

## Synthesis of Cyclometallated Pt(II) Complexes of a Bulky Bipyridine Ligand

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### Abstract

Treatment of 3,4,5,6-tetraphenyl-2,2'-bipyridine (LH) (**7**) with  $[\text{PtCl}_2(\text{dmsO})_2]$  (dmsO = dimethyl sulfoxide) in chloroform afforded the cyclometallated square-planar platinum(II) complex  $[\text{PtCl}(\text{L})]$  (**8**) and the octahedral Pt(IV) complex *mer*- $[\text{PtCl}_3(\text{L})]$  (**9**) containing an anionic tridentate ( $\text{C}^{\wedge}\text{N}^{\wedge}\text{N}$ ) ligand. The chloride of (**8**) can be easily replaced by trifluoroacetate to yield  $[(\text{L})\text{PtO}_2\text{CCF}_3]$  (**10**). Reaction of (**8**) with the alkyne  $\text{HC}\equiv\text{CC}_6\text{H}_4\text{Bu}^t-4$  resulted in the formation of  $[(\text{L})\text{PtC}\equiv\text{CC}_6\text{H}_4\text{Bu}^t-4]$  (**11**). Treatment of (**8**) with 4-dimethylamino-pyridine (DMAP) and  $\text{PPh}_3$  in dichloromethane, and the subsequent addition of  $\text{NH}_4\text{PF}_6$  in methanol produced the salts  $[\text{Pt}(\text{DMAP})(\text{L})]\text{PF}_6$  (**12**) and  $[\text{Pt}(\text{PPh}_3)(\text{L})]\text{PF}_6$  (**13**), respectively. In a similar manner, reaction of (**8**) with 0.5 equiv. of bis(diphenyl-phosphino)methane (dppm) formed the dppm-bridged binuclear dicationic salt  $[(\text{L})\text{Pt}(\mu\text{-dppm})\text{Pt}(\text{L})][\text{PF}_6]_2$  (**14**).


**Keywords:** Pt(II) complexes, cyclometallation, bipyridine, acetylides, bridging complexes

### Introduction

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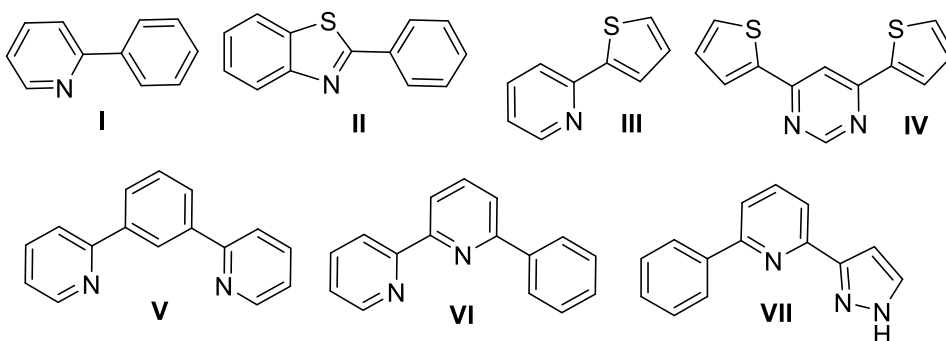
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(Received 14<sup>th</sup> March 2020; Revised 20<sup>th</sup> May 2020; Accepted 27<sup>th</sup> May 2020) © OUSL)



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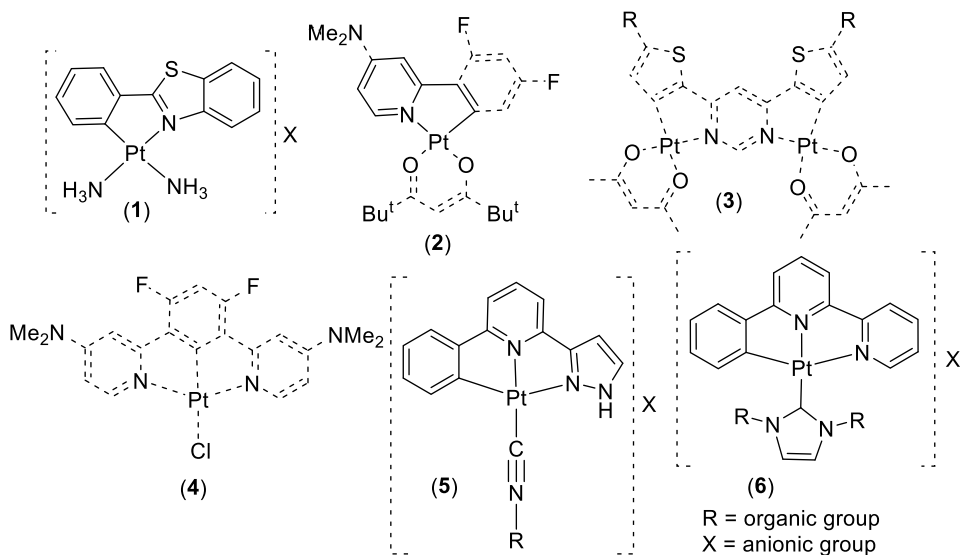
Interest on cyclometallated complexes of the type (C<sup>^</sup>N)M, (N<sup>^</sup>C<sup>^</sup>N)M and (C<sup>^</sup>N<sup>^</sup>N)M of platinum, ruthenium and iridium has risen recently as they are capable of harvesting light (Balzani & Campagna, 2007). Cyclometallated platinum(II) complexes containing a bidentate unit (C<sup>^</sup>N)Pt (Nikolaeva & Puzyk, 2013; Murphy, *et al.*, 2012; Shafikov, 2019), tridentate units (N<sup>^</sup>C<sup>^</sup>N)Pt (Murphy, *et al.*, 2012; Colombo, *et al.*, 2015; Williams, *et al.*, 2003) and (C<sup>^</sup>N<sup>^</sup>N)Pt (Tsai, *et al.*, 2015; Fung, *et al.*, 2016; Feng, *et al.*, 2006; Shao, *et al.*, 2008; Lu, *et al.*, 2004; Nolan, *et al.*, 2013) are derived from aromatic N-donor ligands which display a variety of emissive excited states, including ligand-to-metal and metal-to-ligand charge transfers. Phosphorescent Pt(II) complexes possess many advantages such as a wide emission colour tunability, a better stability towards photo and chemical degradation, a very large stokes shift, and long-lived luminescent excited states (Colombo, *et al.*, 2015). The relative energy of these excited states is strongly affected by the groups attached to these ligands and the other auxiliary ligand bonded to the Pt(II) centre. Some of the basic and well-studied ligand types are given in Figure 1; **I** (Nikolaeva & Puzyk, 2013; Murphy, *et al.*, 2012); **II** (Nikolaeva & Puzyk, 2013); **III** (Shafikov, 2019); **IV** (Shafikov, 2019); **V** (Murphy, *et al.*, 2012; Colombo, *et al.*, 2015; Williams, *et al.*, 2003); **VI** (Fung, *et al.*, 2016; Feng, *et al.*, 2006; Shao, *et al.*, 2008; Lu, *et al.*, 2004; Nolan, *et al.*, 2013); and **VII** (Tsai, *et al.*, 2015).



**Figure 1.** Molecular structures of ligands **I** – **VII**

The cyclometallated platinum(II) complexes of the type [Pt(NH<sub>3</sub>)<sub>2</sub>(C<sup>^</sup>N)]ClO<sub>4</sub> (**1**), where C<sup>^</sup>N is a 2-phenylbenzothiazole ion

showed intense long-lived luminescence (Figure 2) (Nikolaeva & Puzyk, 2013). Williams *et al.* showed that tridentate (N<sup>^</sup>C<sup>^</sup>N)Pt(II) complex (**4**) has slightly superior luminescence quantum yield when compared to that of the bidentate (N<sup>^</sup>C)Pt(II) complex (**2**) (Murphy, *et al.*, 2012).



**Figure 2.** Molecular structures of cyclometallated Pt(II) complexes (**1**) - (**6**)

The binuclear cyclometallated complex (**3**) of a substituted 4,6-bis(2-thienyl)pyrimidine emits in the red region of the spectrum ( $\lambda_{\text{max}} = 610 \text{ nm}$ ,  $\Phi = 0.85$  in deoxygenated dichloromethane at 300 K). Colombo *et al.* described the synthesis of neutral tridentate (N<sup>^</sup>C<sup>^</sup>N)Pt(II) complexes as long-lived bio-imaging probes bearing hydrophilic ethylene glycol chains to increase the water solubility and bio-compatibility. The luminescent complexes of type (**5**) display self-assembly and anti-cancer properties and exert cytotoxicity towards different immortalized cancer cells and primary cells (Tsai, *et al.*, 2015). The Pt(II) complexes of the type [Pt(C<sup>^</sup>N<sup>^</sup>N)(NHC)]O<sub>3</sub>SCF<sub>3</sub> (**6**) (NHC = N-heterocyclic carbene) showed up to 15-fold higher emission intensities upon binding to mismatched DNA over matched DNA, and can be utilized for both detecting DNA abasic sites and identifying cancer cells (Fung, *et al.*,

2016). The photo-physical and third-order nonlinear optical properties of cyclometallated (4,6-diphenyl-2,2'-bipyridyl pentynyl)platinum(II) complex have been investigated (Shao, *et al.*, 2008). Based on their systematic studies, Lu *et al.* suggest that tridentate cyclometallated (C<sup>N</sup>N)Pt(II)  $\sigma$ -alkynyl complexes are promising light-emitting materials, especially as phosphorescent dopants for OLED applications, due to their intense, readily-adjustable triplet emissions under ambient conditions and their thermal stability (Lu, *et al.*, 2004).

Synthesis of the pyridyl-centred polyphenylene (**7**) (see Scheme 1) and its coordination chemistry particularly with rhodium and palladium have been reported (Ollangnier, *et al.*, 2008; Perera & Draper, 2009; Perera, 2018). It is of interest to explore the chemistry of this pyridyl-centred polyphenylene ligand (**7**) with platinum centres in order to prepare possible photoactive luminescent complexes of the type [(C<sup>N</sup>N)PtX] (X = halide, trifluoroacetate, acetylides), [(C<sup>N</sup>N)Pt(L')]PF<sub>6</sub> (L' = pyridine or phosphine) and a binuclear complex containing bridging ligands. In this paper we report studies carried out to devise synthetic routes to such complexes.

## **Methodology**

All the experiments were carried out in an inert atmosphere (dinitrogen or argon). Elemental analyses were carried out on a Carlo Erba 1006 automatic analyser. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer fitted with a universal ATR sampling accessory. Mass spectral data were obtained using a micromass LCT electrospray mass spectrometer. NMR spectra were recorded on a Bruker DPX 400 spectrometer (operating frequencies for <sup>1</sup>H and <sup>13</sup>C are 400.13 and 100.62 MHz, respectively) or Bruker Avance<sup>®</sup> 600 spectrometer (operating frequencies for <sup>1</sup>H and <sup>13</sup>C are 600.13 and 150.9 MHz). <sup>1</sup>H and <sup>13</sup>C chemical shifts ( $\delta$ ) are in ppm with respect to TMS, and coupling constants (J) are in Hz. Single-crystal analyses were performed on a Bruker SMART APEX CCD diffractometer using graphite monochromised Mo-K <sub>$\alpha$</sub>  ( $\lambda=0.71073\text{\AA}$ ) radiation and refinements

were obtained using SHELXS software. Figures 3 and 4 feature the images obtained by using Mercury software. 3,4,5,6-Tetraphenyl-2,2'-bipyridine (**7**) was prepared according to a procedure recorded in relevant literature (Ollangnier, *et al.*, 2008).

**[PtCl(L)] (8) and *mer*-[PtCl<sub>3</sub>(L)] (9)**

Suspension of the ligand (**7**) (60 mg, 0.13 mmol) and [PtCl<sub>2</sub>(dms<sub>o</sub>)<sub>2</sub>] (55 mg, 0.13 mmol) in chloroform (12 mL) was refluxed for 24 h to give an orange precipitate. The solution was concentrated (*ca.* 1.5 mL) and methanol (*ca.* 0.5 mL) was added. The orange precipitate [PtCl(L)] (**8**) was filtered off and washed with methanol (68 mg, 76%). Upon standing, the mother liquor gave yellow crystals of *mer*-[PtCl<sub>3</sub>(L)] (**9**) (16 mg, 16%).

**[PtCl(L)] (8)**

Found: C, 58.23; H, 3.31; N 3.74, calcd. (%) for C<sub>34</sub>H<sub>23</sub>ClN<sub>2</sub>Pt·0.1CHCl<sub>3</sub>: C, 58.34; H, 3.31; N 3.99. IR (neat, ν, cm<sup>-1</sup>): 3059, 1597, 1575, 1466, 1406, 755, 727 and 701. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.37 (m, 1H, H<sup>6</sup>), 8.02 (d, 1H, <sup>3</sup>J(HH) 7.8 Hz, H<sup>8</sup>), 7.55-7.50 (m, 2H, H<sup>5</sup> & H<sup>4</sup>), 7.3-7.2 (m, 7H, H<sup>Ph</sup> & H<sup>9</sup>), 7.13-7.06 (m, 4H, H<sup>Ph</sup>), 6.95-6.91 (m, 3H, H<sup>Ph</sup>), 6.74-6.69 (m, 2H, H<sup>Ph</sup>), 6.61-6.57 (m, 2H, H<sup>3</sup> and H<sup>10</sup>) and 6.02 (d, 1H, <sup>3</sup>J(HH) 7.8 Hz, H<sup>11</sup>). <sup>13</sup>C NMR was not recorded as (**8**) is not very soluble in most of the deuterated solvents.

***mer*-[PtCl<sub>3</sub>(L)] (9)**

Found: C, 52.65; H, 3.03; N 3.24, calcd. (%) for C<sub>34</sub>H<sub>23</sub>Cl<sub>3</sub>N<sub>2</sub>Pt·0.1CHCl<sub>3</sub>: C, 52.98; H, 3.01; N 3.63. IR (neat, ν, cm<sup>-1</sup>): 3006, 1598, 1576, 1470, 1442, 1407, 1276, 1261, 764, 751 and 700. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.51 (m, 1H, H<sup>6</sup>), 8.02 (dd, 1H, <sup>3</sup>J(HH) 7.5 Hz, <sup>4</sup>J(HH) 1.0 Hz, H<sup>8</sup>), 7.69-7.66 (m, 1H, H<sup>5</sup>, overlaps with H<sup>4</sup>), 7.64 (dt, 1H, <sup>3</sup>J(HH) 8.0 Hz, <sup>4</sup>J(HH) 2.0 Hz, H<sup>4</sup>), 7.37-7.30 (m, 6H, H<sup>Ph</sup>), 7.26 (dt, 1H, <sup>3</sup>J(HH) 8.0 Hz, <sup>4</sup>J(HH) 1.5 Hz, H<sup>9</sup>), 7.17-7.14 (m, 4H, H<sup>Ph</sup>), 7.00-6.97 (m, 3H, H<sup>Ph</sup>), 6.84 (dd, 1H, <sup>3</sup>J(HH) 8.0 Hz, <sup>4</sup>J(HH) 1.0 Hz, H<sup>3</sup>), 6.77-6.70 (m, 3H, H<sup>Ph</sup> and H<sup>10</sup>) and 6.20 (dd, 1H, <sup>3</sup>J(HH) 8.5 Hz, <sup>4</sup>J(HH) 1.5 Hz, H<sup>11</sup>). <sup>13</sup>C NMR: δ 148.6 (C<sup>6</sup>), 139.0 (C<sup>4</sup>), 132.4 (C<sup>9</sup>), 132.1 (C<sup>8</sup>), 130.4 (C<sup>11</sup>), 129.3 (C<sup>Ph</sup>), 129.1

(C<sup>Ph</sup>), 129.0 (C<sup>Ph</sup>), 128.8 (C<sup>Ph</sup>), 128.5 (C<sup>Ph</sup>), 128.4 (C<sup>Ph</sup>), 128.1 (C<sup>3</sup>), 127.0 (C<sup>Ph</sup>), 126.9 (C<sup>5</sup>) and 125.3 (C<sup>10</sup>).

### **[PtCl(L)] (8)**

Suspension of the ligand (**7**) (60 mg, 0.13 mmol), [PtCl<sub>2</sub>(dmsO)<sub>2</sub>] (55 mg, 0.13 mmol) and triethylamine (36 mg, 0.36 mmol) in chloroform (12 mL) was refluxed for 20 h to give an orange precipitate. The solution was concentrated (ca. 1.5 mL) and the orange precipitate [PtCl(L)] was filtered off and washed with methanol (83 mg, 92%). The characterizing data as same as above.

### **[Pt(O<sub>2</sub>CCF<sub>3</sub>)(L)] (10)**

Into a warm suspension of [PtCl(L)] (**8**) (30 mg, 0.043 mmol) in dichloromethane (4 mL) was added a solution of silver trifluoroacetate (AgO<sub>2</sub>CCF<sub>3</sub>) (11 mg, 0.049 mmol) in methanol (2 mL). Reaction mixture was stirred at room temperature for 24 h. The solvent was removed, and the residue was extracted with dichloromethane. The combined extract was concentrated to a low volume and methanol was added to give a red solid (31 mg, 93%). Found: C, 56.05; H, 2.95; N 3.25, calcd. (%) for C<sub>36</sub>H<sub>23</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>Pt: C, 56.33; H, 3.02; N 3.65. IR (neat, cm<sup>-1</sup>): 1697, 1576, 1545, 1470, 1444, 1405, 1190, 1135, 1031, 808, 784, 770, 745, 727 and 699. MS (*m/z*-MALDI-TOF, CH<sub>2</sub>Cl<sub>2</sub>): found: 654.1526; calcd. 654.1509 for C<sub>34</sub>H<sub>23</sub>N<sub>2</sub>Pt, [M-O<sub>2</sub>CCF<sub>3</sub>]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 8.81 (br, d, 1H, <sup>3</sup>J(HH) 4.5 Hz, H<sup>6</sup>), 7.79 (t, 1H, <sup>3</sup>J(HH) 7.8 Hz, H<sup>4</sup>), 7.68 (m, 1H, H<sup>5</sup>), 7.42-7.25 (m, 7H, H<sup>Ph</sup> and H<sup>8</sup>), 7.23-7.13 (m, 4H, H<sup>Ph</sup>), 7.10 (m, 1H, H<sup>9</sup>), 7.01-6.91 (m, 3H, H<sup>Ph</sup>), 6.90-6.80 (m, 2H, H<sup>Ph</sup>), 6.69 (t, 1H, <sup>3</sup>J(HH) 7.8 Hz, H<sup>10</sup>), 6.63 (d, 1H, <sup>3</sup>J(HH) 7.8 Hz, H<sup>3</sup>) and 5.94 (d, 1H, <sup>3</sup>J(HH) 7.8 Hz, H<sup>11</sup>). <sup>13</sup>C NMR (100.6 MHz; CD<sub>3</sub>CN, δ<sub>C</sub>): 163.6, 157.1, 156.8, 152.6, 150.0 (C<sup>6</sup>), 147.9, 142.0, 140.4 (C<sup>4</sup>), 136.2, 136.1 (C<sup>8</sup>), 136.0, 135.5, 135.0, 133.7 (C<sup>9</sup>), 130.7 (C<sup>11</sup>), 129.6 (C<sup>Ph</sup>), 129.5 (C<sup>Ph</sup>), 129.3 (C<sup>Ph</sup>), 129.2 (C<sup>Ph</sup>), 128.8 (C<sup>Ph</sup>), 128.4 (C<sup>Ph</sup>), 128.0 (C<sup>3/Ph</sup>), 127.8 (C<sup>3/Ph</sup>), 127.0 (C<sup>Ph</sup>), 126.9 (C<sup>5</sup>) and 124.9 (C<sup>10</sup>). <sup>19</sup>F NMR (376.5 MHz, CDCl<sub>3</sub>): -75.6 (s) ppm.

### **[Pt(C≡CC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>)(L)] (11)**

To a degassed solution containing [PtCl(L)] (**8**) (25 mg, 0.036 mmol), 4-*tert*-butylphenyl acetylene (30 mg, 0.19 mmol) and triethyl amine

(0.5 mL) in dichloromethane (5 mL), CuI (1 mg, 0.005 mmol) was added. The platinum complex went into solution gradually to give a red solution and the reaction mixture was stirred under dinitrogen for 24 h. It was concentrated upon a low volume and methanol was added to give the required product as an orange solid (24 mg, 83%). Found: C, 67.90; H, 4.35; N 3.15, calcd. (%) for  $C_{46}H_{36}N_2Pt$ : C, 68.05; H, 4.47; N 3.45. IR (neat,  $cm^{-1}$ ): 3039, 2964, 2099, 1599, 1575, 1498, 1467, 1442, 1403, 1267, 1107, 1013, 833, 759, 729 and 699. MS ( $m/z$ -MALDI-TOF,  $CH_2Cl_2$ ): found: 811.2547; calcd. 811.2526 for  $C_{46}H_{36}N_2Pt$ ,  $[M]^+$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  9.42 (d, 1H,  $^3J(HH)$  4.0 Hz,  $H^6$ ), 8.08 (d, 1H,  $^3J(HH)$  7.0 Hz,  $^3J(PtH)$  58 Hz,  $H^8$ ), 7.65-7.47 (m, 3H,  $^3J(HH)$  7.8 Hz,  $H^{Ar}$  and  $H^4$ ), 7.44-7.32 (m, 3H,  $^3J(HH)$  7.8 Hz,  $H^{Ar}$  and  $H^5$ ), 7.31-7.21 (m, 7H,  $H^{Ph}$ ), 7.16-7.06 (m, 3H,  $H^{Ph}$ ), 7.06-6.98 (m, 1H,  $H^9$ ), 6.97-6.86 (m, 3H,  $H^{Ph}$ ), 6.82-6.67 (m, 2H,  $H^{Ph}$ ), 6.65-6.51 (m, 2H,  $H^3$  and  $H^{10}$ ), 6.09 (br, d, 1H,  $^3J(HH)$  7.8 Hz,  $H^{11}$ ) and 1.36 (s, 9H,  $CMe_3$ ).  $^{13}C$  NMR (100.6 MHz;  $CDCl_3$ ,  $\delta_c$ ): 148.0 ( $C^6$ ), 138.4 ( $C^8$ ), 137.6 ( $C^4$ ), 130.8 ( $C^9$ ), 129.8 ( $C^{Ar}$ ), 129.7 ( $C^{Ph}$ ), 129.6 ( $C^{Ph}$ ), 129.3 ( $C^{11}$ ), 129.2 ( $C^{Ph}$ ), 128.6 ( $C^{Ph}$ ), 128.4 ( $C^{Ph}$ ), 127.9 ( $C^{Ph}$ ), 127.1 ( $C^{Ph}$ ), 126.9 ( $C^3$ ), 126.8 ( $C^5$ ), 126.7 ( $C^{Ph}$ ), 125.3 ( $C^{Ph}$ ), 124.9 ( $C^{Ar}$ ), 123.1 ( $C^{10}$ ) and 31.4 ( $CMe_3$ ).

### **[Pt(L)(DMAP)]PF<sub>6</sub> (12)**

To a suspension containing [PtCl(L)] (**8**) (20 mg, 0.0289 mmol) and 4-dimethylaminopyridine (DMAP) (10 mg, 0.082 mmol) in chloroform (3 mL) a solution of  $NH_4PF_6$  (12 mg, 0.073 mmol) in methanol (1 mL) was added. The reaction mixture was refluxed for 1h to give a yellow solution which was concentrated to give the required product as a yellow solid (22 mg, 81%). Found: C, 51.91; H, 3.71; N 5.68, calcd. (%) for  $C_{41}H_{33}N_4PF_6Pt \cdot 0.25CHCl_3$ : C, 52.06; H, 3.52; N 5.88. IR (neat, v,  $cm^{-1}$ ): 2961, 1623, 1546, 1396, 835, 771 and 700. ESI-MS (acetone,  $m/z$ ): found: 776.2342; calcd. 776.2353 for  $C_{41}H_{33}N_4Pt$ ,  $[M-PF_6]^+$ .  $^1H$ -NMR (400 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 8.34 (d, 2H,  $^3J(HH)$  7.0 Hz,  $^3J(PtH)$  36 Hz,  $H^{Ar}$ ), 8.20 (d, 1H,  $^3J(HH)$  4.5 Hz,  $H^6$ ), 7.75 (m, 1H,  $^3J(HH)$  7.0 Hz,  $H^5$ ), 7.61 (dt, 1H,  $^3J(HH)$  8.0 Hz,  $^4J(HH)$  1.5 Hz,  $H^4$ ), 7.32-7.28 (m, 6H,  $H^{Ph}$ ), 7.12-7.08 (m, 4H,  $H^{Ph}$ ), 7.01-6.95 (m, 4H,  $^3J(HH)$  7.5 Hz,  $H^{Ph}$  &  $H^9$ ), 6.79 (d, 2H,  $^3J(HH)$  7.0 Hz,  $H^{Ar}$ ), 6.72-6.70 (m, 2H,  $H^{Ph}$ ), 6.66-6.62 (m, 3H,  $H^3$ ,  $H^8$  &  $H^{10}$ ), 6.10 (d, 1H,  $^3J(HH)$  8.0 Hz,  $H^{11}$ ) and 3.25 (s, 6H, Me).  $^{13}C$  NMR (100.6 MHz;

$\text{CDCl}_3$ ,  $\delta_{\text{C}}$ ) : 150.5 ( $\text{C}^{\text{Ar}}$ ), 149.4 ( $\text{C}^6$ ), 139.4 ( $\text{C}^4$ ), 132.7 ( $\text{C}^8$ ), 130.7 ( $\text{C}^9$ ), 129.8 ( $\text{C}^{11}$ ), 129.6 ( $\text{C}^{\text{Ph}}$ ), 129.5 ( $\text{C}^{\text{Ph}}$ ), 129.4 ( $\text{C}^{\text{Ph}}$ ), 128.9 ( $\text{C}^5$ ), 128.4 ( $\text{C}^{\text{Ph}}$ ), 127.6 ( $\text{C}^3$ ), 127.3 ( $\text{C}^{\text{Ph}}$ ), 127.1 ( $\text{C}^{\text{Ph}}$ ), 124.5 ( $\text{C}^{10}$ ), 109.4 ( $\text{C}^{\text{Ar}}$ ) and 39.5 (*Me*).

**[Pt(L)(PPh<sub>3</sub>)]PF<sub>6</sub> (13)**

[PtCl(L)] (**8**) (20 mg, 0.0289 mmol) and triphenylphosphine (12 mg, 0.045 mmol) were heated at 60 °C in chloroform (3 mL) to give a yellow solution.  $\text{NH}_4\text{PF}_6$  (12 mg, 0.073 mmol) in methanol (1 mL) was then added and the solution was concentrated to give the required product as a yellow solid (29 mg, 94%). Found: C, 53.91; H, 3.34; N 2.13, calcd. (%) for  $\text{C}_{52}\text{H}_{38}\text{N}_2\text{P}_2\text{F}_6\text{Pt}$ : C, 53.88; H, 3.33; N 2.37. IR (neat,  $\nu$ ,  $\text{cm}^{-1}$ ): 3006, 1577, 1548, 1472, 1437, 1277, 1261, 833 and 750. ESI-MS (acetone,  $m/z$ ): found: 916.2413; calcd. 916.2420 for  $\text{C}_{52}\text{H}_{38}\text{N}_2\text{PPt}$ ,  $[\text{M}-\text{PF}_6]^+$ .  $^{31}\text{P}$ -NMR (161.9 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 27.6 (s),  $^1\text{J}(\text{PtP}) = 4144$  Hz ( $\text{PPh}_3$ ) and -143.2 (septet),  $^1\text{J}(\text{PF}) = 720$  Hz, ( $\text{PF}_6^-$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90-7.86 (m, 6H,  $\text{H}^{\text{Ph}}$ ), 7.62-7.57 (m, 3H,  $\text{H}^{\text{Ph}}$ ), 7.57-7.51 (m, 4H,  $\text{H}^{\text{Ph}}$  &  $\text{H}^4$ ), 7.31-7.27 (m, 6H,  $\text{H}^{\text{Ph}}$ ), 7.21-7.13 (m, 4H,  $\text{H}^{\text{Ph}}$ ), 7.01-6.94 (m, 4H,  $\text{H}^{\text{Ph}}$  &  $\text{H}^5$ ), 6.88 (br, d, 1H,  $^3\text{J}(\text{HH})$  5.6 Hz,  $\text{H}^6$ ), 6.82 (d, 1H,  $^3\text{J}(\text{HH})$  8.3 Hz,  $\text{H}^3$ ), 6.81-6.76 (m, 2H,  $\text{H}^{\text{Ph}}$ ), 6.56-6.45 (m, 3H,  $\text{H}^8$ ,  $\text{H}^9$  &  $\text{H}^{10}$ ) and 6.28 (d, 1H,  $^3\text{J}(\text{HH})$  7.9 Hz,  $\text{H}^{11}$ ).  $^{13}\text{C}$  NMR:  $\delta$  162.6, 161.0, 158.9, 157.4, 150.9 ( $\text{C}^6$ ), 150.5, 148.8, 139.7 ( $\text{C}^4$ ), 138.4 ( $\text{C}^8$ ), 136.3, 135.8, 135.4, 135.2, 135.1, 134.8, 132.0, 129.8 ( $\text{C}^{11}$ ), 129.7 ( $\text{C}^9$ ), 129.6, 129.5, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.3 ( $\text{C}^3$ ), 128.2, 127.1 ( $\text{C}^5$ ), 126.7 and 124.6 ( $\text{C}^{10}$ ).

**[(L)Pt(dppm)Pt(L)][PF<sub>6</sub>]<sub>2</sub> (14)**

A suspension containing [PtCl(L)] (**8**) (20 mg, 0.029 mmol), bis(diphenylphosphino) methane (dppm) (5.5 mg, 0.014 mmol) and  $\text{NH}_4\text{PF}_6$  (10 mg, 0.061 mmol) in a mixture of degassed acetonitrile (4 mL) and chloroform (1 mL) was heated to 65 °C for 1 h. The resulting yellow solution was allowed to cool and was filtered. The filtrate was concentrated upon a low volume, and ethanol was added to give the required product as yellow needles, (24 mg, 85%). Found: C, 54.03; H, 3.35; N 2.62, calcd. (%) for  $\text{C}_{93}\text{H}_{68}\text{F}_{12}\text{N}_4\text{P}_4\text{Pt}_2 \cdot 1.0\text{CHCl}_3$ : C, 53.69; H, 3.31; N 2.66. IR (neat,  $\nu$ ,  $\text{cm}^{-1}$ ): 1474, 1438, 1405, 1166, 1098, 1015, 832, 770, 757, 734 and

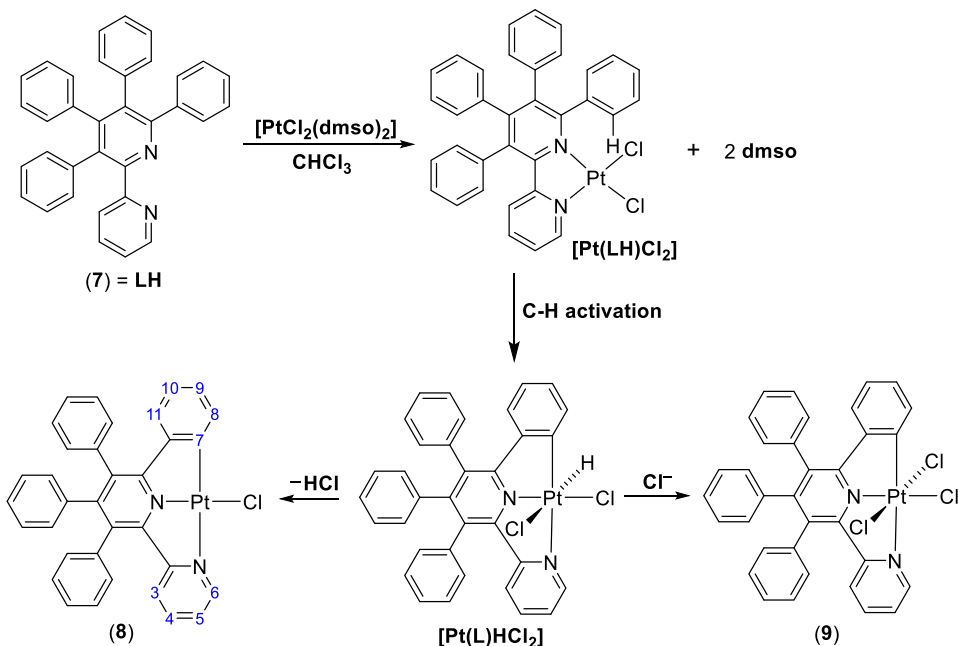


693. MS ( $m/z$ -MALDI-TOF,  $\text{CH}_2\text{Cl}_2$ ): found: 1837.3859; calcd. 1837.3856 for  $\text{C}_{93}\text{H}_{68}\text{F}_6\text{N}_4\text{P}_3\text{Pt}_2$ ,  $[\text{M-PF}_6]^+$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.12-7.91 (m, 8H,  $\text{H}^{\text{Ph}}$ ), 7.56 (t, 2H,  $^3\text{J}(\text{HH}) = 8.0$  Hz,  $\text{H}^4$ ), 7.52-7.46 (m, 4H,  $\text{H}^{\text{Ph}}$ ), 7.46-7.28 (m, 22H,  $\text{H}^6$  &  $\text{H}^{\text{Ph}}$ ), 7.21 (m, 4H,  $\text{H}^{\text{Ph}}$ ), 7.14 (m, 4H,  $\text{H}^{\text{Ph}}$ ), 7.08-7.01 (m, 6H,  $\text{H}^{\text{Ph}}$ ), 6.97 (d, 2H,  $^3\text{J}(\text{HH}) = 7.5$  Hz,  $\text{H}^8$ ), 6.78 (t, 2H,  $^3\text{J}(\text{HH}) = 6.4$  Hz,  $\text{H}^5$ ), 6.69 (d, 2H,  $^3\text{J}(\text{HH}) = 8.3$  Hz,  $\text{H}^3$ ), 6.65 (t, 2H,  $^3\text{J}(\text{HH}) = 7.3$  Hz,  $\text{H}^9$ ), 6.53 (t, 2H,  $^3\text{J}(\text{HH}) = 7.5$  Hz,  $\text{H}^{10}$ ) 6.01 (d, 2H,  $^3\text{J}(\text{HH}) = 8.0$  Hz,  $\text{H}^{11}$ ) and 4.93-4.67 (vt, 4H,  $^2\text{J}(\text{PH}) = 12.7$  Hz,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (100.6 MHz;  $\text{CD}_3\text{CN}$ ,  $\delta_{\text{c}}$ ): 160.2, 158.5, 157.4, 152.8 ( $\text{C}^6$ ), 150.9, 148.8, 139.5 ( $\text{C}^4$ ), 138.6, 137.8 ( $\text{C}^8$ ), 136.5, 136.0, 136.9, 135.4, 135.1, 133.76 ( $\text{C}^{\text{Ph}}$ ), 133.7 ( $\text{C}^{\text{Ph}}$ ), 133.6 ( $\text{C}^{\text{Ph}}$ ), 132.1 ( $\text{C}^{\text{Ph}}$ ), 130.3 ( $\text{C}^{11}$ ), 129.8 ( $\text{C}^{\text{Ph}}$ ), 129.5 ( $\text{C}^{\text{Ph}}$ ), 129.4 ( $\text{C}^{\text{Ph}}$ ), 129.1 ( $\text{C}^9$ ), 129.0 ( $\text{C}^{\text{Ph}}$ ), 129.0 ( $\text{C}^{\text{Ph}}$ ), 128.9 ( $\text{C}^{\text{Ph}}$ ), 128.5 ( $\text{C}^{\text{Ph}}$ ), 127.9 ( $\text{C}^3$ ), 127.2 ( $\text{C}^{\text{Ph}}$ ), 126.8 ( $\text{C}^5$ ) and 124.8 ( $\text{C}^{10}$ ).  $^{31}\text{P}$  NMR (161.9 MHz,  $\text{CD}_3\text{CN}$ ,  $\delta$  in ppm): 13.4,  $^1\text{J}(\text{PtP}) = 4208$  Hz.

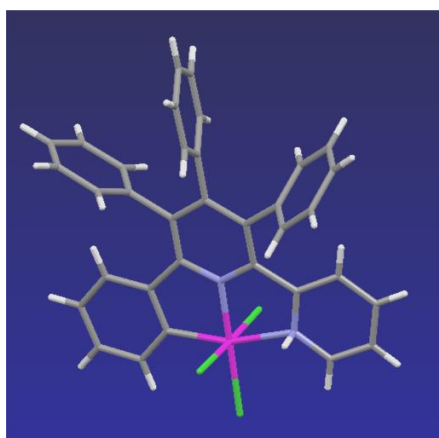
## Results and Discussion

Treatment of (**7**) with  $[\text{PtCl}_2(\text{dmsO})_2]$  (dmsO = dimethyl sulfoxide) in boiling chloroform resulted in the formation of a mixture of cyclometallated square-planar platinum(II) complex  $[\text{PtCl}(\text{L})]$  (**8**) and an octahedral platinum(IV) complex *mer*- $[(\text{L})\text{PtCl}_3]$  (**9**), both containing an anionic tridentate ( $\text{C}^{\wedge}\text{N}^{\wedge}\text{N}$ ) ligand. The orange complex (**8**) was not very soluble in common deuterated solvents and in the proton NMR spectrum, the proton ( $\text{H}^6$ ) on the carbon adjacent to nitrogen was the most deshielded and the resonance appeared as a multiplet at 9.37 ppm. The complex (**9**) was characterised by X-ray crystallography and confirmed the presence of *mer*-geometry around the platinum centre (Figure 3). In the proton NMR spectrum, the  $\text{H}^6$  proton appeared as a multiplet at 9.51 ppm. One can argue that the complex (**5**) could have been formed by the replacement of the platinum hydride of the intermediate  $[\text{Pt}(\text{L})\text{HCl}_2]$  which was due to the oxidative addition of phenyl C-H bond by a chloride ligand formed during the reaction (see Scheme 1). It is clear that the intermediate  $[(\text{L})\text{PtHCl}_2]$  undergoes reductive elimination of HCl to produce the square-planar platinum(II) complex  $[\text{PtCl}(\text{L})]$  (**8**). It is known, in the presence of a base, one could readily remove HCl from a

platinum(IV) complex containing a PtHCl<sub>2</sub> moiety. As expected, addition of triethylamine to the above reaction mixture improved the yield of [PtCl(L)] (**8**).

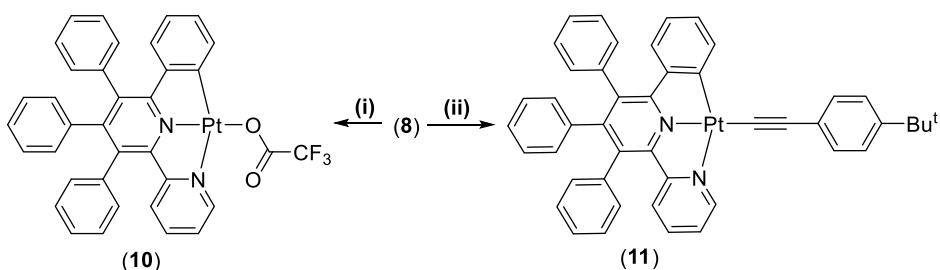


**Scheme 1.** Possible mechanism for the formation of complexes **(8)**-**(9)**; and atom labelling used for the assignment of NMR data



**Figure 3.** Molecular structure of *mer*-[(L)PtCl<sub>3</sub>] (**9**)

Square-planar platinum(II) complexes are being used to study substitution reactions with anionic ligands. The chloride of (**8**) can be easily replaced by trifluoroacetate ion to produce [(L)PtO<sub>2</sub>CCF<sub>3</sub>] (**10**) a red solid with 93% yield. The IR spectrum of (**10**) showed an IR band at 1659 cm<sup>-1</sup> for the C=O group. The complex is quite soluble in organic solvents and it was well characterized. The <sup>19</sup>F NMR spectrum showed a singlet at -75.6 ppm for the fluorine nuclei in the CF<sub>3</sub> group.

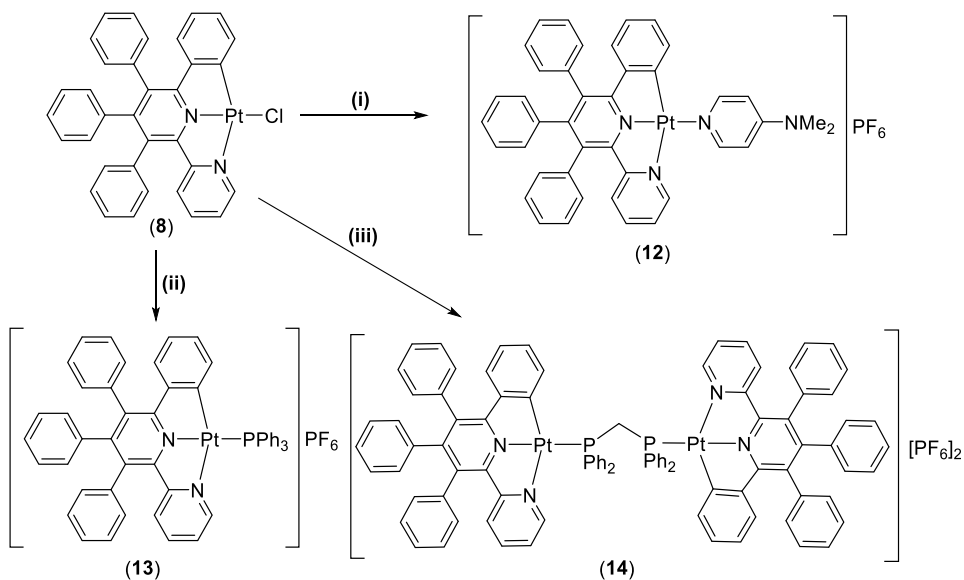


**Scheme 2.** Synthetic routes to complexes (**10**)-(**11**); (i) AgO<sub>2</sub>CCF<sub>3</sub>; (ii) HC≡CC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4

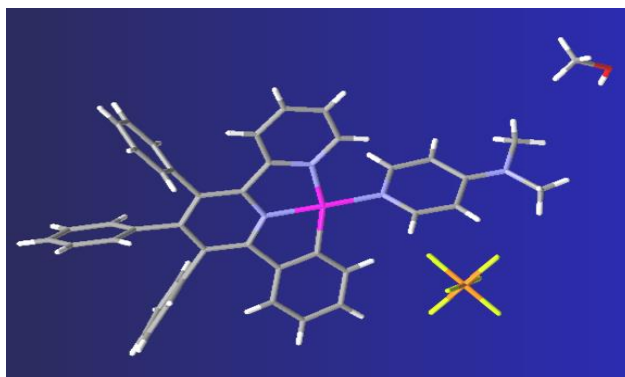
Cyclometallated Pt(II) acetylides have shown interesting photo-physical properties (Feng, *et al.*, 2006; Shao, *et al.*, 2008; Lu, *et al.*, 2004) and the complex (**8**) was converted into its acetylide [(L)PtC≡CC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4] (**11**) of 83% yield, by reacting it with 4-*tert*-butylphenyl acetylene in the presence of triethylamine and catalytic amount of CuI. In the <sup>1</sup>H NMR spectrum, the resonances of the aryl group (-C<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4) appeared as an AB pattern at 7.60 (d) and 7.40 (d) ppm with <sup>3</sup>J(HH) = 7.8 Hz for aryl protons and a singlet at 1.36 ppm for the nine *tert*-butyl protons. The IR spectrum of (**11**) showed an IR band at 2099 cm<sup>-1</sup> for the acetylide ligand.

It is interesting to study the substitution of the chloride ion by neutral ligands such as pyridine and phosphine ligands to make the less soluble platinum(II) complex (**8**) more soluble in the form of a salt. Replacement of the labile chloride ligand with 4-dimethylaminopyridine (DMAP) in the presence of NH<sub>4</sub>PF<sub>6</sub> resulted

in the formation of the salt  $[\text{Pt}(\text{L})(\text{DMAP})]\text{PF}_6$  (**12**). The complex (**12**) was characterised by X-ray crystallography (Figure 4). In its  $^1\text{H}$ -NMR spectrum, the methyl proton resonance of  $\text{NMe}_2$  group appeared as a singlet at 3.25 ppm.



**Scheme 3.** Synthetic routes to complexes **(12)**-**(14)**; (i) DMAP/ $\text{NH}_4\text{PF}_6$ ; (ii)  $\text{PPh}_3/\text{NH}_4\text{PF}_6$ ; (iii) 0.5 equiv.  $\text{dppm}/\text{NH}_4\text{PF}_6$ ;



**Figure 4.** Molecular structure of  $[\text{Pt}(\text{L})(\text{DMAP})]\text{PF}_6$  (**12**)

Replacement of the labile chloride ligand by triphenylphosphine formed the salt **(13)** as a yellow solid of 94% yield.  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR

spectrum of (**13**) showed a singlet at 27.6 ppm with platinum satellites,  $^1J(\text{PtP}) = 4144$  Hz, for  $\text{PPh}_3$  and a septet at -143.2 ppm for the  $\text{PF}_6^-$  group. Replacement of two chloride groups from two complexes of (**8**) by one dppm ligand gave the dppm-bridged binuclear dicationic salt  $[(\text{L})\text{Pt}(\mu\text{-dppm})\text{Pt}(\text{L})](\text{PF}_6)_2$  (**14**). The phosphorus resonance of (**14**) was 13.4 ppm with  $^1J(\text{PtP}) = 4208$  Hz.

## Conclusions

The bulky ligand (**7**) containing four phenyl groups was converted into a quite insoluble cyclometallated terdentate complex  $[(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{PtCl}]$ . However, it can be made more soluble by replacing the chloride ligand to produce the corresponding trifluoroacetate and acetylide. Introduction of a neutral ligand such as pyridine or phosphine generated more soluble salts of the type  $[(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{Pt}(\text{L})]\text{PF}_6$  where  $\text{L}' = \text{PPh}_3, \text{DMAP}$ . A binuclear complex bridging two  $(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{Pt}$  units with dppm was also prepared.

## Acknowledgements

Author wishes to thank the Trinity College Dublin for a Research Fellowship and Professor S. M. Draper for laboratory facilities and other support. Author is also grateful Dr. John O'Brien and Dr. M. Ruether for recording NMR spectra; Dr Martin Feeney for providing mass spectral data; and Dr Thomas McCabe for determining crystal structures. An abstract of this study was presented at the Annual Sessions of the Institute of Chemistry, Ceylon in 2013.

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