donating properties of the substituent R group decrease. Thus, the absence of an extended chromophore such as bipyridine or terpyridine means that MLCT effects are less in the chelating phosphine stabilized systems compared to the related diimine complexes,14 however, the complexes do remain sensitive to the nature of the substituents on the ethynyl ligands. In addition, a comparison of these cis-chelating phosphine complexes (Table 3) with comparable *trans*-diphosphine platinum(II) alkynyls⁹ indicates that there is a blue shift in the absorption spectra of the *cis*-complexes compared to the *trans*-complexes, consistent with a lack of conjugation through the metal centres in the cis-series.



Fig. 4 The UV/visible absorption spectra of complexes 1–4, in CH_2Cl_2 , at room temperature.

The room temperature photoluminescence spectra, in dichloromethane, for complexes 1-4 are shown in Fig. 5. Complexes 2, 3 and 4 display one emission band in the blue region of the electromagnetic spectrum. The feature is attributable to emission from a singlet excited state (fluorescence) because of the small energy shift (Stokes' shift) between the absorption and emission bands; typical values for 2-methoxy-5-[(2'-ethylhexyl)oxy] derivatives of PPV (PPV = poly(pheylenevinylene) and MEH-PPV (MEH-PPV = poly(2'methoxy-5-(2'-ethylhexoxy)-1,4-pheylenevinylene) are in the range 0.2-0.3 eV.23 No phosphorescence is observed for any of these materials at room temperature. However, for 1, a weak, broad emission band in the green region of the spectrum, centred at approximately 565 nm, is observed. For this complex the absorption band is observed at 360 nm (3.43 eV) whereas the emission is at 565 nm (2.19 eV). The large Stokes' shift (1.24 eV)



Fig. 5 The emission spectra of complexes 1-4, in CH₂Cl₂, at room temperature. For complexes 2, 3 and 4 the excitation was in the range 320–350 nm while that for 1 was at 450 nm.

suggests that this emission does not originate from the observed absorption band, and it may be that the emission is from a triplet excited state stabilised by the strong spin–orbit coupling induced by the platinum centre,^{9,24} as has been observed in some platinum(II) alkyl monomers.²⁵ Some related platinum-containing complexes show no fluorescence band but only a phosphorescence band around 2.7 ev.^{2,26}

Conclusions

The new complexes cis-[Pt(dppe)(C=CR)₂] (dppe = 1,2bis(diphenylphosphino)ethane; $R = C_6H_4$ -p-NO₂ 1, C_6H_4 -p-CH₃ 2, C_6H_4 -*p*-C=CH 3 and C_6H_4 -*p*-C₆H₄-*p*-C=CH 4) have been prepared by the coupling reaction of *cis*-[Pt(dppe)Cl₂] with two equivalents of the appropriate alkyne, and have been characterised spectroscopically. The crystal structures of 1, 2 and 4 have been determined and it has been shown that the complexes adopt a square planar coordination geometry around the platinum(II) centre. There are no significant differences in the bonding parameters within the series and no strong intermolecular interactions. The UV/visible absorption and emission spectra, in solution, at room temperature, do show significant differences across the series that can be correlated to the differences in the nature of the R substituents. In this series of compounds, the lowest band gap is associated with complex 1 that has an electron withdrawing NO₂ group. The magnitude of the band gap of this type of system is governed by the π -electron conjugation. Electron withdrawing groups, that increase the electron density along the conjugated path, decrease the band gap.^{9,27} In complexes 1-4 the absorption spectra are dominated by $\pi(C\equiv C) \rightarrow \pi^*(C\equiv C)$ transitions and the higher lying orbitals include some platinum (n + 1)p orbital character. There is a red shift in the energy of the lowest energy band in the order $2 \rightarrow 3 \rightarrow 4 \rightarrow 1$ as the electron donating properties of the substituent R group increase. Thus, the absence of an extended chromophore such as bipyridine or terpyridine means that MLCT effects are less in the chelating phosphine stabilized systems compared to the related diimine complexes. The emission spectra of complexes 2, 3 and 4 display one fluorescence emission band in the blue region of the electromagnetic spectrum. However, for 1, a weak, broad band in the green region of the spectrum, centred at approximately 565 nm, attributable to a phosphorescence emission, is observed. Here, the triplet excited state is stabilised by the strong spin-orbit coupling induced by the platinum centre.

Experimental

All the reactions were performed under an inert atmosphere using standard Schlenk techniques, but no special precautions were taken to exclude oxygen during work-up. Platinum(II) dichloride

Table 4 Crystallographic data for structures 1, 2 and 4^a

Identification code	1	2	4
Empirical formula	$C_{42}H_{32}N_2O_4P_2Pt$	$C_{44}H_{38}P_2Pt$	$C_{61}H_{49}P_2Pt$
Formula weight	885.73	823.77	1039.03
Space group	$P2_1/n$	$P2_1/n$	P2/n
a/Å	8.4730(1)	8.6180(1)	16.3404(2)
b/Å	14.0020(2)	13.9790(2)	8.9013(1)
c/Å	30.4920(6)	29.9090(4)	32.8872(15)
β/°	91.167(1)	91.853(1)	95.902(1)
$V/Å^3$	3616.79(10)	3601.28(8)	4578.11(11)
Ζ	4	4	4
$D(\text{calc})/\text{Mg m}^{-3}$	1.627	1.519	1.450
μ/mm^{-1}	4.014	4.015	3.056
F(000)	1752	1640	2092
Reflections collected	49363	24838	31321
Independent reflections	6288 [R(int) = 0.1457]	10344 [R(int) = 0.0724]	10684 [R(int) = 0.0610]
Goodness-of-fit on F^2	1.165	1.038	1.080
Final <i>R</i> indices $[I > 2\sigma(I)]$: <i>R</i> 1, <i>wR</i> 2	0.0426, 0.1124	0.0404, 0.1015	0.0422, 0.1018
<i>R</i> indices (all data): <i>R</i> 1, <i>wR</i> 2	0.0743, 0.1585	0.0515, 0.1095	0.0669, 0.1300
Largest diff. peak and hole/e Å ⁻³	1.275 and -2.472	2.681 and -3.873	1.384 and -3.442

^{*a*} Common parameters: wavelength, $\lambda = 0.71073$ Å; temperature, T = 150(2) K; space group = monoclinic; absorption correction = semi empirical.

was obtained from Johnson Matthey, and CuI, Pd(OAc)₂, Ph₃P and $HC \equiv C - C_6 H_4 - C H_3$ were purchased from Sigma-Aldrich. Solvents were pre-dried from appropriate drying agents and freshly distilled before use.28 Grade II neutral alumina and Kieselgel 60 (70-230) were used for column chromatography. IR spectra were recorded as CH₂Cl₂ solutions, in a NaCl cell, on a Nicolet Nexus FTIR spectrometer. All the NMR samples were prepared as CDCl_3 solutions and standard ${}^1\text{H}$ NMR, ${}^{13}C{}^{1}H$ NMR and ${}^{31}P{}^{1}H$ NMR spectra were recorded on a Bruker NMR spectrometer at 300.22 MHz, 75.50 MHz and 121.53 MHz respectively. 1H NMR and $^{13}C\{^1H\}$ NMR were referenced to solvent resonances and ³¹P{¹H} NMR was referenced to external trimethyl phosphate. Mass spectra were recorded on Autospec Mass spectrometer by the fast atom bombardment (FAB) technique. Photoluminescence (PL) spectra for all the complexes were taken from 10⁻⁴ M dichloromethane solution. The photoluminescence spectra of the solutions were measured from a 10 mm quartz cuvette at room temperature using a PerkinElmer LS55 Luminescence spectrometer. The spectrometer has a range from 200 nm to 800 nm for excitation. Optical excitation was provided by a Xenon discharge lamp, spectrally resolved by a Monk-Gillieson type monochromator. The PL spectra of 2-4 were taken with excitation from the 320-350 nm light beams. The excitation lines were chosen such that the absorption was enough to excite the polymers. The PL spectrum of 1 was obtained with excitation at 450 nm light beam. The PL signals were passed through a second monochromator and the corrected emission data were collected using a redsensitive (400-900 nm) R928 photomultiplier. Microanalyses were performed at the Department of Chemistry, University of Bath, UK.

cis-[(dppe)PtCl₂],²⁹ HC \equiv C-C₆H₄-NO₂,³⁰ HC \equiv C-C₆H₄-C \equiv CH³⁰ and HC \equiv C-C₆H₄-C₆H₄-C \equiv CH³⁰ were prepared by literature methods.

Synthesis of [Pt(dppe)(C≡C-C₆H₄-NO₂)₂] 1

To a mixture of $CH_2Cl_2/diisopropylamine (3 : 1)$ cis-[(dppe)PtCl₂] (0.300 g, 0.45 mmol), HC=C-C₆H₄-NO₂ (0.198 g, 1.35 mmol) and CuI (17 mg) were sequentially added and the mixture was stirred for 24 h at room temperature under a N₂ atmosphere. The solvent was removed under reduced pressure. The residue was washed 3 times with hot *n*-hexane (50 ml × 3) to remove excess ligand. The precipitate was dissolved in a minimum volume of CH₂Cl₂ and applied to a short alumina column (5 inches). After removal of CH₂Cl₂ the bright yellow solid was isolated in 69% yield (0.275 g). Anal. Calc. for $C_{42}H_{32}O_4N_2P_2Pt:$ C, 56.95; H, 3.64; N, 3.16. Found: C, 57.2; H, 3.64; N, 3.21%.

Synthesis of [Pt(dppe)(C≡C-C₆H₄-CH₃)₂] 2

Similarly, [Pt(dppe)Cl₂] (0.3329 g, 0.05 mmol), HC=C-C₆H₄-CH₃ (0.228 g, 2 mmol) and CuI (15 mg) were stirred in CH₂Cl₂/diisopropylamine (3 : 1) for 24 h. Similar work-up gave a pale yellow solid in 86% yield (0.350 g). Anal. Calc. for C₄₄H₃₈P₂Pt: C, 64.15; H, 4.64. Found: C, 63.9; H, 4.69%.

Synthesis of $[Pt(dppe)(C \equiv C - C_6H_4 - p - C \equiv CH)_2]$ 3

The procedure of 1 was followed, but using $HC\equiv C-C_6H_4$ -*p*- $C\equiv CH$, and this afforded 3 as a pale yellow solid in 58% yield (0. 370 g). Anal. Calc. for $C_{46}H_{34}P_2Pt \cdot 0.5C_6H_{14}$: C, 66.4; H, 4.51. Found: C, 66.6; H, 4.33%.

Synthesis of $[Pt(dppe)(C \equiv C - C_6H_4 - p - C_6H_4 - p - C \equiv CH)_2] 4$

The same procedure as for 1 was followed but using HC=C- C_6H_4 -p- C_6H_4 -p-C=CH to give 4 as off white solid in 50% yield (0.375 g). Anal. Calc. for $C_{58}H_{42}P_2Pt$ -0.5 C_6H_{14} : C, 70.6; H, 4.6. Found: C, 70.4; H, 4.44%.

Crystallography

For crystal data, see Table 4.

Data collection and reduction. The crystals of 1, 2 and 4 were mounted in inert oil on glass fibres. Data were measured using Mo-K_a radiation ($\lambda = 0.71073$ Å) with a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream low-temperature attachment.

Structure solution and refinement. Structures were solved by direct methods (SHELXS-86)³¹ and subjected to fullmatrix least-squares refinement on F^2 (SHELXL-97).³² All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included using rigid methyl groups or a riding model.

CCDC reference numbers 269323–269325.

See http://dx.doi.org/10.1039/b505484b for crystallographic data in CIF or other electronic format.

Acknowledgements

We are grateful to the Leverhulme Trust, the Japanese Society for the Promotion of Science and the Royal Society for financial support (to M. Y.), Shahjalal University for study leave (to M. Y.), the University of Bath for a studentship (to L.-L. O.), and the EPSRC for funding to purchase the X-ray diffractometer. The generous loan of platinum salts by Johnson Matthey plc is gratefully acknowledged.

References

- 1 N. J. Long, Angew. Chem., Int. Ed. Engl., 1995, 34, 21; N. J. Long and C. K. Williams, Angew. Chem., Int. Ed., 2003, 42, 2586.
- 2 I. R. Whittall, A. M. McDonagh and M. G. Humphrey, Adv. Organomet. Chem., 1998, 42, 291; S. R. Marder, in Inorganic Materials, eds. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1996; S. Takahashi, E. Murata, M. Kariya, K. Sonogashira and N. Hagihara, Macromolecules, 1979, 12, 1016; D. W. Bruce, in Inorganic Materials, Eds. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1996; V. W.-W. Yam, K. K. W. Lo and K. M. C. Wong, J. Organomet. Chem., 1999, 578, 3; V. W.-W. Yam, Acc. Chem. Res., 2002, 35, 555; M. P. Cifuentes and M. G. Humphrey, J. Organomet. Chem., 2004, 689, 3968.
- 3 K. Sonogashira, S. Takahashi and N. Hagihara, Macromolecules, 1977, 10, 879; K. Sonogashira, T. Yatake, Y. Tahoda, S. Takahashi and N. Hagihara, J. Chem. Soc., Chem. Commun., 1977, 291.
- 4 B. F. G. Johnson, A. K. Kakkar, M. S. Khan and J. Lewis, J. Organomet. Chem., 1991, 409, C12; Z. Atherton, C. W. Faulkner, S. L. Ingham, A. K. Kakkar, M. S. Khan, J. Lewis, N. J. Long and P. R. Raithby, J. Organomet. Chem., 1993, 462, 265; C. W. Faulkner, S. L. Ingham, M. S. Khan, J. Lewis, N. J. Long and P. R. Raithby, J. Organomet. Chem., 1994, 482, 139.
- 5 M. S. Khan, N. A. Pasha, A. K. Kakkar, P. R. Raithby, J. Lewis, K. Fuhrmann and R. H. Friend, J. Mater. Chem., 1992, 2, 759.
- 6 N. Hagihara, K. Sonogashira and S. Takahashi, Adv. Polym. Sci., 1981, 41, 151; S. Takahashi, M. Kariya, T. Yatake, K. Sonogashira and N. Hagihara, Macromolecules, 1978, 11, 1063.
- 7 S. J. Davies, B. F. G. Johnson, J. Lewis and M. S. Khan, J. Organomet. Chem., 1991, 401, C43.
- 8 K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi and N. Hagihara, J. Organomet. Chem., 1978, 145, 101.
- 9 M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, F. R. Al-Battashi, S. Al-Saadi, B. Ahrens, J. K. Bjernemose, M. F. Mahon, P. R. Raithby, M. Younus, N. Chawdhury, A. Köhler, E. A. Marseglia, E. Tedesco, N. Feeder and S. J. Teat, Dalton Trans., 2004, 2377; M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, N. Feeder, S. Nahar, A. Köhler, R. H. Friend, P. J. Wilson and P. R. Raithby, J. Chem. Soc., Dalton Trans., 2002, 2441; M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, P. R. Raithby, B. Ahrens, L. Male, R. H. Friend, A. Köhler and J. S. Wilson, Dalton Trans., 2003, 65; M. S. Khan, M.R. A. Al-Mandhary, M. K. Al-Suti, P. R. Raithby, B. Ahrens, M. Mahon, L. Male, C. E. Boothby and A. Köhler, Dalton Trans., 2003, 74; N. Chawdhury, A. Köhler, R. H. Friend, M. Younus, N. J. Long and P. R. Raithby, Macromolecules, 1998, 31, 722; M. Younus, A. Köhler, S. Cron, N. Chawdhury, M. R. A. Al-Mandhary, M. S. Khan, N. J. Long, R. H. Friend and P. R. Raithby, Angew Chem., Int. Ed., 1998, 37, 3036; M. S. Khan, S. J. Davies, A. K. Kakkar, D. Schwartz, B. Lin, B. F. G. Johnson and J. Lewis, J. Organomet. Chem., 1992, 424, 87; C. W. Faulkner, S. L. Ingham, M. S. Khan, J. Lewis, N. J. Long and P. R. Raithby, J. Organomet. Chem., 1994, 482, 139; J. Lewis, M. S. Khan, A. K. Kakkar, B. F. G. Johnson, T. B. Marder, H. F. Wittmann, R. H. Friend and A. E. Dray, J. Organomet. Chem., 1992, 425, 165; J. Lewis, M. S. Khan, A. K. Kakkar, B. F. G. Johnson, T. B. Marder, H. F. Wittmann, R. H. Friend and A. E. Dray, J. Mater. Chem., 1992, 2, 759; P. Altamura, G. Giardina, C. L. Sterzo and M. V. Russo, Organometallics, 2001, 20, 4360; J. Lewis, N. J. Long, P. R. Raithby, G. P. Shields, W. Y. Wong and M. Younus, J. Chem. Soc., Dalton Trans., 1997, 4283; P. Haquette, N. Pirio, D. Touchard, L. Toupet and P. H. Dixneuf, J. Chem. Soc., Chem. Commun., 1993, 163; D. Touchard, C. Morice, V. Cadierno, P. Haquette, L. Toupet and P. H. Dixneuf, J. Chem. Soc., Chem. Commun., 1994, 859; D. Touchard, P. Haquette, S. Guesmi, L. L. Pichon, A. Daridor, L. Toupet and P. H. Dixneuf, Organometallics, 1997, 16, 3640; L. D. Field, A. V. George, T. W. Hambley, E. Y. Malouf and D. J. Young, J. Chem. Soc., Chem. Commun., 1990, 931; L. D. Field, A. V. George, E. Y. Malouf, I. H. M. Slip and T. W. Hambley, Organometallics, 1991, 10, 3842; L. D. Field, A. V. George, D. C. R. Hockless, G. R. Purches and A. H. White, J. Chem. Soc., Dalton Trans., 1996, 2011; T. Yamamoto, T. I. Morikita, T. Maruyama, K. Kubota and M. Katada, Macromolecules, 1997, 30, 3590.

- 10 M. I. Bruce, K. Costuas, J.-F. Halet, B. C. Hall, P. J. Low, B. K. Nicholson, B. W. Skelton and A. H. White, J. Chem. Soc., Dalton Trans., 2002, 383.
- 11 S. M. Al-Qaisi, K. J. Galat, M. Chai, D. G. Ray, P. L. Rinaldi, C. A. Tessier and W. J. Youngs, J. Am. Chem. Soc., 1998, 120, 12149; J. A. Whiteford, C. V. Lu and P. J. Stang, J. Am. Chem. Soc., 1997, 119, 2524.
- 12 J. Fornies, M. A. Gomez-Saso, E. Lalinde, M. Martinez and M. T. Moreno, Organometallics, 1992, 11, 2873; S. Yamazaki and A. J. Deeming, J. Chem. Soc., Dalton Trans., 1993, 3051.
- 13 S. L. James, M. Younus and P. R. Raithby, J. Organomet. Chem., 1997, 543, 233; C. J. Adams and P. R. Raithby, J. Organomet. Chem., 1999, 578, 178; C. J. Adams, S. L. James, X. Liu, P. R. Raithby and L. J. Yellowlees, J. Chem. Soc., Dalton Trans., 2000, 63; W.-Y. Wong, G.-L. Lu and K.-H. Choi, J. Organomet. Chem., 2002, 659, 107
- 14 H. Laing, A. del Vilar and G. Rheinwald, J. Organomet. Chem., 1999, 587, 284; P. K. Sui, S.-W. Lai, W. Lu, N. Zhu and C.-M. Che, Eur. J. Inorg. Chem., 2003, 2749; Y. Kong, J. Lee, D. Song and S. Wong, Dalton Trans., 2003, 3483; H. Heisler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte and R. Eisenberg, Inorg. Chem., 2003, 42, 8772; S.-C. Chan, M. C. W. Chan, Y. Wong, C.-M. Che, K.-K. Cheung and N. Zhu, Chem. Eur. J., 2001, 7, 4180; Y.-Y. Ng, C.-M. Che and S. M. Peng, New J. Chem., 1996, 20, 781.
- 15 M. A. Baldo, D. F. O'Brien, Y. Yok, A. A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forest, Nature, 1998, 395, 151; W. Lu, B. X. Mi, M. C. W. Chan, Z. Hui, N. Y. Zhu, S. J. Lu and C.-M. Che, Chem. Commun., 2002, 206; C.-M. Che, S. C. Chan, H. F. Xiang, M. C. W. Chan, Y. Liu and Y. Wong, Chem. Commun., 2004, 1484; B. W. D'Andrade, J. Brooks, V. Adanovich, M. E. Thompson and S. R. Forrest, Adv. Mater., 2002, 14, 1032.
- 16 H.-F. Xiang, S.-C. Chan, K. K.-Y. Wu, C.-M. Che and P. T. Lai, Chem. Commun., 2005, 1408.
- 17 M. V. Russo, C. Lo Sterzo, P. Franceschini, G. Biagini and A. Furlani, J. Organomet. Chem., 2001, 619, 49.
- 18 A. D. Burrows, D. M. P. Mingos, S. E. Lawrence, A. J. P. White and D. J. Williams, J. Chem. Soc., Dalton Trans., 1997, 1295.
- 19 C. J. Cardin, D. J. Cardin and M. F. Lappert, J. Organomet. Chem., 1973, 60, C70; M. A. Cairns, K. R. Dixon and G. A. Rivett, J. Organomet. Chem., 1979, 171, 373.
- 20 L. R. Falvello, J. Fornies, J. Gomez, E. Lalinde, A. Martin, M. T. Moreno and J. Sacristan, Chem. Eur. J., 1999, 5, 474.
- 21 C. E. Whittle, J. A. Weinstein, M. W. George and K. S. Schanze, Inorg. Chem., 2001, 40, 4053.
- 22 T. L. Schull, J. G. Kushmerick, C. H. Patterson, C. George, M. H. Moore, S. K. Pollack and R. Shashidhar, J. Am. Chem. Soc., 2003, 125, 3202; M. Younus, N. J. Long, P. R. Raithby and J. Lewis, J. Organomet. Chem., 1998, 570, 55; H. Masai, K. Sonogashira and N. Hagihara, Bull. Chem. Soc. Jpn., 1971, 44, 2226; Y. Fujikura, K. Sonogashira and N. Hagihara, Chem. Lett., 1975, 1067.
- 23 T. H. Hagler, K. Pakbaz, K. Voss and A. J. Heeger, Phys. Rev. B., 1991, 44, 8652; T. H. Hagler, K. Pakbaaz and A. J. Heeger, Phys. Rev. B., 1995, 51, 14199.
- 24 H. F. Wittman, R. H. Friend, M. S. Khan and J. Lewis, J. Chem. Phys., 1994, 4, 2693.
- 25 I. Fratoddi, C. Battocchio, A. Furlani, P. Mataloni, G. Polzonetti and M. V. Russo, J. Organomet. Chem., 2003, 674, 10.
- 26 M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, A. K. Hisham, P. R. Raithby, B. Ahrens, M. F. Mahon, L. Male, E. A. Marseglia, E. Tedesco, R. H. Friend, A. Köhler, N. Feeder and S. J. Teat, J. Chem. Soc., Dalton Trans., 2002, 1358.
- 27 M. C. B. Colbert, J. Lewis, N. J. Long, P. R. Raithby, M. Younus, A. J. P. White, D. J. Williams, N. N. Payne, L. Yellowlees, D. Beljonne, N. Chawdhury and R. H. Friend, Organometallics, 1998, 17, 3034.
- 28 R. J. Errington, Advanced Practical Inorganic and Metalorganic Chemistry, Chapman and Hall, London, 1997.
- 29 N. J. Long, A. J. P. White, D. J. Williams and M. Younus, J. Organomet. Chem., 2002, 649, 94.
- 30 S. Takahashi, Y. Kuroyama, K. Sonogahara and N. Hagihara, Synthesis, 1980, 627.
- 31 G. M. Sheldrick, SHELXS-86, Program for Crystal Structure Solution, University of Göttingen, Germany, 1986.
- 32 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.