

Synthesis and characterisation of new platinum–acetylide complexes containing diimine ligands

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A new class of platinum–bipyridyl compounds has been synthesized by the dehydrohalogenative reaction of [4,4'-bis(*tert*-butyl)-2,2'-bipyridyl]platinum dichloride [PtCl₂(^tBu₂bipy)] **1** with terminal alkynes HC≡CR, in the presence of copper(I) iodide and diisopropylamine. The products [Pt(C≡CR)₂(^tBu₂bipy)] (R = C₆H₄NO₂-*p* **2**, C₆H₅ **3**, C₆H₄CH₃-*p* **4** or SiMe₃ **5**), have been characterised by spectroscopic and analytical methods, and a single crystal molecular structure determination has been carried out on **4**. Extended Hückel molecular orbital calculations have also been carried out, and the results are used to help rationalise the voltammetric, EPR and spectroelectrochemical properties of the new compounds. These show that compounds **3**, **4** and **5** undergo a one-electron bipyridyl based redox process, but that **2** has an unresolved two-electron process located on the nitro groups.

There has been considerable recent interest in transition metal organometallic compounds that contain two acetylide ligands in a *cis* configuration, due to their suitability as molecular tweezers for the co-ordination of another transition metal fragment in order to form homo- or hetero-bimetallic molecules. Interest arises not only because of their structure, but also their possible catalytic activity and suitability as models for catalytic systems. The complexes are mainly based either upon the bis(cyclopentadienyl)titanium system, or upon platinum systems with tertiary phosphines or C₆F₅⁻ as the auxiliary ligands.^{1,2}

There is also interest in platinum–bipyridyl complexes, either with regard to their solid state structure and how this is related to their luminescence properties,³ the formation of d⁹ metal centres,⁴ or their ability to undergo oxidative addition to form platinum(IV) complexes.⁵ An underlying problem has been the relative insolubility of platinum–bipyridyl complexes in organic solvents, and recent work has started to utilise substituted bipyridines to overcome this problem.⁶

We report here the synthesis and characterisation of a new class of platinum–bipyridyl compounds, containing a substituted bipyridyl ligand and σ-bonded acetylides in the remaining co-ordination sites. A preliminary communication on related work has appeared,⁷ and since this work was started a report containing another platinum–acetylide complex with a diimine ligand has been published.⁸ We know of only four other published platinum–acetylide structures which also contain nitrogen donors, three of which are square planar platinum(II) compounds such as those detailed here,^{2,9} and one of which is an octahedral platinum(IV) compound.¹⁰

Results and discussion

Synthesis of the compounds

The diimine ligand employed in this study is 4,4'-bis(*tert*-butyl)-2,2'-bipyridyl (^tBu₂bipy), which has the chelating properties

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Table 1 Experimental data for compounds **2–5**

Compound	R	Colour	$\tilde{\nu}(\text{C}\equiv\text{C})/\text{cm}^{-1}$	Yield (%)
2	C ₆ H ₄ NO ₂ - <i>p</i>	Yellow	2111, 2123	54
3	C ₆ H ₅	Yellow	2115, 2124	83
4	C ₆ H ₄ CH ₃ - <i>p</i>	Yellow	2114, 2126	69
5	SiMe ₃	Yellow-green	2040, 2056	57

of unsubstituted bipyridine but confers much greater solubility in organic solvents upon metal complexes. It was synthesized from 4-*tert*-butylpyridine, not by the generally used method involving Raney nickel¹¹ but by the lesser known but more convenient method of McGill.¹² Synthesis of the platinum starting material [PtCl₂(^tBu₂bipy)] **1** from this was relatively straightforward; although ^tBu₂bipy is insoluble in water, the method of Morgan and Burstall¹³ involving refluxing the ligand with potassium tetrachloroplatinate in dilute hydrochloric acid still works. However, we found that a more convenient synthesis is to displace the acetonitrile ligands from bis(acetonitrile)platinum dichloride, formed *in situ* from the reaction of platinum dichloride and acetonitrile.¹⁴

From **1**, the synthesis of the acetylide complexes was as previously described.⁷ Stirring overnight with an excess of acetylene in the presence of a catalytic amount of copper(I) iodide and a small amount of diisopropylamine leads to formation of the acetylide complexes [Pt(C≡CR)₂(^tBu₂bipy)] **2–5** in good yield. Purification is easily effected by alumina column chromatography (for **3–5**) and/or recrystallisation, leading to isolation of the products as air stable yellow solids (Table 1).

Characterisation of the complexes

All the compounds show characteristic ¹H NMR spectra which are based upon that of free ^tBu₂bipy. The aromatic protons H⁵ and H⁶ both show a downfield shift upon complexation, whereas H³ moves upfield slightly. There is a relatively small variation in the spectra as the nature of the acetylide group changes, with the exception of compound **2**. The compounds also all show the two $\nu(\text{C}\equiv\text{C})$ bands in their IR spectrum expected for a

Table 2 Absorption maxima (in nm) and absorption coefficients (in parentheses, $/10^4 \text{ M}^{-1} \text{ cm}^{-1}$) for MLCT bands in the UV/visible spectra of compounds **2–5**

Compound	R	Solvent		
		Aceto-nitrile	Dichloro-methane	Ethyl acetate
2	$\text{C}_6\text{H}_4\text{NO}_2\text{-}p$	277 (1.5)	283 (1.4)	286 (1.5)
		371 (2.9)	369 (2.3)	369 (2.5)
3	C_6H_5	284 (3.0)	284 (4.6)	287 (4.0)
		384 (0.5)	395 (1.2)	407 (0.7)
4	$\text{C}_6\text{H}_4\text{CH}_3\text{-}p$	282 (5.0)	286 (7.9)	287 (4.7)
		388 (0.9)	399 (1.1)	412 (0.7)
5	SiMe_3	282 (9.1)	287 (2.4)	290 (3.5)
		375 (2.6)	384 (0.7)	398 (0.9)

cis-bis(acetylide) complex, although they differ from similar phosphine complexes in that the more intense of the two bands is the lower energy and that they are at a slightly higher frequency.¹⁵

The UV/visible spectra of compounds **1–5** in the 250–1000 nm region have been recorded (Table 2). All except **2** show similar spectra consisting of two major bands ($\epsilon \approx 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), one at 380 to 400, and one at 280 to 290 nm. These show a solvatochromic shift, moving to shorter wavelengths with increasing solvent polarity, and, in common with Gidney *et al.*,¹⁶ the bands have been assigned to the first and second metal to ligand charge transfer (MLCT) respectively. These correspond to excitation of an electron from the highest occupied molecular orbital (HOMO) (mainly platinum $d_{x^2-y^2}$ in nature) to the lowest and second lowest unoccupied molecular orbitals (LUMO and SLUMO), which are mainly bipyridyl in nature. The spectra of **1** and **5** also show a double transition at 307 and 320 nm that is not solvatochromic; this may be assigned to a bipyridyl π to π^* transition. It appears as a shoulder on the second MLCT band of **4**.

The spectrum of compound **2** is slightly different. The 280 nm MLCT band is still visible, as is some structure due to the bipyridyl π to π^* transition at around 320 nm. However, there is now one dominant absorption at around 370 nm that is much less solvatochromic than the first MLCT band of compounds **3–5**. The band has an absorption coefficient approximately four times that of the other complexes, and this spectral difference indicates that the origin of this band may be different from that in **3–5**.

A single crystal of complex $4 \cdot 3\text{CHCl}_3$ suitable for an X-ray diffraction study was grown by evaporation of a chloroform–hexane solution. This confirmed the proposed geometry of the compound, revealing it to be essentially planar (apart from the two *tert*-butyl groups) (Fig. 1). The average length of the Pt–C bond is 1.944 Å, a little shorter than is generally found in bis(acetylide) complexes of platinum with phosphine ligands¹⁷ but in good agreement with the other published bis(acetylide) structure containing a diimine ligand.⁸ Conversely, the average carbon–carbon distance in the triple bond of 1.23(2) Å is longer than is generally seen. The two acetylide groups bend away from each other, with the deviation from linearity at the acetylenic carbons averaging around 13°. Selected bond lengths and angles are presented in Table 3. There are hydrogen-bonding interactions between the chloroform solvate molecules, but the only such interaction involving the molecules of **4** is shown in Fig. 2. This involves the platinum atom Pt(1) and one of the hydrogen atoms H(27b) of the tolyl group of a neighbouring molecule (related by the symmetry operation $x, y, z + 1$), at a distance of 2.8 Å.¹⁸ The effect is to link the molecules of **4** into chains that run through the crystal lattice in the *c* direction.

In order to rationalise the differences in the spectra of compounds **2** and **3–5**, some simple MO calculations based on

Table 3 Selected bond lengths (Å) and angles (°) for compound $4 \cdot 3\text{CHCl}_3$

Pt(1)–C(28)	1.940(19)	Pt(1)–C(19)	1.947(17)
Pt(1)–N(2)	2.040(5)	Pt(1)–N(1)	2.065(14)
N(1)–C(5)	1.35(2)	N(2)–C(6)	1.34(2)
C(5)–C(6)	1.44(3)	C(19)–C(20)	1.25(2)
C(20)–C(21)	1.38(2)	C(28)–C(29)	1.20(2)
C(29)–C(30)	1.45(3)		
C(28)–Pt(1)–C(19)	91.7(7)	C(28)–Pt(1)–N(2)	94.7(7)
C(19)–Pt(1)–N(2)	173.6(6)	C(28)–Pt(1)–N(1)	173.1(7)
C(19)–Pt(1)–N(1)	95.0(6)	N(2)–Pt(1)–N(1)	78.6(6)
C(6)–N(2)–Pt(1)	114.7(13)	C(20)–C(19)–Pt(1)	172.1(15)
N(2)–C(6)–C(5)	117.1(17)	N(1)–C(5)–C(6)	113.6(16)
C(19)–C(20)–C(21)	175.0(18)	C(28)–C(29)–C(30)	173(2)

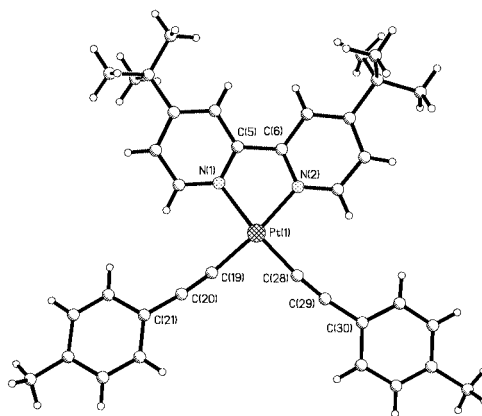


Fig. 1 The crystal structure of compound **4**. Three molecules of CHCl_3 have been omitted for clarity.

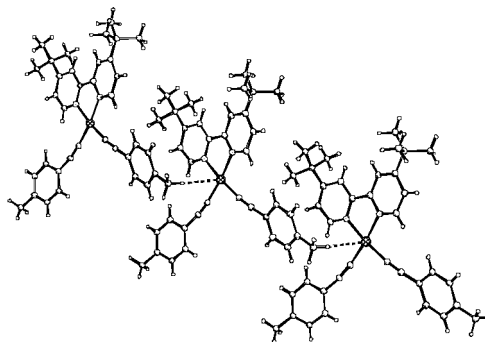


Fig. 2 Part of the crystal structure of compound **4**, showing the intermolecular interaction between H(27b) of one molecule and the platinum atom of a neighbouring molecule.

the structures of **2** and **4** have been performed with the CACAO software package.¹⁹ The results show that for **4** the HOMO is largely metal based, with in-phase overlap of the $d_{x^2-y^2}$ orbital with the in-plane π -bonding combinations of the two acetylide triple bonds. (The compound is lying in the *xy* plane with the acetylide ligands pointing between these axes, in common with the axis system used in ref. 4.) The LUMO is approximately 91% bipyridyl based, in agreement with previous calculations.⁴ In **2**, however, there are two degenerate LUMOs, each being based largely on the p_z orbitals of one of the two nitro groups. The third lowest unoccupied MO is the first to be bipyridine based, but is only approximately 72% bipyridyl in nature and contains a large contribution from the nitro groups of the acetylide ligands.

Spectroelectrochemical behaviour

The electrochemical behaviour of compounds **2** and **3** is consistent with the results of the extended Hückel molecular

Table 4 The parameters used to model the EPR spectra of compounds **2**²⁻ and **3**⁻, and of [Pt(bipy)(CN)₂]⁻ for comparison. This compound shows a further coupling of 2.2 G to two more ¹H nuclei, which is absent for **2**²⁻ and **3**⁻ because of the substitution of the 4 position of the pyridyl rings

Compound	¹⁹⁵ Pt coupling		¹⁴ N coupling		¹ H coupling		ΔH_{pp}
	No.	A_{iso}/G	No.	A_{iso}/G	No.	A_{iso}/G	
2 ²⁻	1	15.8	1	10.1	2	3.37	3.00
3 ⁻	1	21.0	2	3.37	2	2.85	3.2
[Pt(bipy)(CN) ₂] ⁻	1	20.5	2	3.4	2	2.8	

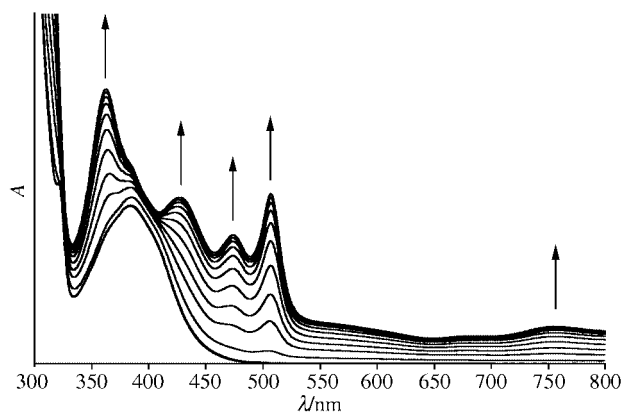


Fig. 3 The spectral changes seen during the reduction of compound **3** to **3**⁻.

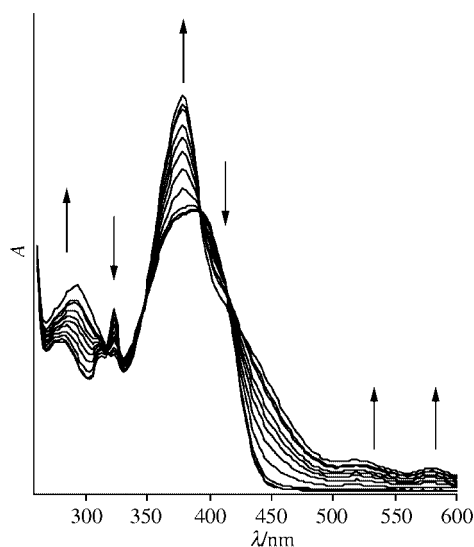


Fig. 4 The spectral changes seen during the reduction of compound **2** to **2**⁻.

orbital (EHMO) calculations. Cyclic voltammetry at 290 K reveals that both systems exhibit reversible reduction processes; complex **3** has a one-electron reversible reduction at -1.32 V, whereas **2** has a two-electron reversible reduction process at -1.08 V. Thus, it is easier to reduce the nitrated complex than the non-nitrated complex, and furthermore the dinitro complex is reduced in a single two-electron step (or in two very closely spaced one-electron steps that are not resolvable in cyclic voltammetry). Both complexes show reversible behaviour on an extended timescale, and were therefore subjected to spectroelectrochemical study.

In situ reduction of compound **3** to the radical monoanion [Pt(C≡CC₆H₅)₂(^tBu₂bipy)]⁻ **3**⁻ at -1.5 V at 240 K is shown in Fig. 3. The spectrum of the electrogenerated species shows a marked resemblance to that previously reported for [Pt(bipy)L₂]⁻,⁴ and so the bands centred at 769, 500 and 370 nm are assigned to $\pi \rightarrow \pi^*$ transitions of the co-ordinated bipyridyl anion, bipy⁻, and the band at 425 nm is assigned to a

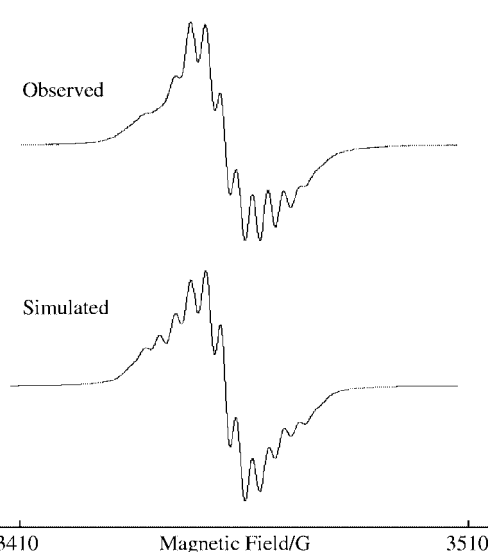


Fig. 5 The observed and simulated EPR spectra of compound **3**⁻.

charge transfer transition. It may be concluded therefore that the one-electron reduction product **3**⁻ should be formulated as [Pt^{II}(C≡CC₆H₅)₂(^tBu₂bipy)]⁻. Note that there are no isosbestic points in the spectra of **3**/**3**⁻ because the spectrum of the latter has a greater absorption coefficient at every wavenumber than that of the former. However, the spectrum of the parent species is completely regenerated if the electrogeneration potential is reset to 0 V after conversion into the anion is complete. The spectra obtained by reducing **2** under the same conditions are quite different from those obtained on reducing **3**. The two absorptions at around 320 nm that are assigned as intra-ligand bipy $\pi \rightarrow \pi^*$ transitions remain relatively unaffected, but the more intense band at 370 nm undergoes a considerable change (Fig. 4). None of the bands associated with the reduced bipyridyl ligand that are seen in Fig. 3 are generated, and so it may be inferred that the co-ordinated bipyridyl ligand is not the site of redox activity in this compound, and that the 370 nm absorption is not the same MLCT band seen for compounds **1** and **3**–**5**.

The *in situ* generated solution EPR spectrum of compound **3**⁻ is shown in Fig. 5, along with an excellent simulation. In the spectrum of the monoreduced anion hyperfine coupling of the unpaired electron to the platinum nucleus and super-hyperfine coupling to the nuclei is observed, which may be modelled using the data given in Table 4. The spectrum shows a great similarity to the previously reported solution EPR spectrum of [Pt(bipy)(CN)₂]⁻,⁴ and the coupling constants (also given in Table 4) are in remarkable agreement. Thus, the conclusions reached for [Pt(bipy)(CN)₂]⁻ must also apply in this system; that is, that the unpaired electron in **3**⁻ resides on the co-ordinated ^tBu₂bipy, in agreement with the predictions of the EHMO calculations and the UV/visible results given above. The simpler EPR spectrum for **3**⁻ as opposed to the cyanide complex confirms that the protons in the 4 and 4' positions in bipy couple to the unpaired electron in [Pt(bipy)(CN)₂]⁻, since by substituting those positions with *tert*-butyl groups one set of

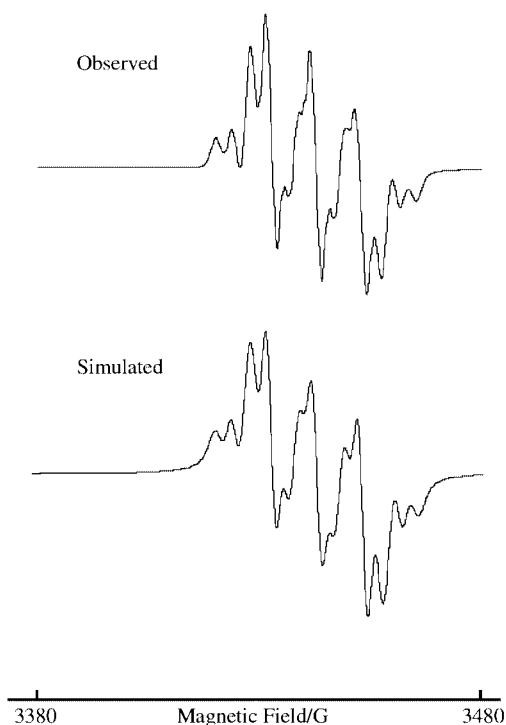


Fig. 6 The observed and simulated EPR spectra of compound 2^{2-} .

superhyperfine coupling is removed. We therefore assign the ^{14}N couplings in 3^- to the bipyridyl nitrogens, and the ^1H couplings to one of the bipyridyl hydrogen atoms, though it is not possible to decide which. In addition, the similar EPR behaviours of 3^- and $[\text{Pt}(\text{bipy})(\text{CN})_2]^-$ indicate that the phenylacetylide ligands are electronically analogous to cyanide ligands.

The solution EPR spectrum of compound 2^{2-} and an excellent simulation of the same are shown in Fig. 6; the simulation parameters are also included in Table 4. The EPR spectra of 2^{2-} and 3^- are obviously very different, and hence require very different coupling constants to model them. The spectrum of 2^{2-} has significantly smaller coupling to the platinum nucleus and a very much larger coupling to ^{14}N . Furthermore note that now the unpaired electron couples to only one ^{14}N nucleus, whereas in 3^- it couples to two such nuclei. Thus we suggest that the site of redox activity in 2 is the nitrophenyl ligand, and more specifically the nitro group which carries much of the electron density when the compound is in the reduced state. It therefore has a degenerate pair of LUMOs based on the nitro groups which are orthogonal to each other and spatially well separated, meaning that the two electrons are not interacting with each other and the diradical complex can satisfactorily be modelled using an $S = 1/2$ system. The ^1H coupling is presumably to two equivalent protons on the phenyl ring.

These findings indicate that the transition forming the 370 nm absorption band of compound 2 is based at least partly upon the nitro groups. The almost non-existent solvatochromism would seem to rule out this transition being charge transfer in nature, and therefore this band may tentatively be assigned as an intra-ligand feature.

Experimental

General

Solvents were pre-dried and distilled from appropriate drying agents.²⁰ All chemicals were obtained from commercial sources and used as received, except for *p*-nitrophenylacetylene, which was prepared according to the literature procedure.²¹ The ^1H NMR spectra were recorded on a Bruker AC 250 spectrometer and referenced to solvent resonances, IR spectra in dichloro-

methane in a NaCl cell on a Perkin-Elmer 1710 Fourier-transform spectrometer and +FAB mass spectra on a Kratos MS890 mass spectrometer. All electrochemical manipulations were performed under an inert atmosphere using a previously described experimental set-up,²² with platinum working and auxiliary electrodes and a Ag–AgCl reference electrode (against which the ferrocene–ferrocenium couple measures +0.55 V), in a 0.1 M solution of $[\text{Bu}_4\text{N}][\text{BF}_4]$ in DMF at 250 mV s^{-1} . UV/visible absorption spectra were obtained on a Perkin-Elmer $\lambda 9$ spectrometer. The EPR spectra were recorded on a Bruker ER200-D X-band spectrometer, and simulations were performed using Bruker Simphonia. Microanalyses were carried out in the Department of Chemistry in Cambridge.

Preparations

4,4'-Bis(*tert*-butyl)-2,2'-bipyridine (Bu_2bipy). This was synthesized by the method of McGill.¹² To 4.4 g (0.338 mmol) of sodium amide under nitrogen in a round bottomed flask were added 50 cm^3 of 4-*tert*-butylpyridine, and the mixture was then heated to 145 $^\circ\text{C}$ (not to reflux) for 6 h, during which time it became metallic purple. The solution was allowed to cool to about 40 $^\circ\text{C}$, during which time it became yellow, and extracted into a separating funnel with approximately 100 cm^3 of xylene; 20 cm^3 of distilled water were carefully added to hydrolyse the sodium amide, and the organic layer was separated off and dried over magnesium sulfate. This mixture was filtered to remove the drying agent, and the liquids (a mixture of unchanged 4-*tert*-butylpyridine and xylene) were distilled off at 60 $^\circ\text{C}$ *in vacuo*, leaving the crude product as a green solid. This was recrystallised twice from the minimum volume of hot acetone, yielding the product as white needles (6.79 g) ($\text{C}_9\text{H}_{12}\text{N}$ requires C, 80.55; H, 9.01; N, 10.43. Found: C, 80.65; H, 8.96; N, 10.53%). ^1H NMR (CDCl_3): δ 1.38 [s, 18 H, 'Bu], 7.29 [dd, 2 H, $^3J(\text{H}^5\text{H}^6) = 5$, $^4J(\text{H}^3\text{H}^5) = 2.5$ Hz, H^5], 8.39 [d, 2 H, H^3] and 8.58 [d, 2 H, H^6].²³

$[\text{PtCl}_2(\text{Bu}_2\text{bipy})]$ 1. A suspension of 0.68 g of platinum dichloride (2.57 mmol) and 0.80 g (2.98 mmol) of Bu_2bipy was refluxed overnight in 40 cm^3 of acetonitrile under a nitrogen atmosphere. Upon cooling the solution the pure product precipitated as a bright yellow solid, which was washed with diethyl ether and dried *in vacuo* (1.05 g, 1.96 mmol, 76%) ($\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Pt}$ requires C, 40.46; H, 4.52; N, 5.24%; M 534. Found: C, 40.38; H, 4.47; N, 5.4%; M^+ , m/z 535). $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2) 281 ($\epsilon/\text{M}^{-1}\text{cm}^{-1} = 2.71 \times 10^4$), 309 (9.4×10^3), 322 (9.4×10^3) and 388 (2.71×10^4). ^1H NMR (CDCl_3): δ 1.45 [s, 18 H, 'Bu], 7.47 [dd, 2 H, $^3J(\text{H}^5\text{H}^6) = 6.25$, $^4J(\text{H}^3\text{H}^5) = 2$ Hz, H^5], 7.88 [d, 2 H, H^3] and 9.45 [d, 2 H, H^6]. m/z 535 ($\text{M}^+ + \text{H}^+$) and 499 ($\text{M}^+ - \text{Cl}$).

Compound 2. Compound **1** (0.15 g, 0.28 mmol) 0.085 g of *p*-nitrophenylacetylene (0.56 mmol) and a catalytic amount (*ca.* 5 mg) of copper(I) iodide were stirred overnight in 10 ml of CH_2Cl_2 and 1 ml of $^i\text{Pr}_2\text{NH}$. The resulting yellow precipitate was filtered out, washed with CH_2Cl_2 , and recrystallised from warm DMF to give 0.114 g (0.15 mmol, 54%) of yellow microcrystalline product ($\text{C}_{34}\text{H}_{32}\text{N}_4\text{O}_4\text{Pt}\cdot\text{C}_3\text{H}_7\text{NO}$ requires C, 52.94; H, 4.81; N, 8.57%; M 756. Found: C, 53.38; H, 4.71; N, 8.43%; M^+ , m/z 756.6). ^1H NMR (CDCl_3): δ 1.45 [s, 18 H, 'Bu], 7.58 [d, 4 H, $^3J(\text{HH}) = 8.8$, phenyl CH], 7.63 [d, 4 H, $^3J(\text{H}^5\text{H}^6) = 6$ Hz, H^5], 7.98 [d, 2 H, H^3], 8.12 [d, 2 H, phenyl CH] and 9.55 [d, 2 H, H^6].

Compounds 3, 4 and 5. These were prepared from compound **1** and the appropriate terminal acetylene by the method detailed here for **5**: to a solution of 0.30 g of **2** (0.56 mmol) in 30 cm^3 of dichloromethane and 1 cm^3 of diisopropylamine was added 0.24 cm^3 (0.17 g, 1.7 mmol, 3 equivalents) of trimethylsilylacetylene (TMSA) and a catalytic amount of

copper(i) iodide (*ca.* 5 mg). This was stirred overnight under a nitrogen atmosphere, before being evaporated to dryness and purified using alumina column chromatography with dichloromethane as eluent. The product was obtained as a yellow-green solid (0.212 g, 0.322 mmol, 57%) following evaporation of the solvent (C₂₆H₄₂N₂PtSi₂ requires C, 51.12; H, 6.43; N, 4.26%; M 658. Found: C, 50.77; H, 6.38; N, 3.98%; M⁺, *m/z* 658.2). ¹H NMR (CDCl₃): δ 0.22 [s, 18 H, SiMe₃], 1.45 [s, 18 H, 'Bu], 7.55 [dd, 2 H, ³J(H⁵H⁶) = 5.9, ⁴J(H³H⁵) = 1.8, H⁵], 7.91 [d, 2 H, H³] and 9.67 [d, 2 H, ³J(PtH⁶) = 28.25 Hz, H⁶].

Compound **3** was a yellow solid obtained using phenylacetylene instead of TMSA, followed by recrystallisation from CH₂Cl₂–hexane. Yield: 0.156 g (0.234 mmol, 83%) (C₃₄H₃₄N₂Pt.CH₂Cl₂ requires C, 56.06; H, 4.84; N, 3.74%; M 666. Found: C, 56.17; H, 4.80; N, 3.40%; M⁺, *m/z* 666.2). ¹H NMR (CDCl₃): δ 1.43 [s, 18 H, 'Bu], 7.1–7.3 [m, 6 H, phenyl CH], 7.5–7.6 [m, 6 H, phenyl CH and H⁵], 7.93 [d, 2 H, ⁴J(H³H⁵) = 1.8, H³] and 9.70 [d, 2 H, ³J(H⁵H⁶) = 5.3 Hz, H⁶].

Compound **4** was a yellow solid obtained using *p*-tolylacetylene instead of TMSA, followed by recrystallisation from CH₂Cl₂–hexane. Yield: 0.255 g (0.37 mmol, 69%) (C₃₆H₃₈N₂Pt requires C, 62.30; H, 5.52; N, 4.04%; M 693. Found: C, 62.04; H, 5.57; N, 4.03%; M⁺, *m/z* 693.3). ¹H NMR (CDCl₃): δ 1.43 [s, 18 H, 'Bu], 2.31 [s, 6 H, tolyl CH₃], 7.04 [d, 4 H, ³J(HH) = 8, tolyl CH], 7.42 [d, 4 H, tolyl CH], 7.54 [dd, 2 H, ³J(H⁵H⁶) = 5.9, ⁴J(H³H⁵) = 1.8 Hz, H⁵], 7.92 [d, 2 H, H³] and 9.72 [d, 2 H, H⁶].

Crystallography

Yellow crystals of compound **4**·3CHCl₃ were obtained by slow evaporation of a chloroform solution. Suitable crystals were mounted using a perfluoroether oil, and cooled to 153 K with an Oxford Cryostream apparatus. Data were collected on a Rigaku AFC7R diffractometer using the ω–2θ technique. Semiempirical absorption corrections based upon ψ scans were applied (TEXSAN).²⁴ The structure was solved by Patterson methods (SHELXS 86)²⁵ and subsequent Fourier-difference syntheses, and refined by full-matrix least squares on *F*² (SHELXL 97).²⁶ The platinum and chlorine atoms were refined with anisotropic displacement factors, and all aromatic hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atoms. Methyl groups were given an idealised tetrahedral geometry and allowed to rotate during the refinement. A final electron density difference map showed no regions of significant electron density.

Crystal data. C₃₉H₄₁Cl₉N₂Pt, *M* = 1051.88, triclinic, space group *P*1̄ (no. 2), *a* = 11.115(3), *b* = 17.187(2), *c* = 10.573(4) Å, *a* = 103.58(2), *β* = 93.90(2), *γ* = 75.67(2)°, *U* = 2123.5(9) Å³, *T* = 290(2) K, *Z* = 2, μ(Mo-Kα) = 3.901 mm⁻¹, 4607 reflections measured, 4382 unique (*R*_{int} = 0.1580) which were used in all calculations. The final residuals on 264 parameters were *R*₁ = 0.068 and *wR*₂ = 0.195 for 3539 reflections with *I* > 2σ(*I*), and *R*₁ = 0.097, *wR*₂ = 0.226 for all data.

CCDC reference number 186/1736.

See <http://www.rsc.org/suppdata/dt/a9/a907028a/> for crystallographic files in .cif format.

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