

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 (C[^]N[^]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 PPh_3 in dichloromethane, and the subsequent addition of NH_4PF_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

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Introduction

Interest on cyclometallated complexes of the type $(C^{\wedge}N)M$, $(N^{\wedge}C^{\wedge}N)M$ and $(C^{\wedge}N^{\wedge}N)M$ 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 $(C^{\wedge}N)Pt$ (Nikolaeva & Puzyk, 2013; Murphy, *et al.*, 2012; Shafikov, 2019), tridentate units $(N^{\wedge}C^{\wedge}N)Pt$ (Murphy, *et al.*, 2012; Colombo, *et al.*, 2015; Williams, *et al.*, 2003) and $(C^{\wedge}N^{\wedge}N)Pt$ (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).

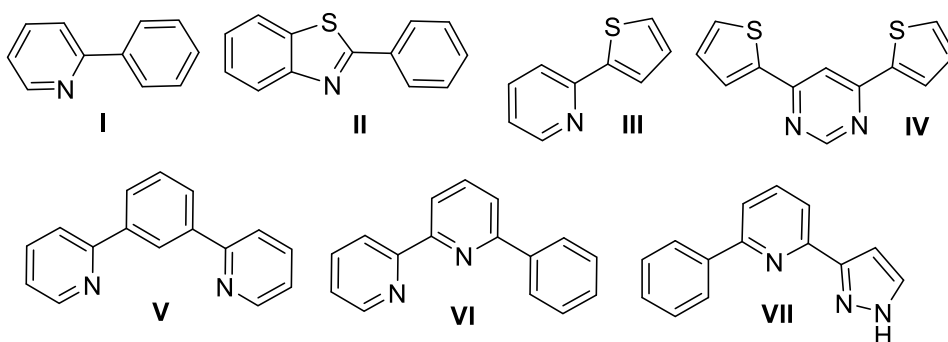


Figure 1. Molecular structures of ligands **I – VII**

The cyclometallated platinum(II) complexes of the type $[\text{Pt}(\text{NH}_3)_2(\text{C}^{\wedge}\text{N})]\text{ClO}_4$ (**1**), where $\text{C}^{\wedge}\text{N}$ is a 2-phenylbenzothiazole ion showed intense long-lived luminescence (Figure 2) (Nikolaeva & Puzyk, 2013). Williams *et al.* showed that tridentate $(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{Pt}(\text{II})$ complex (**4**) has slightly superior luminescence quantum yield when compared to that of the bidentate $(\text{N}^{\wedge}\text{C})\text{Pt}(\text{II})$ complex (**2**) (Murphy, *et al.*, 2012).

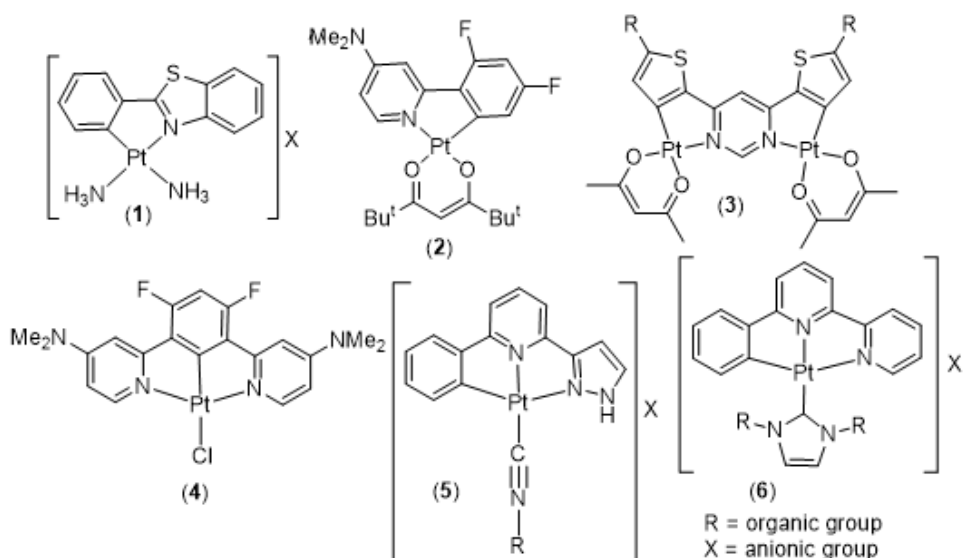


Figure 2. Molecular structures of cyclometallated Pt(II) complexes (**1**) - (**6**)

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 $(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})\text{Pt}(\text{II})$ 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 $[\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})(\text{NHC})]\text{O}_3\text{SCF}_3$ (**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[^]N[^]N)Pt(II) σ -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[^]N[^]N)PtX] (X = halide, trifluoroacetate, acetylides), [(C[^]N[^]N)Pt(L)]PF₆ (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 ¹H and ¹³C are 400.13 and 100.62 MHz, respectively) or Bruker Avance^{II} 600 spectrometer (operating frequencies for ¹H and ¹³C are 600.13 and 150.9 MHz). ¹H and ¹³C

chemical shifts (δ) 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 α ($\lambda=0.71073\text{\AA}$) 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*-[PtCl₃(L)] (9)

Suspension of the ligand (**7**) (60 mg, 0.13 mmol) and [PtCl₂(dms_o)₂] (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*-[PtCl₃(L)] (**9**) (16 mg, 16%).

[PtCl(L)] (8)

Found: C, 58.23; H, 3.31; N 3.74, calcd. (%) for C₃₄H₂₃ClN₂Pt·0.1CHCl₃: C, 58.34; H, 3.31; N 3.99. IR (neat, ν , cm⁻¹): 3059, 1597, 1575, 1466, 1406, 755, 727 and 701. ¹H NMR (400 MHz, CDCl₃): δ 9.37 (m, 1H, H⁶), 8.02 (d, 1H, ³J(HH) 7.8 Hz, H⁸), 7.55-7.50 (m, 2H, H⁵ & H⁴), 7.3-7.2 (m, 7H, H^{Ph} & H⁹), 7.13-7.06 (m, 4H, H^{Ph}), 6.95-6.91 (m, 3H, H^{Ph}), 6.74-6.69 (m, 2H, H^{Ph}), 6.61-6.57 (m, 2H, H³ and H¹⁰) and 6.02 (d, 1H, ³J(HH) 7.8 Hz, H¹¹). ¹³C NMR was not recorded as (**8**) is not very soluble in most of the deuterated solvents.

***mer*-[PtCl₃(L)] (9)**

Found: C, 52.65; H, 3.03; N 3.24, calcd. (%) for C₃₄H₂₃Cl₃N₂Pt·0.1CHCl₃: C, 52.98; H, 3.01; N 3.63. IR (neat, ν , cm⁻¹): 3006, 1598, 1576, 1470, 1442, 1407, 1276, 1261, 764, 751 and 700. ¹H NMR (400 MHz, CDCl₃): δ 9.51 (m, 1H, H⁶), 8.02 (dd, 1H, ³J(HH) 7.5 Hz, ⁴J(HH) 1.0 Hz, H⁸), 7.69-7.66 (m, 1H, H⁵, overlaps with H⁴), 7.64 (dt, 1H, ³J(HH) 8.0 Hz, ⁴J(HH) 2.0 Hz, H⁴), 7.37-7.30 (m, 6H, H^{Ph}), 7.26 (dt, 1H, ³J(HH) 8.0 Hz, ⁴J(HH) 1.5 Hz, H⁹), 7.17-7.14 (m, 4H, H^{Ph}), 7.00-6.97 (m, 3H, H^{Ph}), 6.84 (dd, 1H, ³J(HH)

8.0 Hz, $^4J(\text{HH})$ 1.0 Hz, H^3), 6.77-6.70 (m, 3H, H^{Ph} and H^{10}) and 6.20 (dd, 1H, $^3J(\text{HH})$ 8.5 Hz, $^4J(\text{HH})$ 1.5 Hz, H^{11}). ^{13}C NMR: δ 148.6 (C^6), 139.0 (C^4), 132.4 (C^9), 132.1 (C^8), 130.4 (C^{11}), 129.3 (C^{Ph}), 129.1 (C^{Ph}), 129.0 (C^{Ph}), 128.8 (C^{Ph}), 128.5 (C^{Ph}), 128.4 (C^{Ph}), 128.1 (C^3), 127.0 (C^{Ph}), 126.9 (C^5) and 125.3 (C^{10}).

[PtCl(L)] (8)

Suspension of the ligand (**7**) (60 mg, 0.13 mmol), $[\text{PtCl}_2(\text{dmsO})_2]$ (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 $[\text{PtCl}(\text{L})]$ was filtered off and washed with methanol (83 mg, 92%). The characterizing data as same as above.

[Pt(O₂CCF₃)(L)] (10)

Into a warm suspension of $[\text{PtCl}(\text{L})]$ (**8**) (30 mg, 0.043 mmol) in dichloromethane (4 mL) was added a solution of silver trifluoroacetate (AgO_2CCF_3) (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 $\text{C}_{36}\text{H}_{23}\text{F}_3\text{N}_2\text{O}_2\text{Pt}$: C, 56.33; H, 3.02; N 3.65. IR (neat, cm^{-1}): 1697, 1576, 1545, 1470, 1444, 1405, 1190, 1135, 1031, 808, 784, 770, 745, 727 and 699. MS (*m/z*-MALDI-TOF, CH_2Cl_2): found: 654.1526; calcd. 654.1509 for $\text{C}_{34}\text{H}_{23}\text{N}_2\text{Pt}$, $[\text{M}-\text{O}_2\text{CCF}_3]^+$. ^1H NMR (400 MHz, CD_3CN): δ 8.81 (br, d, 1H, $^3J(\text{HH})$ 4.5 Hz, H^6), 7.79 (t, 1H, $^3J(\text{HH})$ 7.8 Hz, H^4), 7.68 (m, 1H, H^5), 7.42-7.25 (m, 7H, H^{Ph} and H^8), 7.23-7.13 (m, 4H, H^{Ph}), 7.10 (m, 1H, H^9), 7.01-6.91 (m, 3H, H^{Ph}), 6.90-6.80 (m, 2H, H^{Ph}), 6.69 (t, 1H, $^3J(\text{HH})$ 7.8 Hz, H^{10}), 6.63 (d, 1H, $^3J(\text{HH})$ 7.8 Hz, H^3) and 5.94 (d, 1H, $^3J(\text{HH})$ 7.8 Hz, H^{11}). ^{13}C NMR (100.6 MHz; CD_3CN , δ_{C}): 163.6, 157.1, 156.8, 152.6, 150.0 (C^6), 147.9, 142.0, 140.4 (C^4), 136.2, 136.1 (C^8), 136.0, 135.5, 135.0, 133.7 (C^9), 130.7 (C^{11}), 129.6 (C^{Ph}), 129.5 (C^{Ph}), 129.3 (C^{Ph}), 129.2 (C^{Ph}), 128.8 (C^{Ph}), 128.4 (C^{Ph}), 128.0 (C^3/Ph), 127.8 (C^3/Ph), 127.0 (C^{Ph}), 126.9 (C^5) and 124.9 (C^{10}). ^{19}F NMR (376.5 MHz, CDCl_3): -75.6 (s) ppm.

[Pt(C≡CC₆H₄Bu^t)(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 C₄₆H₃₆N₂Pt: 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, CH₂Cl₂): found: 811.2547; calcd. 811.2526 for C₄₆H₃₆N₂Pt, [M]⁺. ¹H NMR (CDCl₃): δ 9.42 (d, 1H, ³J(HH) 4.0 Hz, H⁶), 8.08 (d, 1H, ³J(HH) 7.0 Hz, ³J(PtH) 58 Hz, H⁸), 7.65-7.47 (m, 3H, ³J(HH) 7.8 Hz, H^{Ar} and H⁴), 7.44-7.32 (m, 3H, ³J(HH) 7.8 Hz, H^{Ar} and H⁵), 7.31-7.21 (m, 7H, H^{Ph}), 7.16-7.06 (m, 3H, H^{Ph}), 7.06-6.98 (m, 1H, H⁹), 6.97-6.86 (m, 3H, H^{Ph}), 6.82-6.67 (m, 2H, H^{Ph}), 6.65-6.51 (m, 2H, H³ and H¹⁰), 6.09 (br, d, 1H, ³J(HH) 7.8 Hz, H¹¹) and 1.36 (s, 9H, CMe₃). ¹³C NMR (100.6 MHz; CDCl₃, δ_C): 148.0 (C⁶), 138.4 (C⁸), 137.6 (C⁴), 130.8 (C⁹), 129.8 (C^{Ar}), 129.7 (C^{Ph}), 129.6 (C^{Ph}), 129.3 (C¹¹), 129.2 (C^{Ph}), 128.6 (C^{Ph}), 128.4 (C^{Ph}), 127.9 (C^{Ph}), 127.1 (C^{Ph}), 126.9 (C³), 126.8 (C⁵), 126.7 (C^{Ph}), 125.3 (C^{Ph}), 124.9 (C^{Ar}), 123.1 (C¹⁰) and 31.4 (CMe₃).

[Pt(L)(DMAP)]PF₆ (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 NH₄PF₆ (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 C₄₁H₃₃N₄PF₆Pt·0.25CHCl₃: 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 C₄₁H₃₃N₄Pt, [M-PF₆]⁺. ¹H-NMR (400 MHz, CDCl₃, δ 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, H⁶), 7.75 (m, 1H, ³J(HH) 7.0 Hz, H⁵), 7.61 (dt, 1H, ³J(HH) 8.0 Hz, ⁴J(HH) 1.5 Hz,

H⁴), 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} & H⁹), 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, H³, H⁸ & H¹⁰), 6.10 (d, 1H, ³J(HH) 8.0 Hz, H¹¹) and 3.25 (s, 6H, Me). ¹³C NMR (100.6 MHz; CDCl₃, δ_C): 150.5 (C^{Ar}), 149.4 (C⁶), 139.4 (C⁴), 132.7 (C⁸), 130.7 (C⁹), 129.8 (C¹¹), 129.6 (C^{Ph}), 129.5 (C^{Ph}), 129.4 (C^{Ph}), 128.9 (C⁵), 128.4 (C^{Ph}), 127.6 (C³), 127.3 (C^{Ph}), 127.1 (C^{Ph}), 124.5 (C¹⁰), 109.4 (C^{Ar}) and 39.5 (Me).

[Pt(L)(PPh₃)]PF₆ (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. NH₄PF₆ (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 C₅₂H₃₈N₂P₂F₆Pt: C, 53.88; H, 3.33; N 2.37. IR (neat, ν, cm⁻¹): 3006, 1577, 1548, 1472, 1437, 1277, 1261, 833 and 750. ESI-MS (acetone, m/z): found: 916.2413; calcd. 916.2420 for C₅₂H₃₈N₂PPt, [M-PF₆]⁺. ³¹P-NMR (161.9 MHz, CDCl₃, δ in ppm): 27.6 (s), ¹J(PtP) = 4144 Hz (PPh₃) and -143.2 (septet), ¹J(PF) = 720 Hz, (PF₆⁻). ¹H NMR (400 MHz, CDCl₃): δ 7.90-7.86 (m, 6H, H^{Ph}), 7.62-7.57 (m, 3H, H^{Ph}), 7.57-7.51 (m, 4H, H^{Ph} & H⁴), 7.31-7.27 (m, 6H, H^{Ph}), 7.21-7.13 (m, 4H, H^{Ph}), 7.01-6.94 (m, 4H, H^{Ph} & H⁵), 6.88 (br, d, 1H, ³J(HH) 5.6 Hz, H⁶), 6.82 (d, 1H, ³J(HH) 8.3 Hz, H³), 6.81-6.76 (m, 2H, H^{Ph}), 6.56-6.45 (m, 3H, H⁸, H⁹ & H¹⁰) and 6.28 (d, 1H, ³J(HH) 7.9 Hz, H¹¹). ¹³C NMR: δ 162.6, 161.0, 158.9, 157.4, 150.9 (C⁶), 150.5, 148.8, 139.7 (C⁴), 138.4 (C⁸), 136.3, 135.8, 135.4, 135.2, 135.1, 134.8, 132.0, 129.8 (C¹¹), 129.7 (C⁹), 129.6, 129.5, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.3 (C³), 128.2, 127.1 (C⁵), 126.7 and 124.6 (C¹⁰).

[(L)Pt(dppm)Pt(L)][PF₆]₂ (14)

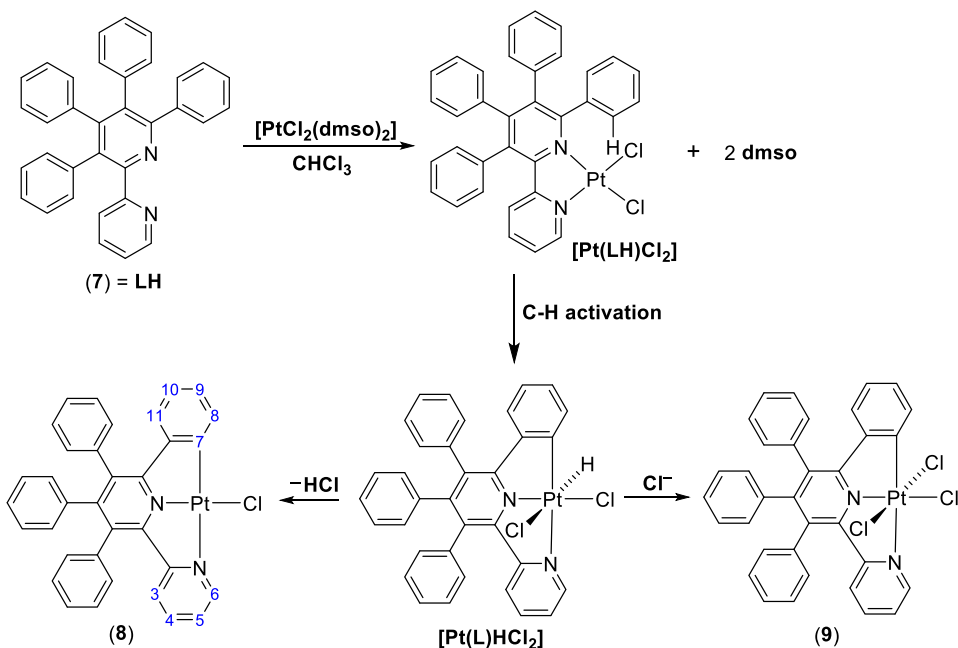
A suspension containing [PtCl(L)] (**8**) (20 mg, 0.029 mmol), bis(diphenylphosphino) methane (dppm) (5.5 mg, 0.014 mmol) and NH₄PF₆ (10 mg, 0.061 mmol) in a mixture of degassed acetonitrile (4 mL) and chloroform (1 mL) was heated to 65 °C for 1 h. The resulting yellow solution was allowed to cool and 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 $C_{93}H_{68}F_{12}N_4P_4Pt_2 \cdot 1.0CHCl_3$: C, 53.69; H, 3.31; N 2.66. IR (neat, ν , cm^{-1}): 1474, 1438, 1405, 1166, 1098, 1015, 832, 770, 757, 734 and 693. MS (m/z -MALDI-TOF, CH_2Cl_2): found: 1837.3859; calcd. 1837.3856 for $C_{93}H_{68}F_6N_4P_3Pt_2$, $[M-PF_6]^+$. 1H NMR (400 MHz, CD_3CN): δ 8.12-7.91 (m, 8H, H^{Ph}), 7.56 (t, 2H, $^3J(HH) = 8.0$ Hz, H^4), 7.52-7.46 (m, 4H, H^{Ph}), 7.46-7.28 (m, 22H, H^6 & H^{Ph}), 7.21 (m, 4H, H^{Ph}), 7.14 (m, 4H, H^{Ph}), 7.08-7.01 (m, 6H, H^{Ph}), 6.97 (d, 2H, $^3J(HH) = 7.5$ Hz, H^8), 6.78 (t, 2H, $^3J(HH) = 6.4$ Hz, H^5), 6.69 (d, 2H, $^3J(HH) = 8.3$ Hz, H^3), 6.65 (t, 2H, $^3J(HH) = 7.3$ Hz, H^9), 6.53 (t, 2H, $^3J(HH) = 7.5$ Hz, H^{10}), 6.01 (d, 2H, $^3J(HH) = 8.0$ Hz, H^{11}) and 4.93-4.67 (vt, 4H, $^2J(PH) = 12.7$ Hz, CH_2). ^{13}C NMR (100.6 MHz; CD_3CN , δ_c): 160.2, 158.5, 157.4, 152.8 (C^6), 150.9, 148.8, 139.5 (C^4), 138.6, 137.8 (C^8), 136.5, 136.0, 136.9, 135.4, 135.1, 133.76 (C^{Ph}), 133.7 (C^{Ph}), 133.6 (C^{Ph}), 132.1 (C^{Ph}), 130.3 (C^{11}), 129.8 (C^{Ph}), 129.5 (C^{Ph}), 129.4 (C^{Ph}), 129.1 (C^9), 129.0 (C^{Ph}), 129.0 (C^{Ph}), 128.9 (C^{Ph}), 128.5 (C^{Ph}), 127.9 (C^3), 127.2 (C^{Ph}), 126.8 (C^5) and 124.8 (C^{10}). ^{31}P NMR (161.9 MHz, CD_3CN , δ in ppm): 13.4, $^1J(PtP) = 4208$ Hz.

Results and Discussion

Treatment of (**7**) with $[PtCl_2(dmsO)_2]$ (dmsO = dimethyl sulfoxide) in boiling chloroform resulted in the formation of a mixture of cyclometallated square-planar platinum(II) complex $[PtCl(L)]$ (**8**) and an octahedral platinum(IV) complex *mer*- $[(L)PtCl_3]$ (**9**), both containing an anionic tridentate ($C^{\wedge}N^{\wedge}N$) ligand. The orange complex (**8**) was not very soluble in common deuterated solvents and in the proton NMR spectrum, the proton (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 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 $[Pt(L)HCl_2]$ 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 $[(L)PtHCl_2]$ undergoes reductive elimination of HCl to produce the square-planar platinum(II) complex $[PtCl(L)]$ (**8**). It is known, in the presence of a base, one could readily remove HCl from a platinum(IV) complex containing a $PtHCl_2$ 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

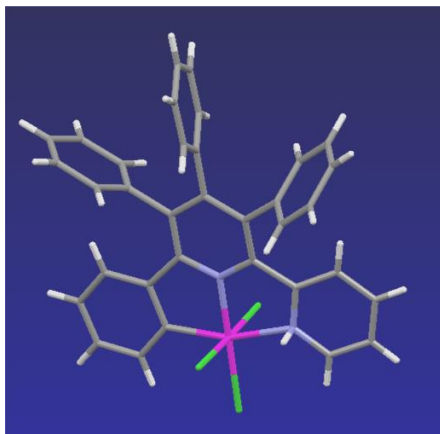
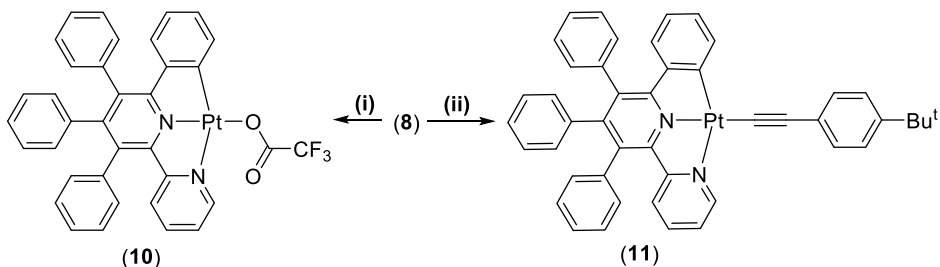


Figure 3. Molecular structure of *mer*-[(L)PtCl₃] (**9**)

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)PtO₂CCF₃] (**10**) a red solid with 93% yield. The IR spectrum of (**10**) showed an IR band at 1659 cm⁻¹ for the C=O group. The complex is quite soluble in organic solvents and it was well characterized. The ¹⁹F NMR spectrum showed a singlet at -75.6 ppm for the fluorine nuclei in the CF₃ group.

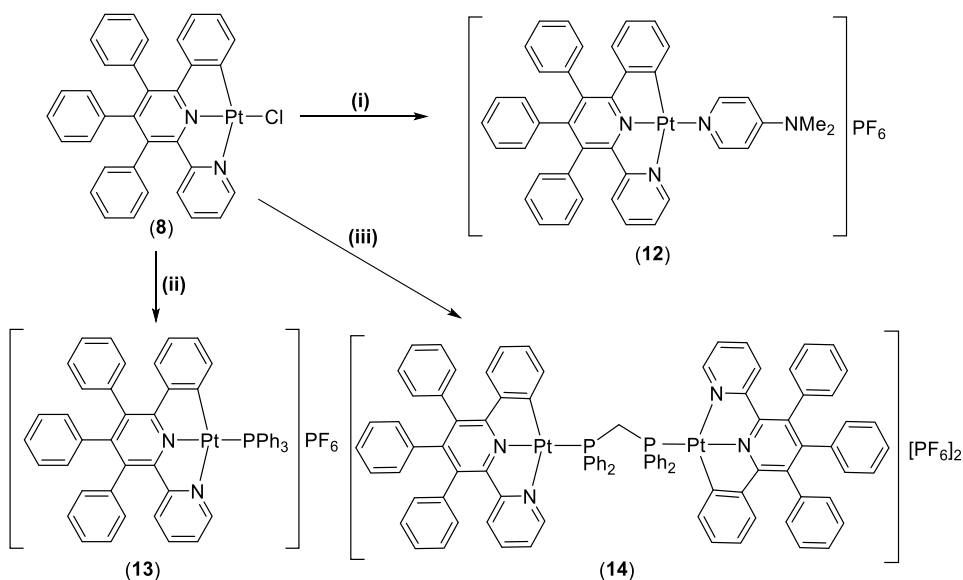


Scheme 2. Synthetic routes to complexes (**10**)-(**11**); (i) AgO₂CCF₃; (ii) HC≡CC₆H₄Bu^t-4

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≡CC₆H₄Bu^t-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 ^1H NMR spectrum, the resonances of the aryl group ($-\text{C}_6\text{H}_4\text{Bu}^t-4$) appeared as an AB pattern at 7.60 (d) and 7.40 (d) ppm with $^3\text{J}(\text{HH}) = 7.8$ 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^{-1} 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_4PF_6 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 ^1H -NMR spectrum, the methyl proton resonance of NMe_2 group appeared as a singlet at 3.25 ppm.



Scheme 3. Synthetic routes to complexes (**12**)-(**14**); (i) DMAP/ NH_4PF_6 ; (ii) $\text{PPh}_3/\text{NH}_4\text{PF}_6$; (iii) 0.5 equiv. dppm/ NH_4PF_6 ;

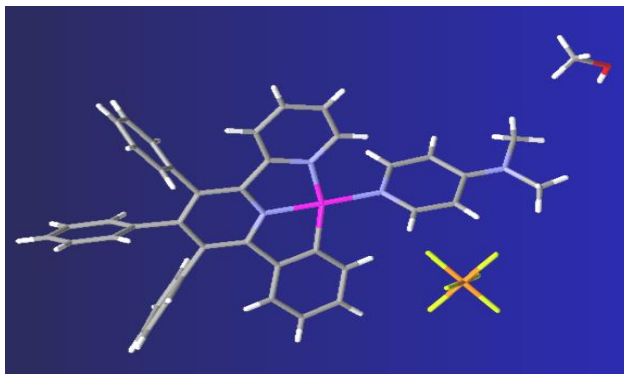


Figure 4. Molecular structure of [Pt(L)(DMAP)]PF₆ (**12**)

Replacement of the labile chloride ligand by triphenylphosphine formed the salt (**13**) as a yellow solid of 94% yield. ³¹P-{¹H} NMR spectrum of (**13**) showed a singlet at 27.6 ppm with platinum satellites, ¹J(PtP) = 4144 Hz, for PPh₃ and a septet at -143.2 ppm for the PF₆⁻ group. Replacement of two chloride groups from two complexes of (**8**) by one dppm ligand gave the dppm-bridged binuclear dicationic salt [(L)Pt(μ-dppm)Pt(L)](PF₆)₂ (**14**). The phosphorus resonance of (**14**) was 13.4 ppm with ¹J(PtP) = 4208 Hz.

Conclusions

The bulky ligand (**7**) containing four phenyl groups was converted into a quite insoluble cyclometallated terdentate complex [(C[^]N[^]N)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 [(C[^]N[^]N)Pt(L')]PF₆ where L' = PPh₃, DMAP. A binuclear complex bridging two (C[^]N[^]N)Pt units with dppm was also prepared.

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