

Synthesis, structural characterisation and photophysics of anionic cyclometalated bis(alkynyl)(benzo[*h*]quinolate)platinate(II) species

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The alkylation of $[\text{Pt}(\text{bzq})(\mu\text{-Cl})_2]$ ($\text{bzqH} = \text{benzo}[h]\text{quinoline}$) with excess of $\text{LiC}\equiv\text{CR}$ in diethyl ether leads to novel (7,8-benzoquinolate)bis(alkynyl)platinate(II) monoanionic species $[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CR})_2]^-$ ($\text{R} = \text{}^t\text{Bu}$ **1**, SiMe_3 , **2**, Ph **3**, Tot **4**, $\text{C}_6\text{H}_4\text{CF}_3$ -**4** **5**, $\text{C}_5\text{H}_4\text{N}$ -**2** **6**, $\text{C}_6\text{H}_4\text{-C}\equiv\text{CPh}$ **7**) which have been isolated as tetrabutylammonium salts. The molecular X-ray structures of **3** and **6** reveal the presence of discrete anions with bond lengths and angles similar to those of related cyclometalated Pt compounds and no evidence of $\pi\text{-}\pi$ or Pt–Pt stacking interactions. The influence of the R substituent on the photophysics of the complexes has been examined by UV-visible absorption, emission spectroscopy and cyclic voltammetry. Complexes **1–6** show a similar strong luminescence in both the solid state (structureless emission) and frozen solutions (well-resolved vibronic structures) while the emissions in solution at room temperature are red shifted (relative to the glass) and weak. For these complexes, on the basis of TD-DFT calculations which reproduce the experimental structure of anion **3**, $[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CPh})_2]^-$, the emissions are proposed to arise from mixed $[\pi \text{C}\equiv\text{CR}/\text{Pt } d/\pi (\text{bzq}) \rightarrow \pi^* \text{bzq}]$ transitions. In contrast, complex **7** which contains the extended *p*-phenylethynylphenylacetylide ligand, $\text{C}\equiv\text{CC}_6\text{H}_4\text{-C}\equiv\text{CPh}$, displays a structured emission both at 298 K and in glassy CH_2Cl_2 solutions. In this case the lack of a significant rigidochromism and DFT theoretical calculations support the involvement of a low-lying, metal perturbed acetylenic ${}^3\pi\pi^*$ ($\text{C}\equiv\text{CC}_6\text{H}_4\text{-C}\equiv\text{CPh}$) excited state.

Introduction

The chemistry of metal alkynyl complexes has long been the subject of intense study mainly due to the versatile reactivity of the unsaturated fragment and its wide variety of modes of interaction with transition metals.¹ Within this field the synthesis of platinum acetylides has recently focused on the preparation of specialty materials including non-linear optical,² luminescent,³ liquid crystalline⁴ materials or the synthesis of conjugated metal containing polymers.⁵ Platinum σ -acetylide has also been employed as a building block for molecular wires,⁶ macrocycles⁷ or hyperbranched⁸ and dendritic molecules⁹ which are particularly attractive due to their potentially useful redox, photophysical or catalytical properties. By far the most work has been carried out with neutral *trans*- and *cis*-platinum phosphine fragments.

The properties of platinum(II) complexes with chelate diimine, terpyridyl or related cyclometalated ligands have attracted considerable attention in recent years¹⁰ and, in this context, a few systems containing alkynyl fragments have been also prepared.^{11–13} These complexes usually exhibit long-lived excited states mainly localized in the aromatic π systems which are attractive for applications in chemical sensing, photocatalysis and in the development of supramolecular systems for solar energy conversion. Additionally, for these square planar d^8 molecules, the axial positions are relatively open and vulnerable to both nucleophilic attack and intermolecular Pt \cdots Pt stacking, facilitating exciplex quenching,^{10g,11a} photoinduced atom-transfer¹⁴ or excimer formation and excimer emission when the excitation is delocalized through metal–metal interactions.^{10k,15} The influence of non-covalent $\pi\text{-}\pi$ ligand contacts on the photoluminescence of this type of luminophores also has many precedents.^{10e,k,16} It has also been shown that the nature of the ancillary ligands can have marked effects on the lowest emitting state. Thus, the incorporation of acetylide groups into these systems usually tunes the energy of the emission attributed to a triplet metal-to-ligand (chelate aromatic π system)

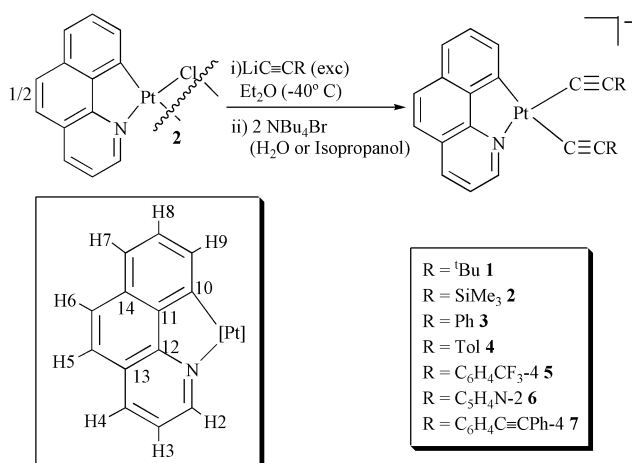
charge transfer by variation of the R substituent through the Pt–C \equiv CR interaction,^{11–13} however, in some complexes, depending on the nature of the R substituent, the photophysics are derived from transitions between π and π^* type orbitals largely located on the aryl acetylide groups.^{11a,12a,c} Despite considerable progress in this area, most of the studies have focused on neutral or cationic species and very little attention has been devoted to exploring anionic systems.¹⁷

Recently, we have described the synthesis of homoleptic $\text{Q}_2[\text{Pt}(\text{C}\equiv\text{CR})_4]^{18a,b}$ and heteroleptic *cis*- and *trans*- $\text{Q}_2[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{C}\equiv\text{CR})_2]$ ($\text{R} = \text{Ph}$, ${}^t\text{Bu}$, SiMe_3)^{18c–e} dianionic alkynyl platinate compounds and have shown that they are suitable precursors for the preparation of homo and hetero (Pt–M, M = Cu(I), Ag(I), Cd(II), Hg(II), Tl(I), Rh(I,III) or Ir(I,III)) polynuclear complexes stabilised by alkynyl and/or by Pt \cdots M bonding interactions.^{19–20} A number of these complexes have been shown to have luminescence properties that are associated with Pt \cdots Pt, Pt \cdots M and $\eta^2\cdots$ M alkynyl bonding interactions.²² In view of these results, we considered it worthwhile to prepare monoanionic bis(alkynyl)cycloplatinate species of type $[\text{Pt}(\text{C}\wedge\text{N})(\text{C}\equiv\text{CR})_2]^-$ in order to study their potential as precursors of novel Pt–M (M = Tl, Cd or Hg) polynuclear complexes and also gain further insights into the involvement of Pt \cdots M or $\eta^2\cdots$ M alkynyl contacts in the excited-state properties of this type of cluster complexes. Here we describe the synthesis, electronic absorption, luminescence and electrochemical properties of a series of bis(alkynyl)platinate compounds (NBu_4)- $[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CR})_2]$ (**1–7**) containing the planar orthometallated 7,8-benzoquinoline ligand (bzq).

Results and discussion

Synthesis and spectroscopic characterisation

The synthesis of the complexes is shown in Scheme 1. Treatment of a yellow suspension of the dinuclear cycloplatinate chloride-bridged complex $[\text{Pt}(\text{bzq})(\mu\text{-Cl})_2]$ ($\text{bzqH} = \text{benzoquinoline}$



Scheme 1

ligand) with an excess of $\text{LiC}\equiv\text{CR}$ in diethyl ether causes partial or total dissolution of the initial yellow suspension, leading to the formation of the anionic species $[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CR})_2]^-$. These anionic species, after usual work up by solvent removal, followed by extraction with deoxygenated H_2O or *i*-PrOH and subsequent addition of NBu_4^+ salts in moderate to good yields (32–83%). While neutral or cationic alkynyl cycloplatinated compounds are known,¹¹ to our knowledge these complexes (1–7) are the first examples of anionic systems. We also noted that whereas Robinson and coworkers,^{11e} in the reaction of $[\text{Pt}\{\text{NCMe}_2\text{NCH}_2(\sigma\text{-Fc})\}\text{Cl}(\text{dmsO})]$ and $\text{LiC}\equiv\text{CPh}$, observed facile reductive elimination giving rise to 1-dimethylamino-methyl-2-phenylethynylferrocene, complexes 1–7 are thermally stable in the solid state and in solution (at low temperature).

The new complexes 1–7 were obtained as bright yellow solids and were fully characterized by elemental analysis, IR and NMR (^1H , ^{13}C) spectroscopy, EI mass spectrometry as well as single crystal X-ray crystallography for 3 and 6. All complexes give the expected negative ion $[\text{M}]^-$ (100%) in their negative-ion ES spectra and conductivity measurements in acetone confirm their behaviour as 1 : 1 electrolytes. The IR spectra show two $\nu\text{C}\equiv\text{C}$ intense absorptions (2008–2108 cm^{-1}) consistent with a *cis* configuration of the alkynyl ligands around the Pt(II) center. For complex 7 one additional absorption is observed at 2209 cm^{-1} which is attributed to terminal free alkyne fragments. The NMR data unambiguously reveal the presence of the 7,8-benzoquinolate ligand and the existence of two inequivalent alkynyl groups. A general labelling scheme for the inequivalent bzq proton and carbon atoms is shown in Scheme 1. The NMR data which were assigned on the basis of ligand spectra, the presence of coupling constants and the results from two dimensional ^1H – ^1H and ^1H – ^{13}C COSY experiments performed on complex 3 are collected in the Experimental section. The ^1H NMR spectra (CD_3COCD_3) exhibit two characteristic low field doublets of doublets with platinum satellites in the ranges 9.39–10.17 (ppm) and 8.37–8.66 (ppm) due to the H^2 and H^9 protons, respectively. Both signals are considerably shifted to high frequencies in comparison with the free ligand (δ H^2 9.29; H^9 7.79) indicating that both rings act as good π acceptors. The ^{195}Pt coupling constants (25–27.3 Hz for H^2 and 35–43 Hz for H^9) are characteristic of values observed for related Pt(II) complexes.^{10b,m,21} In the high-field region, two different Bu^t (δ 1.34, 1.32) or SiMe_3 (δ 0.15, 0.149) resonances in complexes 1 and 2 confirm the presence of non-equivalent alkynyl entities. The low temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of all complexes show the expected resonances for the bzq ligand, in addition to those of the NBu_4^+ cation and the two $\text{C}\equiv\text{CR}$ groups (*trans* to C^{10} and *trans* to N). The metalate C^{10} carbon is found at high frequency (162.0–164.18 ppm) and the expected large $^1J(^{195}\text{Pt}-^{13}\text{C})$ coupling (735–777 Hz) is observed (except for complexes 4 and 7).

Table 1 Selected bond lengths [\AA] and angles [$^\circ$] for $(\text{NBu}_4)[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CPh})_2]$ 3

Pt(1)–C(1)	2.007(9)	Pt(1)–C(9)	1.985(11)
Pt(1)–N(1)	2.065(8)	Pt(1)–C(29)	2.055(7)
C(1)–C(2)	1.183(10)	C(9)–C(10)	1.188(12)
C(1)–Pt(1)–C(9)	92.4(3)	C(1)–Pt(1)–C(29)	93.8(3)
C(9)–Pt(1)–N(1)	94.1(4)	C(29)–Pt(1)–N(1)	79.7(3)

Table 2 Selected bond lengths [\AA] and angles [$^\circ$] for $(\text{NBu}_4)[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CC}_5\text{H}_4\text{N-2})_2]$ 6 (molecules A and B)

Pt(1)–C(1)	1.976(6)	Pt(1)–C(8)	1.992(5)
Pt(1)–N(3)	2.074(4)	Pt(1)–C(25)	2.050(4)
C(1)–C(2)	1.205(7)	C(8)–C(9)	1.201(6)
C(1)–Pt(1)–C(8)	93.74(19)	C(1)–Pt(1)–C(25)	93.65(18)
C(8)–Pt(1)–N(3)	92.06(19)	C(25)–Pt(1)–N(3)	80.60(18)
Pt(2)–C(28)	1.975(6)	Pt(2)–C(35)	1.975(5)
Pt(2)–N(6)	2.063(4)	Pt(2)–C(52)	2.047(4)
C(28)–C(29)	1.182(6)	C(35)–C(36)	1.209(6)
C(35)–Pt(2)–C(28)	93.74(19)	C(28)–Pt(2)–C(52)	92.44(18)
C(35)–Pt(2)–N(6)	92.93(19)	C(52)–Pt(2)–N(6)	80.92(18)

By comparison the $^1J(^{195}\text{Pt}-^{13}\text{C})$ coupling to the cyclometalated C atoms *trans* to alkynyl in complexes $[\text{Pt}(\text{C}\equiv\text{CR})(\text{NMe}_2\text{NCH}_2(\sigma\text{-Fc}))(\text{dmsO})]^{11e}$ and $[\text{Pt}\{\eta^3\text{-}N,C,N\text{-C}_3\text{H}_3(\text{CH}=\text{NR})_2\text{-}2,6\}(\text{C}\equiv\text{CSiMe}_3)]$ ($\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$)^{11d} was 790 and 616 Hz, respectively. For complexes 1–3 the expected two C_α and two C_β alkynyl carbons exhibit platinum satellites allowing unambiguous assignment. In the three cases one of the C_α signals appears at rather high field [δ C_α (*trans* to N) 77.7 1; 119.24 2; 98.05 3] with respect to the other one [δ C_α (*trans* to C^{10}) 110.95 1; 152.38 2; 123.8 3 ($\Delta\delta$ C_α 33.25 1, 33.14 2, 25.75 3)] and exhibits the largest platinum coupling constant [1490 1; 1407 2; 1488 Hz 3 vs. 902 1; 895 Hz 2; not observed for 3], and is therefore attributed to the alkynyl group located *trans* to the iminic N atom. It is remarkable that the high frequency signal, which is assigned to the C_α carbon atom located *trans* to the ortometalated C^{10} atom, is shifted downfield (*ca.* 10 ppm) in relation to the homoleptic species $[\text{Pt}(\text{C}\equiv\text{CR})_4]^-$ species ($\text{R} = \text{Bu}^t$ 98.9; SiMe_3 140.4; Ph 120.9 ppm).²² The observed $^1J(^{195}\text{Pt}-^{13}\text{C})$ coupling for this C_α carbon *trans* to C^{10} decreases slightly from those observed in the dianionic complexes $[\text{Pt}(\text{C}\equiv\text{CR})_4]^{2-}$ ($\text{R} = \text{Bu}^t$ 975 Hz, $\text{R} = \text{SiMe}_3$ 924 Hz, $\text{R} = \text{Ph}$ 982 Hz)²² suggesting a similar *trans* influence for the cyclometalating sp^2 and alkynyl sp carbons. The C_β alkyne carbon of the alkynyl fragment *trans* to the iminic N atom appears also slightly shifted downfield ($\Delta\delta$ C_β 3.8 1 and 2; 2.9 3) and exhibits a notably higher $^2J(^{195}\text{Pt}-^{13}\text{C})$ coupling constant (415 1; 374 2; 433 Hz 3 vs. 230 1; 205 2 and 235 Hz 3) as a result of the very low *trans* influence of the iminic N donor atom. For the remaining complexes the absence of platinum satellites precludes the assignment of these carbons. On the basis of the data on complexes 1–3 and the resonances in the corresponding homoleptic species a tentative assignment is included in the Experimental section.

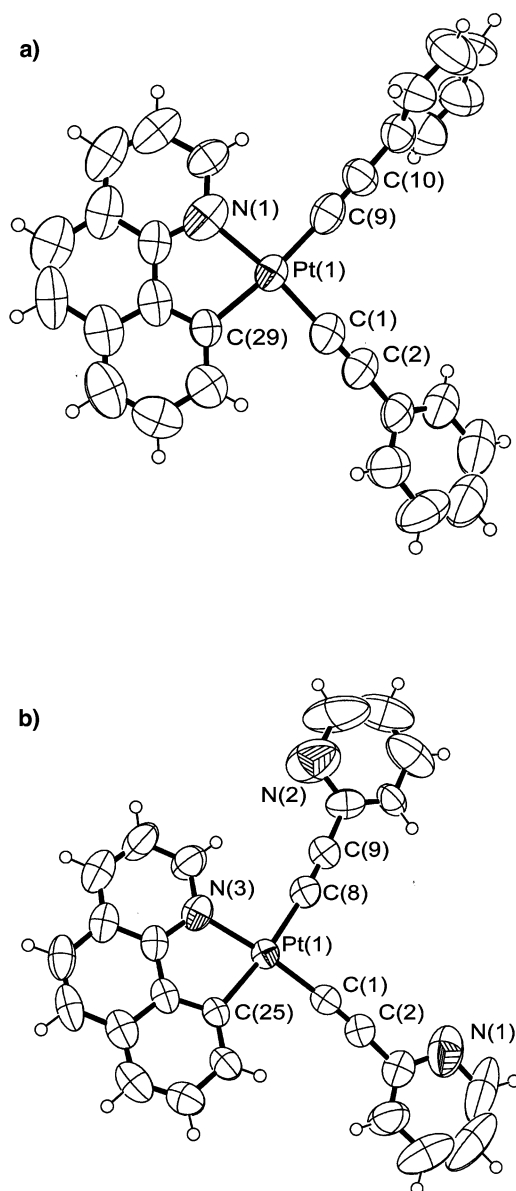
X-Ray crystal structures of $(\text{NBu}_4)[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CR})_2]$, $\text{R} = \text{Ph}$ 3, $\text{R} = \text{C}_5\text{H}_4\text{N-2}$ 6

The X-ray crystal structures of 3 and 6 were obtained, and their structural features are almost identical. For complex 6 two distinct but crystallographically similar anions are found in the unit cell. Selected bond distances and angles are given in Tables 1 and 2. Drawings of the anion of 3 and one of the anions of 6 (anion A) are given in Fig. 1.

In both molecules the platinum center exhibits the expected square planar coordination and the benzoquinoline ligand is essentially flat (the largest deviations from the main planes defined by the metalocycle atoms are 0.102 \AA 3 and 0.144 \AA for

Table 3 Absorption ($\sim 2 \times 10^{-5}$ M solutions) and electrochemical data for complexes 1–7

Compound	Absorption/nm ($10^3 \epsilon/M^{-1} \text{ cm}^{-1}$)	E°/V
1	268(34), 308(14.8), 347(11.3), 409(7.7) (CH_2Cl_2)	0.680
2	272(24.3), 303(10.2), 345(10.4), 392(6.7), 429(2.6) (CH_2Cl_2)	0.852
3	275(231), 351(18.1), 397(10.3) (CH_2Cl_2) 352(14.2), 405(9.1) (acetone) 347(27.0), 392(15.6) (CH_3CN)	0.836
4	270(29.4), 285(29.4), 304(23.6)sh, 351(11.1), 408(7.0) (CH_2Cl_2)	0.820
5	265(406), 306(49.6), 346(30.0), 392(13.0) (CH_2Cl_2) 345(18.3), 398(8.3) (acetone) 329(23.0), 344(23.4), 393(11.9) (CH_3CN)	0.944
6	263(33.9), 308(27.2), 348(16.5), 393(8.9) (CH_2Cl_2)	1.006
7	267(38.5), 335(66.5), 350(67.6), 400(23.2) (CH_2Cl_2)	0.854

**Fig. 1** Molecular structure of a) the anion $[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CPh})_2]^-$ in **3**, b) the anion $[\text{Pt}(\text{bzq})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{N}-2)]^-$ (A) in **6**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

6), while the phenyl or pyridyl rings of the acetylide are tilted (27.6 and 118.2 **3**; 6.9 and 6.2° **6**) from the platinum coordination plane. Bond lengths and angles within the anions are the usual for this type of complex and there are no significant interactions arising from packing arrangements. The small chelate bite N–Pt–C angles of the bzq ligand [$79.7(3)$ **3** and $80.60(18)^\circ$ **6**] are characteristic of five-membered cyclometalated platinum(II) compounds.^{10a-c,m,11d,e,21,23} The $\text{C}_a\text{--Pt--C}_a$ angle [$92.4(3)^\circ$

3 and $93.74(19)^\circ$ for **6**] and the twist angle between the PtNC(bzq) and the PtC_aC_a planes (2.5° for both complexes) are comparable to those observed in the related neutral *cis* complex $[\text{Pt}(\text{phen})(\text{C}\equiv\text{CTol})_2]$ (92.52° ; 9.6°).^{12c} The ethynyl groups in **3** and **6** show the expected linear arrangement. Despite the presence of different *trans* donor atoms (N and C) the Pt–C acetylide bond lengths observed [$1.985(11)$ and $2.007(9)$ Å **3**; $1.976(6)$ and $1.992(5)$ Å **6**] are identical within experimental error. These values are slightly longer than those reported for neutral platinum(II) diimine bis(acetylide) complexes¹² (cf. $1.948(3)$ Å in $[\text{Pt}(\text{phen})(\text{C}\equiv\text{CTol})_2]$ ^{12c}) and in the N–C–N orthometallated derivative $[\text{Pt}\{\eta^3\text{-N,C,N-C}_3\text{H}_3(\text{CH}=\text{NR})_2\text{-2,6}\}(\text{C}\equiv\text{CSiMe}_3)]$ ($\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) ($1.945(2)$ Å)^{11d} but perceptibly shorter than the corresponding distances found in $[\text{Pt}(\text{C}\equiv\text{CR})(\text{Me}_2\text{NCH}_2\text{-}(\sigma\text{-Fc}))(\text{dmsO})]$ ($\text{R} = \text{SiMe}_3$, $2.076(5)$; Fc $2.059(6)$ Å),^{11e} Pt–C bonds to the bzq ring [$2.055(7)$ Å for **3** and $2.050(4)$ Å for **6**] are slightly longer than the corresponding distances in the homoleptic derivative *cis*- $[\text{Pt}(\text{bzq})_2]$ [$1.999(12)$, $1.976(9)$ Å],²¹ a variation that may reflect the high *trans* influence of the alkynyl ligands. The Pt–N bond distances [$2.065(8)$ **3**; $2.074(4)$ **6**] are shorter than those found in *cis*- $[\text{Pt}(\text{bzq})_2]$ [$2.153(8)$ and $2.149(9)$ Å],²¹ probably caused by the higher *trans* influence of the $\text{C}(\text{sp}^2)$ aryl carbon relatively to the $\text{C}(\text{sp})$ acetylide, but compare well with those observed in related cycloplatinate complexes which incorporate a N donor in a five-membered metalacycle.²³

Optical properties and TD-DFT calculations

The UV/Vis absorption data are summarised in Table 3. All complexes show intense absorption bands at 263–351 nm ($\epsilon > 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) which are probably due to ligand-centred transitions ($1\text{IL } \pi \rightarrow \pi^*$) of the bzq cyclometalated and/or alkynide groups. Complexes **1–6** also exhibit a moderately intense low-energy feature (392–409 nm, ϵ $6.7\text{--}13 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) with a shoulder at 429 nm in the case of complex **2**. Complex **7**, containing the extended diynyl ligand, exhibits an absorption spectrum that is significantly different, in particular the low energy band which is located at *ca.* 400 nm possesses a molar absorption coefficient that is substantially higher ($23200 \text{ M}^{-1} \text{ cm}^{-1}$) than the rest of the complexes. In order to check the influence of the solvent, the absorption spectra for some complexes (**3**, **5** and **7**) were also collected in acetone and acetonitrile (see Table 3). The small solvatochromic shift of the lowest energy absorption is indicative of their charge-transfer nature.

In previous studies with homoleptic, heteroleptic and mixed platinum(II) complexes based on cyclometalated C \wedge N aromatic ligands,^{10b,l,m,11a,17,21,23} the solvatochromic low energy absorption bands in the range 350–450 nm have been mainly attributed to metal-to-ligand charge-transfer transitions. In the present work examination of the spectra for complexes **1–7** and comparison with related homoleptic $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{CR})_4]$ complexes indicates the following points. Firstly, it is evident that the aggregate transition comprising the low energy band (~ 400 nm) shifts to lower energy as the electron donating properties of the acetylide substituents increase ($\text{Bu}^t \sim \text{Tol} > \text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CPh} \sim \text{C}\equiv\text{CPh}$

Table 4 Population analysis (%) for the anion [Pt(bzq)(C≡CPh)₂]⁻ **3**

	Pt	(C≡CPh) ₂ [(C≡C) ₂]	bzq
HOMO - 5	8.5	37.9 [6.3]	53.7
HOMO - 4	12.1	58.8 [1.4]	29.1
HOMO - 3	29.1	40.7 [8.1]	30.2
HOMO - 2	15.4	56.3 [20.2]	28.3
HOMO - 1	14.6	60.6 [20.9]	24.8
HOMO	16.0	58.6 [18.4]	25.4
LUMO	7.4	15.2 [4.2]	77.4
LUMO + 1	5.8	22.9 [4.9]	71.2
LUMO + 2	6.4	65.4 [9.9]	28.2
LUMO + 3	4.9	71.6 [9.1]	23.5

> C≡C-C₆H₄-CF₃ ~ C≡C-Py-2 ~ SiMe₃) suggesting that the HOMO is predominantly metal perturbed π C≡CR centred ligand or metal based. Secondly, for complexes **1–6** these bands are significantly red-shifted from the analogous low energy absorptions observed in the corresponding homoleptic complexes (NBu₄)₂[Pt(C≡CR)₄] which are tentatively assigned as ¹MLCT (Pt d/ π C≡CR \rightarrow π^* C≡CR) (*i.e.* 397 nm **3** vs. 362 nm for (NBu₄)₂[Pt(C≡CPh)₄]). This fact suggests that the LUMO of the optical transition is presumably localized on the bzq ligand. For these complexes, the low energy transitions observed are therefore mainly attributed to spin-allowed metal perturbed ligand (acetylide)-to-ligand (benzoquinolate) charge-transfer (Pt d/ π C≡CR \rightarrow π^* bzq). For complex **2** the long wavelength shoulder located at 429 nm is tentatively assigned as a transition to the corresponding triplet state. The proposed assignment is additionally supported by DFT calculations on complex **3**, which give an overall picture of the valence orbitals. The B3LYP density functional theory (DFT) calculations essentially reproduce the experimental structure of complex **3**. The relative compositions of the different energy levels in terms of composing fragments are reported in Table 4. As can be seen the HOMO is a π orbital which is predominantly formed by the C≡CPh fragments with additional contributions from Pt(5d) (16%) and the orthometallated phenyl portion (25%) of the bzq. The HOMO - 1 and HOMO - 2 also consist of a roughly 60% contribution of the C≡CPh fragments and similar contributions of Pt and bzq orbitals. The lowest lying unoccupied molecular orbital LUMO is mainly localised over the bzq ligand with a notable contribution of the orbitals of the pyridyl and central fused aromatic ring. The LUMO + 1 is also centred in the C \wedge N ligand while the following unoccupied molecular orbitals are π^* C≡CR in character, being located 1.47 and 1.73 eV respectively above the LUMO.

The overall picture is similar to those reported recently for model complexes [Pt(C≡CH)₂(COD)] and [Pt(C≡CH)₂-(ⁱPr-DAB)] (ⁱPr-DAB = *N,N'*-diisopropyl-1,4-diazabutadiene) based on DFT calculations.²⁴ In contrast to previous assignments^{12,16a} (as MLCT transitions) the low absorption bands found in complexes [Pt(C≡CH)₂(COD)] and [Pt(C≡CH)₂-(ⁱPr-DAB)] have been also attributed to L'LCT and mixed MLCT/L'LCT or L'LCT [L'LCT = ligand (C≡CR)-to-ligand (π^* diimine) charge transfer] transitions respectively.²⁴ In platinum chemistry L'LCT transitions have been also found in α -diimine bis-thiolate compounds.^{16,25}

For complex **7** the low-energy band has a high extinction coefficient and does not show a notable solvatochromic effect suggesting the notable contribution of an additional different transition. In this case the lowest optical transition is attributed to a transition based on the extended alkynyl ligand having mainly metal perturbed $\pi \rightarrow \pi^*$ (C≡CR) character. Additional evidence supporting this assignment is based on DFT calculations (Table 5). In this case the electronic structure is somewhat different from that of **1–6** and this is due to the fact that the extended C≡C-C₆H₄-C≡C-Ph alkynyl ligands have relatively low-lying unoccupied π^* orbitals. Thus, while the highest-lying four MOs of complex **7** have a similar

Table 5 Population analysis (%) for the anion [Pt(bzq)(C≡CC₆H₄-C≡CPh)₂]⁻ **7**

	Pt	(C≡CC ₆ H ₄ -C≡CPh) ₂	bzq
HOMO - 3	27.7	42.3	30.0
HOMO - 2	11.5	62.6	25.9
HOMO - 1	11.9	67.3	20.7
HOMO	13.6	62.6	23.8
LUMO	2.7	80.0	17.4
LUMO + 1	1.9	76.6	21.5
LUMO + 2	4.3	53.7	41.9
LUMO + 3	0	100	0

composition to complex **3** with π alkynyl contributions of over 60% (Table 5), the first two unoccupied orbitals, LUMO and LUMO + 1, are mainly π^* -C≡C-C₆H₄-C≡CPh in character (*ca.* 80%), the contribution of the Pt to these latter orbitals being negligible (~2%). The contribution of the bzq ligand is only notable in the LUMO + 2, which is a mixed C≡CR (54%)/bzq (42%) orbital, but it is located at 0.79 eV from the LUMO; the LUMO + 3 is again of a virtually pure alkynyl character.

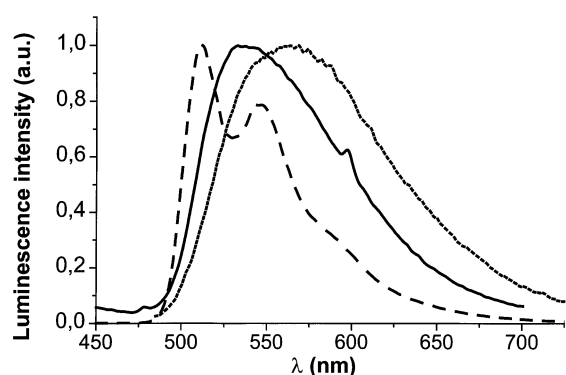
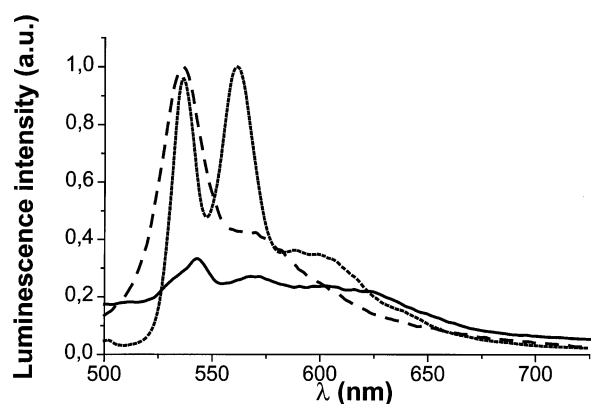
As a further means of examining the properties of the HOMO and LUMO orbitals, we obtained cyclic voltammograms of all complexes in CH₂Cl₂ (0.1 mol dm⁻³ NBu₄PF₆) and the results are also summarized in Table 3. All the complexes exhibit, within the solvent window, only one irreversible oxidation wave in the range of 0.68 to 1.006 eV vs. Fc⁺/Fc. This result is in agreement with previous reports on Pt(II) cyclometalated systems and other Pt(II) complexes containing diimine or related chelating aromatic ligands that show irreversible oxidations usually assigned as metal-centred oxidation from Pt(II) to Pt(III). However, the typical reversible reduction processes usually seen in these systems were not observed in our complexes probably due to the anionic nature of these species. For complex **1** the voltammogram was also recorded in THF and DMF with identical results. The observation that the anodic potential in general decreases as the π -donating abilities of the alkynyl substituents increase is further evidence of the involvement of the Pt(d)- π C≡CR interaction in the HOMO. The oxidation of the bis(*tert*-butylacetylide) complex **1** occurs at a lower potential than for the others. This fact may be ascribed to the presence of the most electron donating alkynyl ligand which increases the energy of the d π (Pt) orbital and is also in agreement with the lowest absorption and emission (see below) energies observed for this complex. In contrast the presence of electron withdrawing alkynyl groups such as C≡C-C₆H₄-CF₃-4 or C≡C-C₆H₄N-2 makes the complexes harder to oxidise.

The emission spectra of all complexes have been recorded in the solid state (RT, KBr pellets), at room temperature in CH₂Cl₂ solution and at 77 K in CH₂Cl₂ glass. The complexes are intensely emissive in the solid state (except complex **7**) and in low temperature glasses and moderately luminescent in fluid solution. Similar spectra were obtained in concentrated solvent glasses excluding excimer formation. Representative comparisons between solid state, fluid solution and glass emission spectra for complexes **1** and **7** are provided in Fig. 2 and 3 while Table 6 summarises the emission maxima, emission lifetimes (solid state) and quantum yields.

With respect to the PL spectra there are several noteworthy features. First, the emissive properties of complexes **1–6** are similar suggesting that the photoluminescence of these derivatives emanates from the same type of excited state. A clear deviation is found in complex **7**, which will be described separately. For complexes **1–6** the solid state emission spectral band shapes (broad with a long tail to lower energies) were similar to the corresponding solution (RT) values, although emission maxima were consistently at shorter wavelengths (except **3**), this hypsochromic shift being, probably, a reflection of restricted excited-state distortion in the solid matrix environment. A second point to be noted is that, upon cooling at 77 K, the

Table 6 Emission and excitation spectral data for complexes 1–7 in KBr and in 10⁻³ M solutions

Compound		$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	ϕ	$\tau/\mu\text{s}$
1	KBr (298)	398, 468	533	0.069	0.82
	CH ₂ Cl ₂ (298)	468	561		
	CH ₂ Cl ₂ (77)	357, 394, 421, 452, 487(sh)	512, 547, 586(sh)		
2	KBr (298)	396, 448, 476	515	0.025	0.73
	CH ₂ Cl ₂ (298)	457	521		
	CH ₂ Cl ₂ (77)	347, 394, 433, 472	493, 532, 570		
3	KBr (298)	401, 427, 462, 499(sh)	527, 598	0.056	0.52
	CH ₂ Cl ₂ (298)	462	526		
	CH ₂ Cl ₂ (77)	352, 400, 447, 473	505, 538, 581		
	Acetone (298)	475	537		
	Acetone (77)	304, 348, 398, 440, 474	493, 526, 569		
	CH ₃ CN (298)	469	534		
	CH ₃ CN (77)	318, 358, 397, 447, 484	509, 541, 594(sh)		
4	KBr (298)	392, 460	530	0.181	0.79
	CH ₂ Cl ₂ (298)	470	534		
	CH ₂ Cl ₂ (77)	345, 398, 444, 477	505, 540, 581(sh)		
5	KBr (298)	333, 393, 458	513, 530	0.023	0.78
	CH ₂ Cl ₂ (298)	461	511		
	CH ₂ Cl ₂ (77)	354, 398, 433, 473	492, 526, 568		
	Acetone (298)	473	521		
	Acetone (77)	330, 393, 435, 473	495, 528, 567(sh)		
	CH ₃ CN (298)	454	516		
	CH ₃ CN (77)	357, 395, 429, 473	488, 524, 564		
6	KBr (298)	333, 394, 459	508, 583(sh)	0.012	0.13
	CH ₂ Cl ₂ (298)	456	517		
	CH ₂ Cl ₂ (77)	354, 399, 432, 474	495, 530, 569		
7	KBr (298)	356, 393, 473	544, 570, 604, 622	0.067	—
	CH ₂ Cl ₂ (298)	473	537, 567		
	CH ₂ Cl ₂ (77)	356, 392, 424, 445, 471	535, 562, 589, 598, 636		

**Fig. 2** Normalised emission spectra of **1** in KBr (—), in fluid CH₂Cl₂ solution at room temperature (···) and at 77 K (---).**Fig. 3** Normalised emission spectra of **7** in KBr (—), in fluid CH₂Cl₂ solution at room temperature (---) and at 77 K (···).

emission profiles of these complexes (1–6) became intensified and structured with maxima shifted to higher energies. The vibronic interval is *ca.* 1300 cm⁻¹ which is indicative of cyclometalated bzq ligand involvement in the emissive excited state. The small rigidochromic blue shift (19–49 nm) observed is

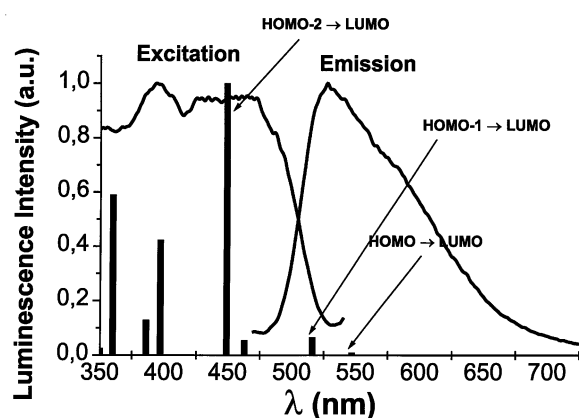
comparable to those reported for many cyclometalated and diimine platinum(II) complexes and has been linked to solvent–solute interactions in fluid solution which seem to stabilise the excited state emissive. Intrinsic lifetimes (solid state, KBr pellets) in the submicrosecond range and the separation between the lowest energy excitation and the highest energy emission band (Table 6) are indicative of metal complex phosphorescence. The solution emission quantum yields determined according to the method described by Demas and co-workers²⁶ (Table 6) are in the range 0.012 to 0.181 and compare well with those observed for analogous cyclometalated neutral complexes such as [Pt(C[^]N)(O[^]O)]^{10b} (0.02–0.25).

For complexes **3** and **5** the emission spectra were also recorded in acetone and acetonitrile. The observation of small solvatochromic shifts (see Table 6) is consistent with charge-transfer excited states. The emission maxima in CH₂Cl₂ at 298 K are modified from 561 nm for **1** to 511 nm for **5** (1711 cm⁻¹) illustrating the slight tunability of the emission depending on the nature of the acetylide substituent. Clearly, the emission maximum shifts to lower energy as the π orbital energy and donor capability of the acetylide ligand increase, in keeping with a mainly π C \equiv CR or Pt(d)/ π C \equiv CR based HOMO. Therefore, for these complexes the origin of this emission band is assigned as a triplet metal-perturbed L'LCT ³[Pt(d)/ π C \equiv CR \rightarrow π^* bzq] excited state. The main TD-DFT calculated excitation energies for the anion of complex **3**, which are tabulated in Table 7 and shown in Fig. 4, are in good agreement with the experimental excitations. The two intense calculated excitations at *ca.* 397 and 449 nm are mainly attributed to HOMO \rightarrow LUMO + 1 and HOMO - 2 \rightarrow LUMO supporting a metal-perturbed L'LCT assignment. The lowest calculated singlet (HOMO \rightarrow LUMO 547 nm, HOMO - 1 \rightarrow LUMO 516 nm and HOMO - 3 \rightarrow LUMO 463 nm) and triplet (576, 559 and 518 nm) excitations are in reasonable agreement with the experimental emission (λ_{max} 527 nm).

Complex **7** (with *cis*-configured C \equiv C-C₆H₄-C \equiv CPh moieties) displays different solid-state, solution and glassy emissions in comparison to complexes 1–6 (Fig. 3). The observed structured emission in CH₂Cl₂ solution and the absence of rigidochromic behaviour suggest that the nature of the excited state is

Table 7 TD-DFT RPA (random phase approximation) singlet excitation calculations for $[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CPh})_2]^- \mathbf{3}$

Transition	Contributions	o.s.	$\lambda_{\text{exc}}(\text{calc.})/\text{nm}$
HOMO - 2 \rightarrow LUMO	0.58	0.148	448.8
HOMO - 1 \rightarrow LUMO	0.22		
HOMO - 3 \rightarrow LUMO	0.20		
HOMO \rightarrow LUMO + 1	0.66	0.062	396.8
HOMO - 1 \rightarrow LUMO + 1	0.12		
HOMO - 4 \rightarrow LUMO	0.11		
HOMO - 2 \rightarrow LUMO + 1	0.66	0.088	365.7
HOMO - 5 \rightarrow LUMO	0.14		
HOMO - 5 \rightarrow LUMO	0.65	0.045	347
HOMO - 2 \rightarrow LUMO + 1	0.13		

**Fig. 4** Calculated excitation spectrum (bars) of $[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CPh})_2]^-$ and experimental solid-state (RT, KBr pellets) excitation and emission spectra of complex **3**.

different. Significantly, the glassy (77 K) peak maxima are similar to the emission peaks observed for the homoleptic derivative $(\text{NBu}_4)_2[\text{Pt}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CPh})_4]$ (541, 570, 588, 607 nm). In complex **7** a mixed IL/MLCT excited state that originates from the alkynyl entities or the existence of two closely emissive states of type $\pi-\pi^* \text{C}\equiv\text{CR}/\text{Pt}(\text{d})-\pi \text{C}\equiv\text{CR} \rightarrow \pi^* \text{C}\equiv\text{CR}$ is tentatively suggested as the origin of the emission. The considerable red shift of its glassy emission (535 nm) relative to **1-6** could be tentatively attributed to the low-lying delocalized nature of the butadiynyl moieties, which affords LUMO stabilisation.

Conclusion

In summary the synthesis, electronic absorption, luminescence and electrochemical properties of novel bis(alkynyl)platinate compounds $(\text{NBu}_4)_2[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CR})] \mathbf{1-7}$ containing the planar orthometallated 7,8-benzoquinoline ligand (bzq) have been described. For complex **1-6** the low energy transitions observed are mainly attributed on the basis of TD-DFT calculations to metal perturbed ligand (acetylide)-to-ligand(benzoquinolate) charge transfer. For complex **7** containing the extended dialkynyl ligand $\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{Ph}$ the lowest optical transition (absorption and emission) is attributed to a transition having mainly metal perturbed $\pi-\pi^*(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{Ph})$ character.

Experimental

General procedures

All reactions were carried out under nitrogen atmosphere and solvents were dried by standard procedures and distilled under dry N_2 before use. Proton (300 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker ARX-300 spectrometer with chemical shifts externally referenced to SiMe_4 . Infrared spectra were recorded with a Perkin-Elmer FT-IR1000 spectrometer as Nujol mulls between polyethylene sheets and C, H and N

analyses were carried out with a Carlo Erba EA1110 CHNS-O microanalyzer. Mass spectra were obtained on a HP-5989B mass spectrometer (ES(-) technique) and conductivities were measured in acetone solutions (*ca.* $5 \times 10^{-4} \text{ mol}^{-1}$) with a Crison GLP 31 conductimeter. Emission and excitation spectra were obtained on a Perkin-Elmer Luminescence Spectrometer LS 50B and emission lifetime measurements were performed with a dye laser (Lamda-Physik, LPD 3002 CES, $\Delta\lambda = 0.2 \text{ cm}^{-1}$; $\lambda = 337$, $> 5 \text{ mJ pulse}^{-1}$ in the range 332–350 nm, dye *p*-terphenyl in dioxane) pumped by an excimer XeCl laser (Lamda-Physik, LPX 105i, $\lambda = 308 \text{ nm}$, $200 \text{ mJ pulse}^{-1}$, FWHM $\sim 20 \text{ ns}$). The solution emission quantum yields were measured by the Demas and Crosby²⁶ method using $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ in degassed acetonitrile as the standard. The platinum precursor $[\text{Pt}(\text{bzq})-(\mu-\text{Cl})_2 (\text{bzqH} = \text{benzo}[h]\text{quinoline})]$ was prepared according to the reported procedure.²⁷ Alkynes, except for $\text{H}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CPh}$ which was prepared following a standard procedure,²⁸ were purchased from commercial suppliers and used as received. Cyclic voltammetric studies were performed using an EG&G 283 potentiostat/galvanostat. Anhydrous CH_2Cl_2 was used as the solvent under a nitrogen atmosphere, and 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate was used as the supporting electrolyte.

Computational details

In this work, the experimental crystal structure of the anion $[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CPh})_2]^- \mathbf{3}$, and a model of the anion $[\text{Pt}(\text{bzq})(\text{C}\equiv\text{C}_6\text{H}_4\text{C}\equiv\text{CPh})_2]^- \mathbf{7}$, based on the structure of **3**, were used. The density functional calculations were performed on isolated molecules using the Gaussian 98 program package²⁹ at the B3LYP level.³⁰ The basis set for the platinum atom was LANL2DZ,³¹ with the corresponding ECP (effective core potential), and 6-31G(d,p) for the C, N and H atoms. The excitation energies for **3** were obtained using the Time Dependent Theory (TD-DFT).

Crystal structure determinations for **3** and **6**

Both experiments were performed at 293 K in a κ -CCD area diffractometer using graphite-monochromated Mo-K_α radiation. All calculations were carried out using the SHELXL-97³² program and the data reduction with HKL Denzo ScalePack.³³ The structures were solved by direct methods and refined on F^2 . All hydrogen atoms were constrained to idealised geometries and were assigned isotropic displacement parameters equal to 1.2 times the U_{iso} value of their attached carbon for the aromatic and CH_2 hydrogens and 1.5 times for the methyl groups. Absorption corrections were carried out using the SORTAV³⁴ program.

Crystallographic data for **3**: $\text{C}_{45}\text{H}_{54}\text{N}_2\text{Pt}$, $M = 817.99$, monoclinic, space group $P2_1/n$, $a = 20.7488(4)$, $b = 8.6637(2)$, $c = 24.5454(6) \text{ \AA}$, $\beta = 113.3822(8)^\circ$, $V = 4049.97(16) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.342 \text{ g cm}^{-3}$, $F(000) = 1664$, $\mu(\text{Mo-K}_\alpha) = 3.495 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$. The 23343 reflections measured yielded 8130 unique data ($\theta_{\text{max}} = 26.37^\circ$, $R_{\text{int}} = 0.0515$), 437 parameters, $R1 = 0.0599 [I > 2\sigma(I)]$, $wR2 = 0.1472$.

Crystallographic data for **6**: $C_{43}H_{52}N_4Pt$, $M = 818.46$, monoclinic, space group $P2_1/n$, $a = 19.3798(2)$, $b = 16.8231(2)$, $c = 25.2980(4)$ Å, $\beta = 108.9762(5)^\circ$, $V = 7799.62(17)$ Å³, $Z = 8$, $\rho_{\text{calc}} = 1.394$ g cm⁻³, $F(000) = 3316$, $\mu(\text{Mo-K}\alpha) = 3.631$ mm⁻¹, $\lambda = 0.71073$ Å. The 47259 reflections measured yielded 15798 unique data ($\theta_{\text{max}} = 26.37^\circ$, $R_{\text{int}} = 0.0531$), 872 parameters, $R1 = 0.0417$ [$I > 2\sigma(I)$], $wR2 = 0.0796$.

CCDC reference numbers 197073 and 197074.

See <http://www.rsc.org/suppdata/dt/b2/b210907g/> for crystallographic data in CIF or other electronic format.

Synthesis of $(\text{NBu}_4)[\text{Pt}(\text{bzq})(\text{C}\equiv\text{C}^t\text{Bu})_2]$ **1**

$[\text{Pt}(\text{bzq})(\mu\text{-Cl})_2]$ (0.25 g, 0.306 mmol) was added to a fresh solution of $\text{LiC}\equiv\text{C}^t\text{Bu}$ (2.446 mmol) (1 : 8 molar ratio) in diethyl ether/hexane (25 mL) at low temperature (-40°C) and the mixture was allowed to warm to room temperature. After stirring for 30 min the solvent was evaporated and the resulting yellow solid was extracted with cold deoxygenated water (50 mL). The resulting yellow aqueous solution was rapidly filtered under N_2 through celite and, the filtrate treated with vigorous stirring with a solution of $(\text{NBu}_4)\text{Br}$ (0.197 g, 0.611 mmol) in 10 mL of H_2O . The resulting yellow solid **1** was filtered, washed with deoxygenated water and air-dried (0.34 g, 83%); (Found: C, 62.34; H, 7.61; N, 3.92. $C_{41}H_{62}N_2Pt$ requires C, 62.26; H, 8.03; N, 3.60%); $\nu_{\text{max}}/\text{cm}^{-1}$ (C≡C) 2108s and 2099vs (Nujol); $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3, J/\text{Hz})$: 9.39 (dd, $J = 5.4, 1.2$, $^3J(\text{Pt-H}) = 25.5$, H^2); 8.66 (dd, $J = 6, 2.4$, $^3J(\text{Pt-H}) = 40.2$, H^9); 8.40 (dd, $J = 7.8, 1.2$, H^4); 7.72 (d, $J = 8.7$, H^5); 7.57 (d, $J = 8.7$, H^6); 7.5 (dd, $J = 7.8, 5.4$, H^3); 7.45 (m, $\text{H}^{7,8}$); 3.46 (m, NCH_2 , NBu_4); 1.62 (m, $-\text{CH}_2-$, NBu_4); 1.34 (s, ^tBu); 1.32 (s, ^tBu); 1.22 (q, $-\text{CH}_2-$, NBu_4); 0.83 (t, $-\text{CH}_3$, NBu_4). $\delta_{\text{C}}\{^1\text{H}\}$ ($\text{CDCl}_3, J/\text{Hz}$, 233 K): 164.18 ($^1J_{\text{Pt-C}} = 770$, C^{10}); 157.75 ($^2J_{\text{Pt-C}} = 48$, C^{12}); 149.71 ($^2J_{\text{Pt-C}} \sim 40$, C^2); 143.3 (C^{11}); 134.94 (C^4); 134.5 (C^9); 133.26 ($\text{C}^{13,14}$); 129.14, 128.99 ($\text{C}^{7,8}$); 125.65 ($\text{C}^{13,14}$); 122.08 ($\text{C}^{5,6}$); 120.7 (C^3); 118.8 ($\text{C}^{5,6}$); 113.36 ($^2J_{\text{Pt-C}\beta} = 230$, $\equiv\text{C}_\beta\text{Bu}^t$ *trans* to C^{10}); 110.95 ($^1J_{\text{Pt-C}\alpha} = 902$, $\text{C}_\alpha\equiv\text{CBu}^t$ *trans* to C^{10}); 109.5 ($^2J_{\text{Pt-C}\beta} = 415$, $\equiv\text{C}_\beta\text{Bu}^t$ *trans* to N); 77.7 ($^1J_{\text{Pt-C}\alpha} = 1490$, $\text{C}_\alpha\equiv\text{CBu}^t$ *trans* to N); 57.5 (N- CH_2); 32.95 (C(CH_3)); 32.26 (C(CH_3)); 29.37 (C(CH_3)); 29.00 (C(CH_3)); 23.34 (CH_2); 18.90 (CH_2); 13.74 (CH_3 , NBu_4); m/z 535 (M^- , 100%), 1071 (M_2^- , 20), 989 ($\text{M}_2 - \text{C}\equiv\text{C}^t\text{Bu}^-$, 20). A_M (acetone): 101 mol⁻¹ cm² Ω⁻¹.

Synthesis of $(\text{NBu}_4)[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CSiMe}_3)_2]$ **2**

To a solution of $\text{LiC}\equiv\text{CSiMe}_3$ (2.446 mmol) prepared from $\text{HC}\equiv\text{CSiMe}_3$ (0.338 mL, 2.446 mmol) and LiBu^n (2.43 mmol) in Et_2O (30 mL) at -25°C [$[\text{Pt}(\text{bzq})(\mu\text{-Cl})_2]$ (0.25 g, 0.306 mmol) was added and the mixture was stirred at this temperature for 10 min. The reaction mixture was then allowed to warm to 25°C and, after stirring for 30 min, all volatile materials were removed *in vacuo*. The resulting residue was extracted with cold *i*-PrOH, filtered and treated with $(\text{NBu}_4)\text{Br}$ (0.197 g, 0.611 mmol) affording **2** as a yellow solid (0.25 g, 51%); (Found: C, 57.53; H, 7.66; N, 3.40. $C_{39}H_{62}N_2PtSi_2$ requires C, 57.82; H, 7.71; N, 3.46%); $\nu_{\text{max}}/\text{cm}^{-1}$ (C≡C) 2031vs and 2008vs (Nujol). $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3, J/\text{Hz})$: 10.16 (dd, $J = 5.2, 1.2$, $^3J_{\text{Pt-H}} = 25.9$, H^2); 8.58 (dd, $J = 6.4, 1.6$, $^3J_{\text{Pt-H}} = 40.2$, H^9); 8.45 (dd, $J = 8, 1$, H^4); 7.76 (d, $J = 8.7$, H^5); 7.61 (d, $J = 8.7$, H^6); 7.55 (dd, $J = 8; 5.2$, H^3); 7.48 (m, $\text{H}^{7,8}$); 3.45 (m, NCH_2 , NBu_4); 1.68 (m, $-\text{CH}_2-$, NBu_4); 1.27 (q, $-\text{CH}_2-$, NBu_4); 0.85 (t, $-\text{CH}_3$, NBu_4); 0.15 (s, SiMe_3); 0.149 (s, SiMe_3). $\delta_{\text{C}}\{^1\text{H}\}$ ($\text{CDCl}_3, J/\text{Hz}$, 233 K): 163.0 ($^1J_{\text{Pt-C}} = 759.9$, C^{10}); 157.49 ($^2J_{\text{Pt-C}} = 28.2$, C^{12}); 152.38 ($^1J_{\text{Pt-C}\alpha} = 895$, $\text{C}_\alpha\equiv\text{CSiMe}_3$ *trans* to C^{10}); 149.77 ($^2J_{\text{Pt-C}} \sim 45$, C^2); 149.28 (s, C^{11}); 135.9 (C^4); 135.8 ($^2J_{\text{Pt-C}} = 94$, C^9); 132.68 ($\text{C}^{13,14}$); 129.2 ($\text{C}^{7,8}$); 125.9 ($\text{C}^{13,14}$); 122.19 ($\text{C}^{5,6}$); 120.8 (C^3); 119.9 ($\text{C}^{5,6}$); 119.24 ($^1J_{\text{Pt-C}\alpha} = 1407$, $\text{C}_\alpha\equiv\text{CSiMe}_3$ *trans* to N); 107.71 ($^2J_{\text{Pt-C}\beta} = 205$, $\equiv\text{C}_\beta\text{SiMe}_3$ *trans* to C^{10}); 103.9 ($^2J_{\text{Pt-C}\beta} = 374$, $\equiv\text{C}_\beta\text{SiMe}_3$ *trans* to N); 57.6 (N- CH_2); 23.40 (CH_2); 18.94

(CH_2); 13.75 (CH_3 , NBu_4); 1.85 (s, SiMe_3); 1.54 (s, SiMe_3); $m/z = 567$ (M^- , 100%). A_M (acetone): 81 mol⁻¹ cm² Ω⁻¹.

Synthesis of $(\text{NBu}_4)[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CPh})_2]$ **3**

To a fresh (-25°C) solution containing 8 equiv. of $\text{LiC}\equiv\text{CPh}$ (2.446 mmol) in Et_2O (30 mL) was added $[\text{Pt}(\text{bzq})(\mu\text{-Cl})_2]$ (0.25 g, 0.306 mmol) and the mixture was allowed to reach room temperature. The mixture was then stirred for 2.5 h and the remaining steps were identical to the procedure described for **2** (0.25 g, 50%). (Found: C, 66.00; H, 7.09; N, 3.23. $C_{45}H_{54}N_2Pt$ requires C, 66.07; H, 6.65; N, 3.42%); $\nu_{\text{max}}/\text{cm}^{-1}$ (C≡C) 2103s and 2080s (Nujol). $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3, J/\text{Hz})$: 10.17 (d, $J = 4.3$, $^3J(\text{Pt-H}) = 25$, H^2); 8.63 (dd, $J = 5.9, 1.8$, $^3J(\text{Pt-H}) = 43$, H^9); 8.49 (dd, $J = 7.22, 1.2$, H^4); 7.79 (d, $J = 8.8$, H^5); 7.64 (m); 7.53 (m); 7.39 (m) (H^3 , H^{6-8} , 4H Ph); 7.20 (4H, Ph); 7.04 (m, 2H, Ph); 3.43 (m, NCH_2 , NBu_4); 1.65 (m, $-\text{CH}_2-$, NBu_4); 1.24 (q, $-\text{CH}_2-$, NBu_4); 0.81 (t, $-\text{CH}_3$, NBu_4). $\delta_{\text{C}}\{^1\text{H}\}$ ($\text{CDCl}_3, J/\text{Hz}$, 240 K): 162.73 ($^1J_{\text{Pt-C}} = 777$ C^{10}); 157.49 ($^2J_{\text{Pt-C}} \sim 50$, C^{12}); 150.04 (C^2); 143.46 (C^{11}); 135.96 (C^4); 134.49 ($^2J_{\text{Pt-C}} \sim 90$, C^9); 132.87 ($\text{C}^{13,14}$); 131.41 (Co, Ph); 131.01 (Co, Ph); 130.09 ($\text{C}^{7,8}$); 129.4 ($\text{C}^{7,8}$); 129.22 (C_β , Ph); 129.12 (C_β , Ph); 127.6 (C_m , Ph); 127.54 (C_m , Ph); 127.3 (C_β , Ph); 126.0 ($\text{C}^{13,14}$); 124 (C_β , Ph); 123.8 ($\text{C}_\alpha\equiv\text{CPh}$ *trans* to C^{10} , ^{195}Pt are not clearly resolved); 122.49 ($\text{C}^{5,6}$); 121.14 (C^3); 120.10 ($\text{C}^{5,6}$); 106.4 ($^2J_{\text{Pt-C}\beta} = 235$, $\equiv\text{C}_\beta\text{Ph}$ *trans* to C^{10}); 103.49 ($^2J_{\text{Pt-C}\beta} = 433$, $\equiv\text{C}_\beta\text{Ph}$ *trans* to N); 98.05 ($^1J_{\text{Pt-C}\alpha} = 1488$, $\text{C}_\alpha\equiv\text{CPh}$ *trans* to N); 57.7 (N- CH_2); 23.34 (CH_2); 19.12 (CH_2); 13.66 (CH_3 , NBu_4); $m/z = 576$ (M^- , 100%). A_M (acetone): 90 mol⁻¹ cm² Ω⁻¹.

Synthesis of $(\text{NBu}_4)[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CTol})_2]$ **4**

To a fresh (-15°C) solution containing 8 equiv. of $\text{LiC}\equiv\text{CTol}$ (2.446 mmol) in Et_2O (30 mL) [$[\text{Pt}(\text{bzq})(\mu\text{-Cl})_2]$ (0.25 g, 0.306 mmol) was added and the mixture was stirred at this temperature for 2 h. The mixture was then allowed to reach room temperature (*ca.* 1 h.). The solvent was evaporated to dryness and the yellow solid residue extracted with a mixture of *i*-PrOH/deoxygenated water (10/50 mL). The resulting yellow aqueous solution was rapidly filtered under N_2 through celite and, the filtrate treated with vigorous stirring with a solution of $(\text{NBu}_4)\text{Br}$ (0.197 g, 0.611 mmol) in 10 mL of H_2O ; (0.13 g, 32%); (Found: C, 66.73; H, 6.81; N, 3.59%. $C_{47}H_{58}N_2Pt$ requires C, 66.72; H, 6.90; N, 3.30%); $\nu_{\text{max}}/\text{cm}^{-1}$ (C≡C) 2105s and 2082s (Nujol). $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3, J/\text{Hz})$: 10.17 (d, $J = 4.3$, $^3J(\text{Pt-H}) = 25.8$, H^2); 8.63 (dd, $J = 6.0, 1.7$, $^3J(\text{Pt-H}) = 41$, H^9); 8.48 (d, $J = 7.9$, H^4); 7.78 (d, $J = 8.7$, H^5); 7.62 (m); 7.52 (m) (H^3 , H^{6-8}); 7.30 (d, $J = 7.7$ 4H, CH, Tol); 7.02 (d, $J = 7.7$, 4H, CH, Tol); 3.47 (m, NCH_2 , NBu_4); 2.88 (s, 6H, CH_3 , Tol); 1.66 (m, $-\text{CH}_2-$, NBu_4); 1.29 (m, $-\text{CH}_2-$, NBu_4); 0.80 (t, $-\text{CH}_3$, NBu_4). $^{13}\text{C}\{^1\text{H}\}$ ($\text{CDCl}_3, 260$ K): 162.94 (C^{10}); 157.67 (C^{12}); 149.97 (C^2); 143.5 (C^{11}); 135.6 (C^4); 134.6 (C^9); 133.4 ($\text{C}^{13,14}$); 133.10 (C^4 , Tol); 132.9 (C^4 , Tol); 131.00 (CH, Tol); 130.75 (CH, Tol); 129.19 (C^{7+8} bzq); 128.31 (CH, Tol); 128.20 (CH, Tol); 128.03 (s, this signal could be tentatively assigned to $\text{C}_\alpha\equiv\text{CTol}$ *trans* to C^{10}); 127.18 (C_1 , Tol); 126.53 (C_1 , Tol); 122.97 ($\text{C}^{13,14}$); 122.22 ($\text{C}^{5,6}$); 120.88 (C^3 , bzq); 119.84 ($\text{C}^{5,6}$); 106.3 ($\equiv\text{C}_\beta\text{Tol}$ *trans* to C^{10}); 103.3 ($\equiv\text{C}_\beta\text{Tol}$ *trans* to N); 97.0 ($\text{C}_\alpha\equiv\text{CTol}$ *trans* to N, ^{195}Pt satellites are not resolved); 57.93 (N- CH_2); 23.53 (CH_2); 21.2 (CH_3 , Tol); 19.13 (CH_2); 13.49 (CH_3 , NBu_4); $m/z = 603$ (M^- , 100%); A_M (acetone): 110 mol⁻¹ cm² Ω⁻¹.

Synthesis of $(\text{NBu}_4)[\text{Pt}(\text{bzq})(\text{C}\equiv\text{CC}_6\text{H}_4\text{CF}_3)_2]$ **5**

$[\text{Pt}(\text{bzq})(\mu\text{-Cl})_2]$ (0.20 g, 0.245 mmol) was added to a solution containing 10 equiv. of the lithiated ligand ($\text{HC}\equiv\text{CC}_6\text{H}_4\text{CF}_3$ -4, 0.4 mL, 2.45 mmol, and $n\text{-BuLi}$ 1.52 mL, 2.45 mmol) in ether (30 mL) at -15°C . The reaction mixture was allowed to warm slowly to room temperature (*ca.* 1 h) and then evaporated to dryness. The residue was extracted with cold *i*-PrOH (30 mL), filtered under nitrogen and the filtrate stirred with a solution of

(NBu₄)Br (0.16 g, 0.5 mmol) in deoxygenated H₂O to yield complex **5** as a yellow solid (0.27g, 57%); (Found: C, 58.88; H, 5.23; N, 2.66. C₄₇H₅₂N₂Pt requires C, 59.17; H, 5.49; N, 2.93%); $\nu_{\max}/\text{cm}^{-1}$ (C≡C) 2105vs and 2082vs (Nujol). δ_{H} (CD₃COCD₃, *J*/Hz): 10.1 (dd, *J* = 5.4, 1.2, ³*J*(Pt–H) = 27.3, H²); 8.54 (dd, *J* = 6.3, 1.5, ³*J*(Pt–H) = 41, H⁹); 8.53 (d, *J* = 10.4, H⁴); 7.8 (d, *J* = 8.7, H⁵); 7.65 (m, H^{6,3}); 7.53 (dbr, 10H, H^{7,8} bzq and CH, C₆H₄CF₃); 3.45 (m, NCH₂, NBu₄); 1.74 (m, –CH₂–, NBu₄); 1.35 (q, –CH₂–, NBu₄); 0.89 (t, –CH₃, NBu₄). δ_{F} (CDCl₃): –145.58 (s, CF₃); –145.67 (s, CF₃). $\delta_{\text{C}}\{^1\text{H}\}$ (CDCl₃, *J*/Hz, 240 K): 162.0 (¹*J*_{Pt–C} = 735, C¹⁰); 157.37 (C¹²); 149.94 (C²); 143.4 (C¹¹); 136.37 (C⁴); 134.4 (C⁹); 133.7 (C–CF₃); 133.01 (C^{13,14}, C–CF₃); 131.17 (C_o; C₆H₄–CF₃); 131.03 (C_o–C₆H₄–CF₃); 129.34 (C⁷⁺⁸); 128.15 (C_i; C₆H₄–CF₃); 127.04 (C_i; C₆H₄–CF₃); 126.17 (C^{13,14}); 125.06 (C_o≡CC₆H₄CF₃ *trans* to C¹⁰); 124.56 (C_m; C₆H₄–CF₃); 127.7 (CF₃); 125.0 (CF₃); 122.62 (C^{5,6}); 121.26 (C³); 120.59 (C^{5,6}); 105.8 (²*J*_{Pt–Cβ} = 234, ≡C_βC₆H₄CF₃ *trans* to C¹⁰); 102.93 (C_o≡CC₆H₄CF₃ *trans* to N); 102.67 (≡C_βC₆H₄CF₃ *trans* to N); 57.82 (N–CH₂); 23.36 (CH₂); 19.07 (CH₂); 13.53 (CH₃, NBu₄); *m/z* = 710 (M⁺; 100%); *A*_M (acetone): 93 mol^{–1} cm² Ω^{–1}.

Synthesis of (NBu₄)[Pt(bzq)(C≡CC₅H₄N-2)] **6**

[Pt(bzq)(μ-Cl)]₂ (0.25 g, 0.306 mmol) was added to a solution containing 10 equiv. of the lithiated ligand (HC≡CC₅H₄N-2, 0.308 mL, 3.06 mmol, and n-BuLi 1.91 mL, 3.06 mmol) in ether (30 mL) at –78 °C. The reaction mixture was allowed to warm slowly to room temperature (*ca.* 2.5 h) and then evaporated to dryness. The remaining steps were identical to the procedure described for **5**, using 0.197 g, 0.611 mmol of (NBu₄)Br in deoxygenated H₂O complex **6** precipitated as a yellow solid (0.31g, 62%); (Found: C, 62.78; H, 6.57; N, 6.56. C₄₃H₅₂N₄Pt requires C, 62.98; H, 6.39; N, 6.82%); $\nu_{\max}/\text{cm}^{-1}$ (C≡C) 2110vs and 2086vs (Nujol). δ_{H} (CD₃COCD₃, *J*/Hz): 10.13 (dd, *J* = 5.1, 1, ³*J*(Pt–H) = 27 H², bzq); 8.65 (dd, *J* = 6.9, 1.3, ³*J*(Pt–H) = 35 H⁹, bzq); 8.51 (dd, *J* = 7.1, 1, H⁴, bzq); 8.39 (m, 2H, H⁶, 2-Py); 7.8 (d, *J* = 8.7, H⁵, bzq); 7.65 (m, H^{6,3}, bzq); 7.54 (m, 4H, H^{7,8}, bzq and 2 H⁴, 2-Py); 7.32 (d, 2H, H³, 2-Py); 7.00 (m, 2H, H⁵, 2-Py); 3.53 (m, NCH₂, NBu₄); 1.72 (m, –CH₂–, NBu₄); 1.27 (q, –CH₂–, NBu₄); 0.79 (t, –CH₃, NBu₄). The low solubility of this complex at low temperature precludes its characterisation by ¹³C NMR spectroscopy; *m/z* = 577 (M⁺, 100%). *A*_M (acetone): 81 mol^{–1} cm² Ω^{–1}.

Synthesis of (NBu₄)[Pt(bzq)(C≡CC₆H₄C≡CC₆H₅)] **7**

To a solution containing 8 equiv. of LiC≡CC₆H₄C≡CPh (1.987 mmol) in Et₂O (30 mL, –40 °C) was added [Pt(bzq)(μ-Cl)]₂ (0.203 g, 0.248 mmol) and the mixture was allowed to reach room temperature. Once at room temperature, the mixture was stirred for 2 h and then evaporated to dryness. The resulting residue was extracted with a cold mixture of i-PrOH and EtOH, filtered and treated with (NBu₄)Br (0.200 g, 0.62 mmol) affording **7** as a yellow solid (0.153 g, 31%); (Found: C, 71.91; H, 6.47; N, 2.67. C₆₁H₆₂N₂Pt requires C, 71.95; H, 6.14; N, 2.75%); $\nu_{\max}/\text{cm}^{-1}$ (C≡C) 2209s, 2098s and 2074s (Nujol). δ_{H} (CD₃COCD₃, *J*/Hz): 10.11 (d, *J* = 4.6, ³*J*(Pt–H) = 26.8, H²); 8.59 (d, *J* = 4.6, ³*J*(Pt–H) = 31, H⁹); 8.51 (d, *J* = 7.8, H⁴); 7.81 (d, *J* = 8.7, H⁵); 7.67 (m); 7.64 (m); 7.59 (m); 7.54 (H³, H^{6–8}, 6H, C₆H₄, Ph); 7.42 (m, 12H, C₆H₄, Ph); 3.43 (m, NCH₂, NBu₄); 1.68 (m, –CH₂–, NBu₄); 1.28 (q, –CH₂–, NBu₄); 0.83 (t, –CH₃, NBu₄). $\delta_{\text{C}}\{^1\text{H}\}$ (CDCl₃, *J*/Hz, 233 K): 162.4 (C¹⁰); 157.46 (C¹²); 149.88 (C²); 143.42 (C¹¹); 136.16 (C⁴); 134.45 (C⁹); 133.11–130.89 (C^{13,14}, C₆H₄, Ph); 129.65 (C^{7,8}); 129.29 (C^{7,8}); 128.26–127.93 (C₆H₄, Ph); 126.6 (C^{13,14}); 123.07 (C₆H₄, Ph); 122.5 (C^{5,6}); 121.13 (C³); 120.37 (C^{5,6}); 117.89 (C₆H₄, Ph); 117.57 (C₆H₄, Ph); 106.71, 103.79, 102.55 (C_o≡CC₆H₄); 90.11, 90.02, 89.40, 89.32 (C₆H₄C≡CPh); 57.77 (N–CH₂); 23.38 (CH₂); 19.09 (CH₂); 13.55 (CH₃, NBu₄). MS ES(–): molecular peak not observed. *A*_M (acetone): 96 mol^{–1} cm² Ω^{–1}.

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