# Synthesis, characterisation and photochemistry of platinum diselenolenes†

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The reaction between  $[Pt(PPh_3)_4]$  and cycloocteno-1,2,3-selenadiazole or bis-cycloocteno-1,4-diselenin in toluene under reflux yielded the poorly soluble mononuclear platinum diselenolene  $[Pt(Se_2C_8H_{12})(PPh_3)_2]$ , **1c**. Treatment of  $[Pt(C_2H_4)(PR_3)_2]$  with a bis-cycloalkeno-1,4-diselenin in a mixture of 1,4-dioxane, THF and toluene under reflux led in good yield to the platinum diselenolenes  $[Pt(Se_2C_{n+4}H_{2n+4})(PR_3)_2]$  (R = Et (**2**), Bu (**3**); n = 3 (**b**), 4 (**c**)). The analogous complexes  $[Pt(Se_2C_8H_{12})(L)]$  (L = dppm: **4c**; L = dppe: **5c**; L = dppp: **6c**) were prepared from **1c** *via* ligand exchange with chelating phosphines. All new compounds have been characterised by multinuclear NMR, IR and UV-visible spectroscopy and mass spectrometry, and their luminescence properties have been examined. The molecular structures of  $[Pt(Se_2C_7H_{10})(PEt_3)_2]$  (**2b**),  $[Pt(Se_2C_8H_{12})(PEt_3)_2]$  (**2c**) and  $[Pt(Se_2C_8H_{12})(dppm)]$  (**4c**) have been determined by X-ray crystallography.

# Introduction

Since the 1960s transition metal dithiolenes have attracted the attention of chemists, physicists and materials scientists,<sup>1</sup> as a result of their unusual electrochemical and optical properties, which have many potential applications in fields such as molecular electronics, infrared dyes, liquid crystals and catalysis.<sup>24</sup> The luminescent properties of platinum dithiolenes have received particular attention.<sup>5</sup> By contrast, the selenium analogues of dithiolenes (diselenolenes) have been little studied,<sup>6-12</sup> largely because of the lack of generally applicable preparative methods.

One possible route to diselenolenes involves the addition of an activated alkyne to a metal polyselenide,<sup>13</sup> as utilised by us to prepare  $[Pt{Se_2C_2(CO_2Et)_2}(PPh_3)_2]$ .<sup>14</sup> This method is, however, restricted to diselenolenes bearing electron-withdrawing substituents. The reactions of 1,2,3-selenadiazoles with low-valent transition metal compounds have previously been used, by us<sup>15</sup> and others,<sup>16</sup> to prepare a wide variety of selenium-containing complexes. In particular we have shown that cyclopentadienylcobalt<sup>17</sup>

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§Current address: Chemistry Group, Multidisciplinary Nanotechnology Centre, School of Engineering, Swansea University, Singleton Park, Swansea SA2 8PP, U.K. and palladium<sup>18</sup> diselenolenes bearing hydrocarbon substituents may be produced by this route. Palladium diselenolenes can also be prepared from 1,4-diselenins, the products of thermolysis of 1,2,3-selenadiazoles.<sup>19</sup>

In 1995 we reported the outcome of the reaction between  $[Pt(PPh_3)_4]$  and cycloocteno-1,2,3-selenadiazole (4,5,6,7,8,9-hexahydrocycloocta-1,2,3-selenadiazole).<sup>20</sup> We were unable at that time to characterise the products fully, but have now re-visited this reaction as the starting point for an investigation of possible synthetic routes to platinum diselenolenes. We also report here the results of some preliminary photochemical studies of this class of compounds, prompted by our recently reported discovery of near-infrared luminescence from their palladium analogues.<sup>21</sup>

# **Results and discussion**

## Synthesis of [Pt(Se<sub>2</sub>C<sub>8</sub>H<sub>12</sub>)(PPh<sub>3</sub>)<sub>2</sub>], 1c

The reaction of  $[Pt(PPh_3)_4]$  with cycloocteno-1,2,3-selenadiazole in refluxing toluene gave two products, the compound  $[Pt(SeC_8H_{12})(PPh_3)_2]$  containing a selenaketocarbene ligand, and a poorly soluble yellow powder with empirical formula  $[Pt(Se_2C_8H_{12})(PPh_3)_2]$ . In addition to poor solubility the latter product had a high melting point (>300 °C) and so was believed, at the time, to be polymeric. The poor solubility prohibited a full spectral analysis, but we have now been able to obtain a MALDI mass spectrum of this species in which the molecular ion (m/z = 987) for the monomer has high relative abundance. On the basis of this result, as well as the outcomes of the phosphine exchange reactions described below, we conclude that the poorly soluble yellow powder is, in fact, the monomeric diselenolene  $[Pt(Se_2C_8H_{12})(PPh_3)_2]$ , **1c** (see eqn (1)).



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Due to the moderate yield (26%) reported for **1c** (which was not exceeded in this study) some alternative routes to this compound were investigated. The reaction of  $[Pt(PPh_3)_4]$  with bis-cycloocteno-1,4-diselenin in refluxing toluene was found to give **1c** in 33% yield; there was no evidence of the formation of  $[Pt(SeC_8H_{12})(PPh_3)_2]$ . Reaction of  $[Pt(n^2-C_2H_4)(PPh_3)_2]$  with cycloocteno-1,2,3-selenadiazole in refluxing toluene also gave **1c** (eqn (2)). There was again no evidence for the formation of  $[Pt(SeC_8H_{12})(PPh_3)_2]$  under these conditions, although  $[Pt(n^2-C_2H_4)(PPh_3)_2]$  has been observed to react with cycloocteno-1,2,3-selenadiazole at room temperature in Et<sub>2</sub>O to give small amounts of  $[Pt(SeC_8H_{12})(PPh_3)_2]$ .<sup>22</sup>

Reaction of  $[Pt(SeC_8H_{12})(PPh_3)_2]$  with elemental selenium or with cycloocteno-1,2,3-selenadiazole in refluxing toluene did not yield 1c,<sup>20</sup> indicating that  $[Pt(SeC_8H_{12})(PPh_3)_2]$  is not an intermediate in the formation of 1c. On the basis of these results we postulate that both products of the original reaction are formed *via* the well-known thermal decomposition<sup>23,24</sup> of cycloocteno-1,2,3-selenadiazole to generate a selenaketocarbene: if this intermediate is intercepted by a source of the Pt(PPh\_3)\_2 fragment,  $[Pt(SeC_8H_{12})(PPh_3)_2]$  will be formed; otherwise the selenaketocarbene will dimerise to generate bis-cycloocteno-1,4diselenin, which on reaction with "Pt(PPh\_3)\_2" will yield 1c(Scheme 1).

# Attempted syntheses of $[Pt(Se_2C_6H_8)(PPh_3)_2]$ , 1a, and $[Pt(Se_2C_7H_{10})(PPh_3)_2]$ , 1b

Attempts to prepare and isolate pure  $[Pt(Se_2C_6H_8)(PPh_3)_2]$ , **1a**, and  $[Pt(Se_2C_7H_{10})(PPh_3)_2]$ , **1b**, by analogous procedures were unsuccessful. Interestingly in the reaction of  $[Pt(PPh_3)_4]$ (or  $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$ ) with cyclohexeno-1,2,3-selenadiazole, the reaction mixture became a purple colour at both room temperature and at reflux probably due to the formation of  $[Pt\{SeC(R^1)=C(R^2)N=NC(R^1)=C(R^2)Se\}(PPh_3)]$  ( $R^1-R^2$  =  $(CH_2)_4$ ). A similar colour change was observed when  $[Pt(PPh_3)_4]$  was reacted with cyclohepteno-1,2,3-selenadiazole at room temperature (although the reaction took several days), but not when cycloocteno-1,2,3-selenadiazole was used. Details of the synthesis and characterisation of other examples of this type of compound will be reported separately.<sup>25</sup>

## Reactions of 1c with trialkylphosphines and chelating diphosphines

Prolonged stirring of **1c** with an excess of PR<sub>3</sub> or a chelating diphosphine, L (L = dppm, dppe, dppp), in toluene at elevated temperatures yielded diselenolenes of the type [Pt(Se<sub>2</sub>C<sub>8</sub>H<sub>12</sub>)(PR<sub>3</sub>)<sub>2</sub>](R = Et, **2c**; Bu, **3c**) or [Pt(Se<sub>2</sub>C<sub>8</sub>H<sub>12</sub>)(L)](L = dppm, **4c**; dppe, **5c**; dppp, **6c**) (Scheme 2). Since **1c** is immobile on alumina, its separation from the products was straightforward. The trialkylphosphine derivatives **2c** and **3c** are more easily and directly synthesised by an alternative route (see below), and their full characterisation is discussed later.

Compounds **4c**, **5c** and **6c** were isolated as green-yellow solids in good yield. They are soluble in a wide range of organic solvents, and are generally air-stable both in the solid state and in solution, although standing in CHCl<sub>3</sub> does eventually lead to some decomposition, evidenced by the formation of a blue solid.

# Synthesis of $[Pt(Se_2C_{n+4}H_{2n+4})(PR_3)_2]$ (*n* = 3, 4; R = Et, Bu), 2b-c and 3b-c

The platinum diselenolenes  $[Pt(Se_2C_{n+4}H_{2n+4})(PR_3)_2]$  (n = 3, 4; R = Et, Bu) were obtained by refluxing  $[Pt(C_2H_4)(PR_3)_2]$ with the corresponding bis-cycloalkeno-1,4-diselenin in a dioxane/toluene/THF mixture (eqn (3)). Subsequent column chromatography led to the isolation of  $[Pt(Se_2C_{n+4}H_{2n+4})(PR_3)_2]$  as pale green solids. The synthesis of **2b–c** and **3b–c** in this way provides further evidence that in the reaction of  $[Pt(PPh_3)_4]$ with cycloocteno-1,2,3-selenadiazole, **1c** is produced *via* biscycloocteno-1,4-diselenin.



Scheme 1 Postulated mechanism of reaction leading to  $[Pt(SeC_8H_{12})(PPh_3)_2]$  and  $[Pt(Se_2C_8H_{12})(PPh_3)_2]$  (1c).

(3)



Scheme 2 Phosphine exchange reactions of 1c.

The cyclohexeno- derivatives **2a** and **3a** could not be prepared by an analogous procedure. It is believed that a cycloalkyne is generated in the reaction pathway (Scheme 3) and the greater ring strain of cyclohexyne will inhibit its formation.<sup>26</sup> A similar situation was encountered in the synthesis of  $[Pd(Se_2C_6H_8)(PBu_3)_2]$ from  $[Pd_2(dba)_3]$ -dba, PBu<sub>3</sub> and bis-cyclohexeno-1,4-diselenin, where a prolonged reflux in xylene was necessary to give the product,<sup>19</sup> in the platinum case the ethereal solvents used in the *in situ* synthesis of  $[Pt(C_2H_4)(PR_3)_2]$  limit the temperature at which the reaction can be carried out.

We have obtained further indirect evidence for the validity of this mechanism. The attempted synthesis of diselenolenes of the type [Pt(Se<sub>2</sub>C<sub>*n*+4</sub>H<sub>2*n*+4</sub>)(L)] (L = dppm, dppe) by reaction of [Pt(C<sub>2</sub>H<sub>4</sub>)(L)] with bis-cycloalkeno-1,4-diselenins was unsuccessful; there was no trace of the desired products. Compounds **4c** and **5c** could therefore only be prepared by phosphine exchange (see above). These results reinforce the proposed inclusion of a phosphine dissociation step in the reaction pathway, which for chelating phosphines (dppm, dppe) is not favoured.

Although it is possible to synthesise mononuclear or dinuclear palladium diselenolenes (Scheme 4),<sup>18,19,27</sup> there is no evidence for the formation of dinuclear platinum diselenolenes in these reactions. This is probably due to the platinum–phosphine stoichiometry of 1:2 imposed by the starting material; with the palladium compounds the palladium–phosphine stoichiometry could be altered to give either the mononuclear or dinuclear product.

 Table 1
 Selected bond lengths (Å) and angles (°) for 2b

Pt-P(1)	2.289(2)	Pt-P(2)	2.296(2)
Pt-Se(1)	2.4167(8)	Pt-Se(2)	2.4136(9)
$Se(1) \cdots Se(2)$	3.318(1)		
P(1)-Pt-P(2)	95.72(8)	Se(1)-Pt-Se(2)	86.77(3)
P(1)-Pt-Se(1)	89.20(5)	P(2)-Pt-Se(2)	88.58(6)

Compounds **2b–c** and **3b–c** are generally air-stable and soluble in hexane, toluene, EtOAc, acetone and dichloromethane; they do however decompose within a few hours on exposure to air in CHCl<sub>3</sub> solution.

## X-Ray crystallography<sup>†</sup>

It was possible to obtain crystals of **2b**, **2c**, **3b** and **4c** suitable for X-ray diffraction by recrystallisation from hexane–dichloromethane. However, the crystals of **3b** diffracted poorly, and although it was possible to confirm that the molecular structure was analogous to that of **2b**, satisfactory geometric parameters were not obtained. The structure of **2c** is affected by the disordered arrangement of several ethyl chains and of the cyclooctene ring in one of the two independent molecules forming the asymmetric unit. The molecular structures of **2b**, **2c** and **4c** are shown in Fig. 1, 2 and 3 respectively. Selected bond lengths and angles are listed in Tables 1, 2 and 3 respectively.

As expected, each molecule has a square-planar  $PtP_2Se_2$  core. In the case of **4c** the square plane is quite distorted as a result

Table 2   Selected bo	nd lengths (Å)	and angles (°) for <b>2c</b>	
Pt(1) - P(1)	2.289(2)	Pt(2)–P(3)	2.282(2)
Pt(1) - P(2)	2.283(2)	Pt(2)-P(4)	2.287(2)
Pt(1)-Se(1)	2.417(1)	Pt(2)-Se(3)	2.414(1)
Pt(1)-Se(2)	2.422(1)	Pt(2)-Se(4)	2.429(1)
$Se(1) \cdots Se(2)$	3.321(1)	$Se(3) \cdots Se(4)$	3.325(1)
P(1) - Pt(1) - P(2)	96.94(6)	P(3)-Pt(2)-P(4)	98.39(6)
Se(1)-Pt(1)-Se(2)	86.67(2)	Se(3) - Pt(2) - Se(4)	86.73(2)
P(1)-Pt(1)-Se(1)	90.03(4)	P(3) - Pt(2) - Se(3)	89.58(4)
P(2)-Pt(1)-Se(2)	86.53(5)	P(4)-Pt(2)-Se(4)	85.47(4)

of the acute P-Pt-P angle (73.92(9)°) imposed by the dppm

ligand, which is 23° smaller than the average of the P-Pt-

Table 3Selected bond lengths (Å) and angles (°) for 4c

Pt-P(1)	2.257(3)	Pt-P(2)	2.253(2)
Pt-Se(1)	2.395(1)	Pt-Se(2)	2.404(1)
$Se(1) \cdots Se(2)$	3.357(2)		
P(1)-Pt-P(2)	73.92(9)	Se(1)-Pt-Se(2)	88.79(4)
P(1)-Pt-Se(1)	98.30(7)	P(2)-Pt-Se(2)	99.18(7)

P angles formed by the monodentate phosphines in the other two compounds. This will probably result in a poorer Pt–P orbital overlap, which may be reflected in the lower  ${}^{31}P_{-}{}^{195}Pt$  and  ${}^{31}P_{-}{}^{77}Se$  coupling constants observed for 4c (see below). Possibly as a consequence of such a small P–Pt–P angle in 4c the opposite



Scheme 3 Postulated mechanism of reaction leading to 2b-c and 3b-c (R = Et, Bu; n = 3, 4).



Scheme 4 Preparation of mono- and dinuclear palladium diselenolenes.<sup>19</sup>





Fig. 1 View of the molecule in the structure of 2b with the atomic numbering scheme adopted. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.



**Fig. 2** Views of the two independent molecules in the structure of **2c** with the atomic numbering scheme adopted. The disordered arrangement of part of the cyclooctene ring in one of the molecules is shown, but only the major fraction of each of the disordered methyl or ethyl groups is shown for simplicity. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.



**Fig. 3** View of the molecule in the structure of **4c** with the atomic numbering scheme adopted. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Se-Pt-Se angle in that molecule is larger, by ca. 2°, than the corresponding angles in 2b and 2c. Also the value of the Se  $\cdots$  Se separation in 4c (3.357(2) Å) is higher, by at least 0.04 Å, than those found for the other structures. These differences in the geometry of the metal environment, between 4c and the other compounds, exceed those existing between 2b and 2c, in spite of the fact that the latter compounds are formed from ligands having different cycloalkene ring sizes. The most significant differences between the coordination geometries of 2b and 2c are in their P-Pt-Se angles: both molecules of 2c are slightly unsymmetrical, each with a 3-4° difference in the values of its opposite P-Pt-Se angles, whereas only a 0.6° difference is found for the 2b molecule, which is essentially symmetrical. Also the arrangements of the triethylphosphine ligands are different in the two compounds, as may be appreciated from Fig. 1 and 2: that of 2b is symmetrical with respect to a plane bisecting the molecule, normal to the coordination plane, whereas those of both molecules of 2c are unsymmetrical. Asymmetry of the metal atom environment and of the phosphine arrangement, similar to that of the present 2c molecules, was previously detected for a set of palladium diselenolene complexes having tributylphosphine coligands.<sup>19</sup> These aspects are considered in detail in the ESI,<sup>†</sup> with the support of the results of quantum mechanical calculations: the same factors that were considered to be responsible for the asymmetry in the palladium complexes appear to be effective also in the present compounds.

In all present structures the metal and ligand atoms, as well as the nearest four carbon atoms of the cycloalkene ring, lie in a plane, with largest deviations from the plane of 0.151(2) Å (P(2) in **2b**), 0.124(2) Å and 0.295(7) Å (P(2) and, respectively, C(28) in the two molecules of **2c**) and 0.27(1) Å (C(8) in **4c**). In all the structures, the other atoms deviate considerably from such molecular planes, with ring conformations of the chair and open envelope types, respectively for the seven-membered and the eight-membered ring; these arrangements match those previously verified for the Pd derivatives (ESI<sup>†</sup>).<sup>19</sup>

As a further note to the comparison between closely related Pt and Pd complexes, the mean value of the present Pt-P distances in 2c, 2.285(4) Å, is 0.045 Å smaller than the mean of Pd-P distances in the previous derivative with the cyclooctene-1,2diselenolate ligand,<sup>19</sup> characterised by the same unsymmetrical setting of phosphines as 2c. The Pt-Se distances in 2c, spanning the range 2.414(1)-2.429(1) Å, are closer to the Pd-Se ones (2.4034(8) and 2.4223(9) Å) in the other compound. If, on the other hand, the Pt-Se bond lengths in all of the present compounds 2b, 2c and 4c (spanning the range 2.395(1)–2.429(1) Å, only marginally wider than that of the 2c molecules) are compared with those presented by a broader selection of diselenolene derivatives, they are found to be slightly longer than in the anionic complex  $[Pt{Se_2C_2(CF_3)_2}_2]^-$ (average 2.375(6))<sup>28,29</sup> or in the neutral one  $[Pt(Se_2C_6H_4)(bipy)]$ (average 2.367(7) Å, bipy = 2,2'-bipyridyl),<sup>30</sup> but agree with those of the dianionic  $[Pt{Se_2C_2(CN)_2}_2]^{2-}$  (2.401(1) Å).<sup>31</sup> The Se-Pt-Se angles in 2b and 2c (average 86.7(1)°) are smaller than those in the  $[Pt{Se_2C_2(CF_3)_2}_2]^-$  salts (88.27(7)–91.64(7)°) and  $[Pt(Se_2C_6H_4)(bipy)](89.6(2)^\circ);$  this is probably a result of the large P-Pt-P angles of  $95.72(8)-98.39(6)^{\circ}$  in **2b** and **2c**, which are due to the steric repulsions between ethyl groups. As already said, the larger Se-Pt-Se angle of 4c is rationalised by the presence of a small P-Pt-P angle in that compound.

#### NMR spectroscopy

The NMR spectroscopic data for compounds **2b–c**, **3b–c**, **4c**, **5c** and **6c** are shown in Tables 4, 5 and 6, and are in accord with the proposed structures.

The <sup>77</sup>Se NMR spectra show the patterns expected for the X part of an AA'X spin system (a result of the <sup>31</sup>P nuclei being chemically but not magnetically equivalent). These consist of five lines (ignoring the satellites due to <sup>77</sup>Se–<sup>195</sup>Pt coupling) from which the coupling constants <sup>1</sup>J(<sup>77</sup>Se–<sup>195</sup>Pt), <sup>2</sup>J(<sup>77</sup>Se–<sup>31</sup>P<sub>cis</sub>), <sup>2</sup>J(<sup>77</sup>Se–<sup>31</sup>P<sub>trans</sub>) and <sup>2</sup>J(<sup>31</sup>P–<sup>31</sup>P) can be established by calculation based on the relative intensities of the lines (these parameters are usually more precisely accessible by analysis of the <sup>77</sup>Se satellite structure of the single <sup>31</sup>P resonance, but difficulties were encountered in obtaining <sup>31</sup>P NMR spectra with sufficiently good signal-to-noise ratios). All five lines of the AA'X pattern were observed for **2b–c**, **3b–c** and **5c**; as an example Fig. 4 shows the <sup>77</sup>Se resonance of **3c**.

There are large differences between the *cis*- and *trans*- coupling constants; the small <sup>77</sup>Se-<sup>31</sup>P<sub>cis</sub> coupling in these complexes is in part the reason why the AA'X pattern was not always fully resolved. For **2b–c** and **3b–c** the two <sup>31</sup>P-<sup>77</sup>Se coupling constants (avg. <sup>2</sup>*J*(<sup>77</sup>Se-<sup>31</sup>P<sub>trans</sub>) = 65 Hz; avg. <sup>2</sup>*J*(<sup>77</sup>Se-<sup>31</sup>P<sub>cis</sub>) = 16 Hz) are almost identical to those of the analogous palladium complexes [Pd(Se<sub>2</sub>C<sub>n+4</sub>H<sub>2n+4</sub>)(PBu<sub>3</sub>)<sub>2</sub>] (avg. <sup>2</sup>*J*(<sup>77</sup>Se-<sup>31</sup>P<sub>trans</sub>) = 66 Hz, <sup>2</sup>*J*(<sup>77</sup>Se-<sup>31</sup>P<sub>cis</sub>) = 16 Hz).<sup>19</sup> The calculated <sup>31</sup>P-<sup>31</sup>P coupling constants are quite different however: avg. <sup>2</sup>*J*(<sup>31</sup>P-<sup>31</sup>P) = 19 Hz, *cf*. <sup>2</sup>*J*(<sup>31</sup>P-<sup>31</sup>P) = 44 Hz in [Pd(Se<sub>2</sub>C<sub>n+4</sub>H<sub>2n+4</sub>)(PBu<sub>3</sub>)<sub>2</sub>]. The calculated <sup>2</sup>*J*(<sup>77</sup>Se-<sup>31</sup>P<sub>trans</sub>) coupling constant of 86 Hz for compound **5c** is greater than those for **2b–c** and **3b–c**; this could be a result of the geometrical constraints placed on the PtSe<sub>2</sub>P<sub>2</sub> core by the chelating phosphine, or reflect the change from a trialkyl- to a diarylalkylphosphine.

	Compound	2b	2c	3b	3c
<sup>1</sup> H: $\delta$ (ppm)	$\alpha$ -CH <sub>2</sub>	2.29–2.50 (4H, m)	2.42-2.56 (4H, m)	2.40-2.50 (4H, m)	2.41–2.46 (4H, m)
	$\beta$ -CH <sub>2</sub>	1.27–1.35 (4H, m)	1.24–1.34 (4H, m)	1.25–1.60 (4H, m)	1.24–1.50 (4H, m)
	$\gamma$ -CH <sub>2</sub>	1.75–1.83 (2H, m)	1.41–1.57 (4H, m)	1.85–2.10 (2H, m)	1.90–2.01 (4H, m)
	$CH_2P$	1.78–1.90 (12H, m)	1.90–2.10 (12H, m)	1.85–2.10 (12H, m)	1.90–2.01 (12H, m)
	$CH_2CH_2CH_2$	_	_	1.25-1.60 (24H, m)	1.24–1.50 (24H, m)
	$CH_3$	0.89 (18H, dt) <sup>a</sup>	0.99 (18H, dt) <sup>a</sup>	0.81 (18H, t) <sup>a</sup>	0.80 (18H, t) <sup>a</sup>
<sup>13</sup> C: $\delta$ (ppm)	$\alpha$ -CH <sub>2</sub>	39.3 <sup>r</sup>	37.0	39.3 <sup>r</sup>	37.0 <sup>r</sup>
	$\beta$ -CH <sub>2</sub>	33.8	31.2	33.8	31.2
	$\gamma$ -CH <sub>2</sub>	27.7	26.7	27.7	26.7
	$CH_2P$	17.9 <sup>c</sup>	$18.0^{c}$	25.9 <sup>c</sup>	$26.0^{\circ}$
	$CH_2CH_2CH_2$	_	_	24.5 <sup>d</sup>	24.5 <sup>d</sup>
	$CH_3CH_2$	_	_	26.7 <sup>e</sup>	26.7 <sup>e</sup>
	CH <sub>3</sub>	8.2	8.2	13.9	14.0
	C = C	131.1	130.2	130.8	130.0

**Table 4** <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data for **2b–c**, and **3b–c** in  $d_6$ -acetone solution

<sup>*a*</sup>  $^{3}J(^{1}H^{-1}H) = 7.6 \text{ Hz} (2\mathbf{b}-\mathbf{c}, 3\mathbf{c}), 7.2 \text{ Hz} (3\mathbf{b}), {}^{3}J(^{1}H^{-3!}P) = 16 \text{ Hz} (2\mathbf{b}-\mathbf{c}). {}^{b} {}^{3}J(^{13}C^{-195}Pt) = 20 \text{ Hz} (2\mathbf{c}). {}^{c} \text{ AA'X system, avg. } J(^{13}C^{-3!}P) = 16 \text{ Hz} (2\mathbf{b}), 18 \text{ Hz} (2\mathbf{c}, 3\mathbf{b}-\mathbf{c}), {}^{2}J(^{13}C^{-195}Pt) = 26 \text{ Hz} (2\mathbf{b}-\mathbf{c}), 25 \text{ Hz} (3\mathbf{b}-\mathbf{c}). {}^{d} \text{ AA'X system, avg. } J(^{13}C^{-3!}P) = 7 \text{ Hz}. {}^{e}J(^{13}C^{-195}Pt) = 19 \text{ Hz}. {}^{f^{2}}J(^{13}C^{-195}Pt) = 45 \text{ Hz} (2\mathbf{b}), 44 \text{ Hz} (2\mathbf{c}), 47 \text{ Hz} (3\mathbf{b}), 46 \text{ Hz} (3\mathbf{c}).$ 

Table 5 <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data for 4c, 5c and 6c in CDCl<sub>3</sub> solution

	Compound	4c	5c	6с
<sup>1</sup> H: $\delta$ (ppm)	$\alpha$ -CH <sub>2</sub>	2.73–2.90 (4H, m)	2.55–2.70 (4H, m)	2.45–2.70 (4H, m)
	$\beta$ -CH <sub>2</sub>	1.56–1.69 (4H, m)	1.29–1.59 (4H, m)	1.20–1.60 (4H, m)
	$\gamma - CH_2$	1.32–1.46 (4H, m)	1.29–1.59 (4H, m)	1.20–1.60 (4H, m)
	$CH_2P$	$4.61 (2H. t)^a$	2.20–2.45 (4H, m)	1.20 - 1.60 (4H, m)
	$CH_2CH_2CH_2$			0.76-0.90 (2H, m)
	$C_6H_5-o, p$	7.25–7.42 (12H, m)	7.25–7.45 (12H, m)	7.15–7.45 (12H, m)
	$C_6H_5-m^2$	7.72–7.78 (8H, m)	7.70–7.80 (8H, m)	7.50–7.65 (8H, m)
<sup>13</sup> C: $\delta$ (ppm)	$\alpha$ -CH <sub>2</sub>	37.3 <sup>b</sup>	36.7 <sup><i>b</i></sup>	37.6 <sup>b</sup>
	$\beta$ -CH <sub>2</sub>	31.4	30.3	31.2
	$\gamma$ -CH <sub>2</sub>	27.1	26.1	27.1
	CH <sub>2</sub> P	$48.0^{c}$	$28.5^{c}$	26.5°
	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	_	_	24.5
	$C_6 H_{s-0}$	133.6 <sup>d</sup>	133.1 <sup>d</sup>	$134.1^{d}$
	$C_6 H_5$ -ipso	132.6	130.9	Not observed
	$C_6 H_5 - p$	131.9	130.7	131.2
	$C_6H_5-m$	129.5 <sup>e</sup>	$128.2^{e}$	128.4 <sup>e</sup>
	C = C	Not observed	139.2	Not observed

 ${}^{a}{}^{2}J({}^{1}\text{H}{}^{-31}\text{P}) = 10 \text{ Hz}, {}^{3}J({}^{1}\text{H}{}^{-195}\text{Pt}) = 42 \text{ Hz}. {}^{b}{}^{3}J({}^{13}\text{C}{}^{-195}\text{Pt}) = 49 \text{ Hz}$  (**4c**), 47 Hz (**5c**, **6c**).  ${}^{c}{}^{1}J({}^{13}\text{C}{}^{-31}\text{P}) = 31 \text{ Hz}$  (**4c**), for **5c** complex multiplet with avg.  $J({}^{13}\text{C}{}^{-31}\text{P}) = 21 \text{ Hz}$ , for **6c** coupling unresolved.  ${}^{d}\text{ AA'X}$  system, avg.  $J({}^{13}\text{C}{}^{-31}\text{P}) = 6 \text{ Hz}$  (**4c**, **5c**), 5 Hz (**6c**).  ${}^{c}\text{ AA'X}$  system, avg.  $J({}^{13}\text{C}{}^{-31}\text{P}) = 6 \text{ Hz}$  (**4c**, **5c**), 5 Hz (**6c**).  ${}^{c}\text{ AA'X}$  system, avg.  $J({}^{13}\text{C}{}^{-31}\text{P}) = 6 \text{ Hz}$  (**4c**, **5c**), 5 Hz (**6c**).  ${}^{c}\text{ AA'X}$  system, avg.  $J({}^{13}\text{C}{}^{-31}\text{P}) = 6 \text{ Hz}$  (**4c**, **5c**), 5 Hz (**5c**).

One point of note is that the <sup>77</sup>Se resonances of compounds **2b** and **3b** are at much lower field (approximately 30 ppm) than those of **2c** and **3c**. This phenomenon is also observed in other diselenolenes,<sup>18,19</sup> 1,2,3-selenadiazoles and 1,4-diselenins (see ESI†): the number of carbon atoms in the aliphatic ring appears to have an influence on the electronic environment of the selenium atoms, with the C<sub>7</sub> ring giving lower field <sup>77</sup>Se NMR resonances than the C<sub>6</sub> and C<sub>8</sub> ring analogues. It is not clear why this is the case, nor whether it is limited to the C<sub>6</sub>–C<sub>8</sub> ring sizes. This effect of ring size upon chemical shift is also observed in the <sup>13</sup>C NMR spectra of these compounds:<sup>32</sup> the resonances of the aliphatic ring carbons are all at lower field for **2b** and **3b**. The resonances associated with the C=C group were weak, and as such the coupling constants associated with these atoms could not be determined.

#### UV-visible spectroscopy

The colours of **2b–c** and **3b–c** (pale green/yellow) differ significantly from those of their palladium analogues  $[Pd(Se_2C_{n+4}H_{2n+4})-(PBu_3)_2]$  and  $[Pd_2(Se_2C_{n+4}H_{2n+4})_2(PBu_3)_2]$  (purple).<sup>24</sup> The UVvisible spectra of the palladium diselenolenes show absorption maxima in both the UV and visible regions; by contrast compounds **2b–c**, **3b–c**, **4c**, **5c** and **6c** absorb relatively weakly in the visible region with absorption maxima in the UV region only (see Table 7). This indicates that the lowest excited state in these compounds is unlikely to have MLCT character, and is therefore different from that in a related series of bis(phosphine)platinum dithiolenes.<sup>33</sup> There are two significant differences between the two systems: firstly, the change from sulfur to selenium makes the ligand more electron-rich; secondly, the dithiolenes concerned carry

	Compound	2b	2c	3b	3c	4c	5c	6c
<sup>31</sup> P	$\delta$ (ppm) $^{1}J(^{31}P_{-}^{195}Pt)/Hz$	2.5 2767	2.4 2781	-5.3 2767	-5.1 2780	-47.4 2377	44.2 2784	-6.6 2676
<sup>77</sup> Se	$\delta$ (ppm)	481	441	474	454	457	452	466
	$^{1}J(7^{77}Se^{-195}Pt)/Hz$	268	268	264	256	294	268	260
	avg. ${}^{2}J({}^{77}\text{Se}{}^{-31}\text{P})/\text{Hz}$	41	40	40	41	35	46	47
	$^{2}J(77 \text{Se}^{-31}\text{P}_{cis})/\text{Hz}$	14	16	16	18	<i>a</i>	6	a
	$^{2}J(^{77}\text{Se}-^{31}\text{P}_{trans})/\text{Hz}$	67	63	64	64	a	86	a
	${}^{2}J({}^{31}P-{}^{31}P)/Hz$	20	20	19	18	a	7	a

**Table 6** <sup>31</sup>P and <sup>77</sup>Se NMR spectroscopic data for **2b–c**, **3b–c** in  $d_6$ -acetone solution and **4c**, **5c** and **6c** in CDCl<sub>3</sub> solution



Fig. 4 <sup>77</sup>Se NMR spectrum of 3c in CDCl<sub>3</sub> solution.

Table 7 Solution phase UV-visible data for compounds 2b-c, 3b-c, 4c, 5c and 6c

Compound	$\lambda_{\rm max}/{ m nm}~(\epsilon/{ m cm}^{-1}~{ m M}^{-1})$			
<b>2</b> b <sup><i>a</i></sup>	220 (26 400), 235 (29 500), 320 (4500)			
2c <sup>a</sup>	215 (26 300), 240 (29 200), 320 (4700)			
3b <sup>a</sup>	220 (28 100), 240 (36 900), 320 (5100)			
3c <sup>a</sup>	215 (37 500), 240 (37 500), 320 (5500)			
4c <sup>b</sup>	365 (3700)			
5c <sup>b</sup>	350 (3050)			
6c <sup>b</sup>	325 (4000)			

<sup>*a*</sup> Recorded in CH<sub>2</sub>Cl<sub>2</sub> solution ( $10^{-5}$  M) between 200 and 800 nm. <sup>*b*</sup> Recorded in MeCN solution ( $10^{-4}$  M) between 300 and 800 nm; typically there is a 5 nm bathochromic shift on changing the solvent to toluene.

electron-withdrawing substituents, making them much better  $\pi$ -acceptors.

The red shift in the lowest energy absorption band for compound 4c is intriguing. We speculate that the distortion at platinum imposed by the four-membered chelate ring is responsible, as complexes with monodentate phosphines resemble the dppp complex 6c, and the behaviour of the dppe complex 5c is intermediate.

#### Photochemistry

Compounds 1c, 2c, 3b, 4c, 5c and 6c were examined for luminescence under steady-state (usually 380 nm) and pulsed laser UV (355 nm) excitation in: the solid state at room temperature and at 77 K; aerated and nitrogen-purged room temperature (RT) toluene solution (except 1c because of solubility problems); a toluene–diethyl ether–ethanol (1:2:1) (TDE) glass at 77 K (again excepting 1c because of solubility problems). Table 8 collects photochemical data.

In nitrogen-purged toluene solution all the soluble platinum diselenolenes show a weak and narrow emission band at *ca*. 650–660 nm (see Fig. 6 for an example) with a shoulder at *ca*. 700 nm which is perhaps a vibronic feature. Emission decays are acceptable fits to single exponentials, the lifetimes are quite long (*ca*. 50–90  $\mu$ s), and quantum yields are low. We assign this RT emission to molecular phosphorescence because of the long lifetime and the observation that it is quenched by oxygen at the diffusion-controlled rate.

In the solid state at 77 K all the complexes exhibit long-lived intense emission. Emission decays are acceptable fits to single exponentials with lifetimes of ca. 14-20 µs. The emission spectra are all broad and structureless (Fig. 5) but show emission maxima ranging from ca. 550-680 nm depending upon the ligands. Only 1c and 4c show strong emission in the solid state at RT, and this is even broader than that at 77 K and is somewhat reduced in intensity (Fig. 5). Examination of the emission decay kinetics across the emission bands for these two compounds, *i.e.* 1c and 4c, showed no wavelength dependence of emission decay at either 77 K or RT. For 2c and 6c a combination of a small sample and relatively weak emission made collection of data difficult. For all the compounds solid state room temperature decay lifetimes are ca. 1.4–3.2  $\mu$ s, significantly shorter than those at 77 K. It is interesting to note that while the emission quantum yield for 4c increases by perhaps only a factor of 1.5 in going from RT to 77 K the lifetime increases by a factor of 10.

When examined at 77 K in a TDE glass the general behaviour of all the compounds is similar in that an intense broad emission band with emission maximum in the 580–620 nm range is observed.

	Emission in nitrogen-purged room temperature toluene solution			Emission in toluene–diethyl ether–ethanol (1 : 2 : 1) glass at 77 K		Emission in the solid state				
							298 K		77 K	
Compound	$\lambda_{\rm max}/{\rm nm}$	τ/10 <sup>-6</sup> s	$k_{ m q}/10^{10}~{ m M}^{-1}~{ m s}^{-1}$	${oldsymbol{\Phi}}_{ m phos}$	$\lambda_{\rm max}/{\rm nm}$	τ/10 <sup>-6</sup> s	$\overline{\lambda_{\max}/nm}$	$\tau/10^{-6}$ s	$\lambda_{\rm max}/{\rm nm}$	τ/10 <sup>-6</sup> s
1c 2c	650	$50 \pm 2$			600	$22.5 \pm 1.1$	675 Weak⁵	$3.21\pm0.02$	675	$16.7 \pm 0.7$
3b	647 <sup>c</sup>				614	$18.3 \pm 1.7$	Weak <sup>b</sup>		672 <sup>d</sup>	$14.2 \pm 0.5$
4c	647	$80 \pm 6$	1.08"	$0.0007 \pm 0.0001^{e}$	600 (broad) 645 (sharp)	$\begin{array}{c} 10.8 \pm 1.2 \\ 60.1 \pm 0.7^{f} \end{array}$	630	$1.89\pm0.04$	619	$20.1 \pm 1.5$
5c 6c	662 649	$\begin{array}{c} 87\pm7\\ 55\pm5\end{array}$			581 610	$\begin{array}{c} 22.8 \pm 2.1 \\ 22.7 \pm 2.5 \end{array}$	Weak <sup>b</sup> Weak <sup>b</sup>	$1.51\pm0.05$	600 556	$14.7 \pm 0.9$ $14.1 \pm 0.6$

#### Table 8 Photophysical data for compounds 1c, 2c, 3b, 4c, 5c, and 6c

<sup>*a*</sup> From a comparison of emission lifetimes in nitrogen-purged and air-equilibrated solutions. <sup>*b*</sup> Weak emission and broad noisy spectrum made assignment of  $\lambda_{max}$  difficult. <sup>*c*</sup> Weak emission. <sup>*d*</sup> Excitation at 470 nm. <sup>*e*</sup> Excitation at 416 nm. <sup>*f*</sup> Long-lived component from a double exponential fit.



Fig. 5 Emission spectra of 4c in the solid state at room temperature and 77 K. Insets show emission decay curves, with best-fit single exponentials (solid lines).

However for 4c (Fig. 6) there is also a distinct feature at 645 nm which, by comparison with the solution phase emission spectrum we assign to molecular phosphorescence. Decay kinetics for the broad emission, measured at 600 nm, and the sharp band, at 645 nm, are different, with the latter showing a long-lived component (Table 8). Because of the presence of this phosphorescence band in the emission spectrum of 4c and the two decay times, we tentatively suggest that both the broad emission component seen in TDE glasses at 77 K and the broad band solid state emission are intermolecular in origin, from either the solid state lattice, or aggregates in the glass. Initially we thought that the emissions might have a similar origin to the broad band emission seen in stacked platinum complexes such as the tetracyanoplatinates,<sup>34</sup> but the X-ray diffraction data for 2b, 2c and 4c show the closest intermolecular distances to be greater than 500 pm which is too large for this to be the case.

Fig. 7 shows the emission from **3b** in TDE glass at 77 K. We include this spectrum because it most clearly shows an additional emission band in the blue spectral region which is short lived ( $\tau < ca. 25$  ns, the time resolution of our ns laser system) with vibronic

structure. A similar band can be observed with varying clarity when any of the complexes is irradiated with UV light under any of the conditions we have used, *i.e.* aerated or nitrogen-purged solution, solid state at RT or 77 K, or TDE glass at 77 K, even when the broad orange/red emission is absent. The short lifetime and position suggest this feature may be fluorescence.

We are currently examining the photochemistry of these complexes in more detail in an attempt to identify the origins of these various emission bands

### Conclusion

The poorly soluble product of the reaction between cycloocteno-1,2,3-selenadiazole and  $[Pt(PPh_3)_4]$  has been confirmed as the mononuclear platinum diselenolene  $[Pt(Se_2C_8H_{12})(PPh_3)_2]$ , **1c**. The phosphine ligands in **1c** may be exchanged to generate more soluble species, including those containing the chelating bidentate phosphines dppm, dppe and dppp. The complexes containing trialkylphosphines are best prepared by the reaction between  $[Pt(C_2H_4)(PR_3)_2](R = Et, Bu)$  and a bis-cycloalkeno-1,4-diselenin,

![](_page_9_Figure_1.jpeg)

Fig. 6 Emission spectra of 4c in room temperature nitrogen-purged toluene solution (dashed line) and in a toluene-diethyl ether-ethanol (1:2:1) glass at 77 K (solid line).

![](_page_9_Figure_3.jpeg)

Fig. 7 Emission spectrum of **3b** in a toluene–diethyl ether–ethanol (1:2:1) glass at 77 K.

and this represents an efficient and potentially versatile route to platinum diselenolenes. These compounds display unusual luminescent properties, which are the subject of ongoing investigation in our laboratories.

# Experimental

#### Materials and general procedures

All the reactions below were performed using standard Schlenk techniques under an atmosphere of dry argon. Dry solvents, when required, were distilled over molten potassium (hexane, THF), molten sodium (1,4-dioxane, toluene) or  $CaH_2$  (CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, MeCN). Solvents were degassed by repeated boiling under reduced pressure followed by saturation with inert gas.

Cycloalkeno-1,2,3-selenadiazoles,<sup>23</sup> bis-cycloalkeno-1,4-diselenins,<sup>24</sup> [Pt(PPh<sub>3</sub>)<sub>4</sub>],<sup>35</sup> [Pt(Se<sub>2</sub>C<sub>8</sub>H<sub>12</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**1c**),<sup>20</sup> [PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]<sup>36</sup> and [PtCl<sub>2</sub>(PBu<sub>3</sub>)]<sup>37</sup> were synthesised by literature procedures (slightly adapted in some cases<sup>22</sup>). Platinum salts were obtained on loan from Johnson Matthey plc; PEt<sub>3</sub> was obtained from Strem Chemicals Inc.; cyclohexanone, cycloheptanone, cyclooctanone, dppm, dppe, dppp, ethene, naphthalene, PBu<sub>3</sub>, P(*i*-C<sub>5</sub>H<sub>11</sub>)<sub>3</sub>, P(OMe)<sub>3</sub>, potassium, and sodium were obtained from Aldrich Chemical Company. All chemicals were used as supplied.

#### Physical measurements

<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded at 400.1 MHz, 100.6 MHz and 162.0 MHz respectively using a Bruker AC400 with tetramethylsilane as internal standard (<sup>1</sup>H, <sup>13</sup>C) or 85% phosphoric acid as external standard (<sup>31</sup>P). <sup>77</sup>Se NMR spectra were recorded at 47.7 MHz on a Bruker WM250 with dimethyl selenide as external standard. All <sup>13</sup>C, <sup>31</sup>P and <sup>77</sup>Se NMR spectra were <sup>1</sup>H decoupled. IR spectra were recorded using a Perkin-Elmer Spectrum One FTIR spectrometer with ATR; the data obtained are included in the ESI. UV-visible spectra were recorded on either a Unicam UV300 spectrometer or an HP 8452A diode array spectrophotometer, using quartz cuvettes. Mass spectra were recorded by the EPSRC Mass Spectrometry Service Centre using fast atom bombardment (FAB) or MALDI (for 1c); m/z values have been rounded to the nearest integer; assignments are based on isotopomers containing <sup>1</sup>H, <sup>12</sup>C, <sup>31</sup>P, <sup>80</sup>Se and <sup>195</sup>Pt; expected isotope distribution patterns were observed.

### Syntheses of 2c and 3c from [Pt(Se<sub>2</sub>C<sub>8</sub>H<sub>12</sub>)(PPh<sub>3</sub>)<sub>2</sub>], 1c

Under argon in a pre-dried Schlenk tube, **1c** (50 mg, 0.05 mmol) was slurried in dry toluene (4 mL); the slurry was treated with 1 mL of PEt<sub>3</sub> (**2c**) or PBu<sub>3</sub> (**3c**) and stirred at approximately 70 °C for 3 days. After this time a green/yellow solution had formed. This was concentrated *in vacuo* and the residue chromatographically separated on Al<sub>2</sub>O<sub>3</sub> with toluene–EtOAc (1:1) elution; collection of the green/yellow fraction and subsequent concentration *in vacuo* gave **2c** (yellow solid, 32 mg, 93% yield) or **3c** (yellow solid, 40 mg, 90% yield).

#### Syntheses of 4c, 5c and 6c from [Pt(Se<sub>2</sub>C<sub>8</sub>H<sub>12</sub>)(PPh<sub>3</sub>)<sub>2</sub>], 1c

Under argon in a pre-dried Schlenk tube, a mixture of **1c** (60 mg, 0.06 mmol) and dppm (230 mg, 0.6 mmol), dppe (240 mg, 0.6 mmol) or dppp (250 mg 0.6 mmol) in dry toluene (8 mL) was heated to 90 °C for 4 days. After this time a green solution had formed. This was concentrated *in vacuo*, and the residue chromatographically separated on alumina with toluene–CH<sub>2</sub>Cl<sub>2</sub> (1:1) elution; collection of the green fraction and subsequent concentration *in vacuo* gave **4c** (yellow solid, 44 mg, 86% yield), **5c** (yellow solid, 36 mg, 69% yield) or **6c** (yellow solid, 36 mg, 68% yield). NMR spectroscopic data for **4c**, **5c** and **6c** are summarised in Tables 5 and 6. FAB MS, m/z (relative abundance, assignment): **4c**, 847 (100, [M]<sup>+</sup>); **5c**, 861 (100, [M]<sup>+</sup>); **6c**, 875 (100, [M]<sup>+</sup>). Crystals of **4c** suitable for an X-ray diffraction study were obtained from a hexane–CH<sub>2</sub>Cl<sub>2</sub> solution at –20 °C.

### Syntheses of 2b-c and 3b-c from [Pt(C<sub>2</sub>H<sub>4</sub>)(PR<sub>3</sub>)<sub>2</sub>]

All experiments were carried out according to the following general procedure. Under argon  $[PtCl_2(PR_3)_2]$  (0.4 mmol; R = Et, Bu) was taken up in 1,4-dioxane (20 mL) and the solution degassed. This solution was put under an ethene atmosphere and treated dropwise with NaC<sub>10</sub>H<sub>8</sub> (~0.12 M solution in THF), complete conversion to  $[Pt(C_2H_4)(PR_3)_2]$  being evidenced by the solution holding the green colour for approximately 2–3 min before clearing. The ethene atmosphere was replaced with an argon atmosphere, and the reaction mixture was treated with a solution of bis-cycloalkeno-1,4-diselenin (0.6 mmol) in degassed

toluene (8 mL). The reaction mixture was heated to reflux for 1 h after which time it was pale green in colour; concentration *in vacuo* gave a green oil, which was purified by column chromatography on alumina with a 3 : 1 mixture of toluene and ethyl acetate. Collection of the pale green band gave **2b–c** and **3b–c** as analytically pure yellow solids. Yields: **2b**, 218 mg, 80%; **2c**, 192 mg, 69%; **3b**, 201 mg, 59%; **3c**: 218 mg, 63%. NMR spectroscopic data for **2b–c** and **3b–c** are summarised in Tables 4 and 6. FAB MS, m/z (relative abundance, assignment): **2b**, 685 (50,  $[M]^+$ ), 431 (100,  $[Pt(PEt_3)_2]^+$ ); **2c**, 699 (20,  $[M]^+$ ), 431 (100,  $[Pt(PEt_3)_2]^+$ ); **3b**, 839 (30,  $[M]^+$ ), 599 (100,  $[Pt(PBu_3)_2]^+$ ); **3c**, 867 (30,  $[M]^+$ ), 599 (100,  $[Pt(PBu_3)_2]^+$ ). Crystals of **2b** and **2c** suitable for an X-ray diffraction study were obtained by recrystallisation from toluene–hexane at -20 °C.

# X-Ray crystallography†

X-Ray diffraction data for **2b**, **2c** and **4c** were collected at room temperature on an Oxford Diffraction Xcalibur 3 CCD diffractometer, using Mo K $\alpha$  radiation. Crystal data and the main data collection and structure refinement parameters are given in Table 9.

Lattice constants were determined from the settings of 6990 (2b), 13 233 (2c) and 1962 (4c) reflections. Corrections for absorption were applied with SADABS.<sup>38</sup> The structures of 2b and 2c were solved by direct methods<sup>39</sup> and that of 4c by heavy-atom methods; they were all refined by full-matrix least-squares on  $F^2$  values, with SHELXL.<sup>40</sup> In the case of the acentric 4c the absolute structure was assigned on the basis of *R* values and Flack's test;<sup>41</sup> a correction for the presence of a small twinning component generated by rotation around [100] was also applied. All nonhydrogen atoms were refined anisotropically and hydrogens were placed in idealized positions, each riding on the respective carrier atom, with  $U_{\rm H} = 1.2 U_{\rm C}^{\rm eq} (U_{\rm H} = 1.5 U_{\rm C}^{\rm eq}$  for methyl groups). Effects of disorder in the chains of 2c were accounted for. Programs used in the crystallographic calculations included PARST for analysis of geometries,<sup>42</sup> and ORTEP for graphics.<sup>43</sup>

#### Photochemistry

Steady-state room temperature and 77 K emission measurements were performed using a Perkin Elmer MPF-44E fluorescence spectrometer with a 150 W xenon arc lamp and a Hamamatsu R928 photomultiplier. An excitation wavelength of 380 nm was generally used, with excitation and emission slitwidths of between 6 nm and 8 nm. A 420 nm cut-off filter on the emission monochromator was used for studies at wavelengths longer than 450 nm. At room temperature a 1 cm  $\times$  1 cm quartz fluorescence cell was used; at 77 K an NMR tube cooled by liquid nitrogen in a phosphorescence Dewar was used. The quantum yield of room temperature phosphorescence for 4c was measured using tetraphenylporphyrin in ethanol at 298 K  $(\Phi_{\rm em} = 0.15)^{44}$  as emission standard. Nanosecond laser kinetic measurements were obtained using an Applied Photophysics Laser Kinetic Spectrometer with the 355 nm emission from a Spectron frequency tripled Nd/YAG laser as excitation pulse, and emission slitwidths of 19 nm. The averaged data from 8-16 decay curves were recorded using a LeCroy 9304AM oscilloscope. For samples which gave relatively weak emission, amplification of the laser pulse was used in order to improve the signal-to-noise ratio. Low

 Table 9
 Crystallographic data collection and refinement parameters for 2b, 2c and 4c

Compound	2b	2c	4c	
Empirical formula	$C_{19}H_{40}P_{2}PtSe_{2}$	$C_{20}H_{42}P_2PtSe_2$	$C_{33}H_{34}P_2PtSe_2$	
Formula weight	683.46	697.48	845.55	
T/K	293(2)	293(2)	293(2)	
Wavelength/Å	0.71069	0.71069	0.71069	
Crystal system	Orthorhombic	Triclinic	Orthorhombic	
Space group	Pbca	$P\overline{1}$	$Pc2_1n$	
a/Å	11.584(1)	12.836(1)	13.504(1)	
b/Å	15.516(2)	14.189(1)	14.049(2)	
c/Å	27.248(2)	16.900(1)	16.183(2)	
$\alpha/^{\circ}$	90.00	110.62(1)	90.00	
$\beta/^{\circ}$	90.00	108.63(1)	90.00	
$\gamma/^{\circ}$	90.00	99.46(1)	90.00	
Volume/Å <sup>3</sup>	4897.5(8)	2593.5(2)	3070.2(6)	
Ζ	8	4	4	
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.854	1.786	1.829	
Absorption coefficient/mm <sup>-1</sup>	8.834	8.343	7.067	
F(000)	2640	1352	1632	
Crystal size/mm	$0.45 \times 0.40 \times 0.36$	0.70  imes 0.60  imes 0.40	$0.40 \times 0.40 \times 0.25$	
$\theta$ range for data collection/°	4.04 to 26.37	4.26 to 26.37	4.05 to 27.33	
Reflections collected	34 446	18 863	27 746	
Independent reflections [Rint]	4986 [0.0761]	10048 [0.0265]	6358 [0.0610]	
Observed reflections $[I > 2\sigma(I)]$	3813	8049	4882	
Parameters [restraints]	229	560 [348]	344 [1]	
Goodness-of-fit on $F^2$	1.001	1.082	1.061	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0490$	$R_1 = 0.0324$	$R_1 = 0.0489$	
	$wR_2 = 0.1256$	$wR_2 = 0.0776$	$wR_2 = 0.1137$	
R indices (all data)	$R_1 = 0.0649$	$R_1 = 0.0454$	$R_1 = 0.0596$	
	$wR_2 = 0.1356$	$wR_2 = 0.0812$	$wR_2 = 0.1207$	
Largest diff. peak/hole/e Å <sup>-3</sup>	2.310/-2.251	1.197/-1.180	2.457/-1.799	

temperature emission spectra of frozen solutions were recorded in a toluene–diethyl ether–ethanol (1:2:1) glass.<sup>45</sup> The kinetic data were analysed using Jandel Table-Curve<sup>TM</sup>.

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