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## Synthesis of Platinum(II) Complexes of a Pyridyl Azafluoranthene Ligand

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### ABSTRACT

Pyridyl azafluoranthene ligand (LH, **2**) was prepared by a Diels-Alder cycloaddition reaction between 2-cyanopyridine and bis(4-*tert*-butylphenyl)-8H-cyclopenta[*l*]acenaphthylene-8-one (**1**). Treatment of (**2**) with  $[\text{PtCl}_2(\text{dms})_2]$  (dms = dimethyl sulfoxide) in the presence of triethylamine in chloroform afforded the cyclometallated square-planar platinum(II) complex  $[(\text{L})\text{PtCl}]$  (**3**) containing an anionic terdentate ( $\text{C}^{\wedge}\text{N}^{\wedge}\text{N}$ ) ligand. The reaction of (**2**) with 0.5 equivalent of  $[(\eta^3\text{-methylallyl})\text{Pt}(\mu\text{-Cl})_2]$  in dichloromethane and subsequent addition of  $\text{NH}_4\text{PF}_6$  in methanol resulted in the formation of the salt  $[(\eta^3\text{-methylallyl})\text{Pt}(\text{2})]\text{PF}_6$  (**4**). The chloride ligand in (**3**) can be replaced by iodide and trifluoroacetate to yield  $[(\text{L})\text{PtI}]$  (**5**) and  $[(\text{L})\text{PtO}_2\text{CCF}_3]$  (**6**), respectively. Treatment of (**3**) with  $\text{HC}\equiv\text{CC}_6\text{H}_4\text{Bu}^t$  in the presence of triethylamine and CuI yielded the acetylide  $[(\text{L})\text{PtC}\equiv\text{CC}_6\text{H}_4\text{Bu}^t]$  (**7**). Treatment of (**3**) with  $\text{PPh}_3$  in dichloromethane and subsequent addition of  $\text{NH}_4\text{PF}_6$  in methanol gave the salt  $[(\text{L})\text{Pt}(\text{PPh}_3)]\text{PF}_6$  (**8**). Similarly, the salt  $[(\text{L})\text{Pt}(\text{DMAP})]\text{PF}_6$  (**9**) was prepared by the reaction between (**3**) and 4-dimethylaminopyridine (DMAP). All the complexes were characterized by elemental analysis, IR, Mass and NMR spectroscopy.

### 1. Introduction

Fluoranthene **I** has an extended  $\pi$ -system in which three benzene rings are fused to a central 5-membered ring; they have been used to prepare curved aromatic ring systems such as corannulene, circumtrindene and fullerenes [1]. Fluoranthene derivatives such as 7,8,10-trisubstituted fluoranthenes **II** [2-4], 7,8,9,10-tetrasubstituted fluoranthenes **III** [3, 5-7], bisfluoranthenes **IV** [4, 8] and **V** [4, 8], benzo[*k*]fluoranthenes **VI** [9,10] and **VII** [9,10] have been prepared (Figure 1). Substituted fluoranthenes have been extensively studied due to their potential as organic light emitting devices (OLEDs) [3-10].

Some of these molecules present a pre-fused moiety that is readily extended to larger polyaromatic hydrocarbon (PAH) derivatives [9]. Tetrasubstituted fluoranthenes of the type **III** can be cyclodehydrogenated to prepare PAH known as dibenzotetraphenylperiflanthene with 23 fused rings [11,12]. Incorporation of different substituents at the fluoranthene moiety can have an impact on optoelectronic and luminescence properties in the solid state which are desirable to use them as optoelectronic devices. Fluoranthene based fluorescent chemo-sensors have been used in light emitting devices and detection of explosives [2-5, 7]. Materials based on bis{4-(7,9,10-triphenylfluoranthene-8-yl)phenyl} sulfone **V** and 2,8-

bis(7,9,10-triphenylfluoranthene-8-yl)dibenzo[*b,d*]thiophene-5,5-dioxide **IV** exhibit deep blue fluorescence emission in both solution and thin film [8].

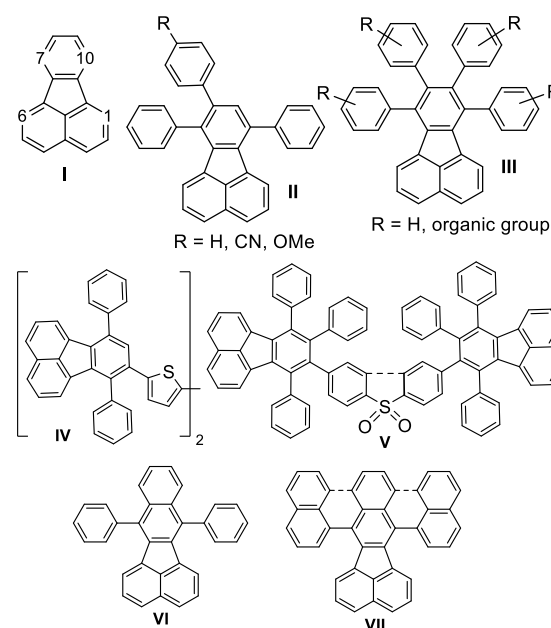
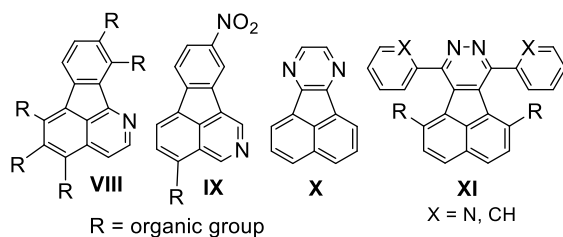


Figure 1 Structures of compounds I-VII

### Azafluoranthene

The fluoranthene compounds with the N-functionality at the periphery are called azafluoranthene. Azafluoranthene are not very common but a few azafluoranthene and diazafluoranthenes are known in the literature [13-18] (Figure 2).



**Figure 2 Structures of azafluoranthenes VIII-XI**

Wang *et al.*, have isolated two 1-azafluoranthene alkaloids **VIII** from the stems of *Cyclea barbata* Miers [13]. Brinie *et al.*, have prepared derivatives of 2-azafluoranthene **IX** from methyl 9-fluorene-1-carboxylate [15]. 7,10-diazafluoranthenes **X** has shown strong mutagenic activity and has been prepared by treating 7,10-diaza-8,9-dihydro fluoranthene with DDQ in dioxane [16]. Due to anisotropic charge transport properties, 7,10-diphenyl-8,9-diazafluoranthene **XI** has the potential to be a good n-type organic semiconductor [17].

### Platinum complexes

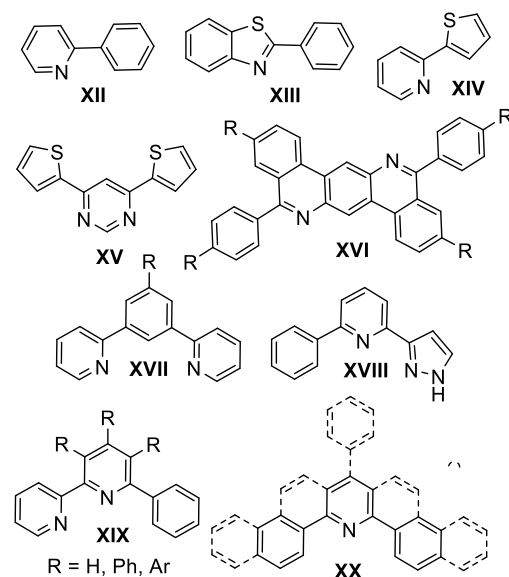
Cyclometallated platinum(II) complexes possess many advantages such as a wide emission colour tunability, a better stability towards photo and chemical degradation, a very large Stokes shift, and long-lived luminescent excited states [19-34]. Cyclometallated Pt(II) complexes containing a bidentate unit (C<sup>^</sup>N)Pt [19, 21], and tridentate units (N<sup>^</sup>C<sup>^</sup>N)Pt [20,22,23], (C<sup>^</sup>N<sup>^</sup>N)Pt [24-29] and (C<sup>^</sup>N<sup>^</sup>C)Pt [30-34] derived from aromatic N-donor ligands display interesting photophysical properties which can be tuned by the groups attached to these ligands in addition to the other auxiliary ligand bonded to the Pt(II) centre. Some of the basic and well-studied ligand types are given in Figure 3: **XII** [19,20], **XIII** [19], **XIV** [21], **XV** [21], **XVI** [22], **XVII** [20,23,24], **XVIII** [25], **XIX** [26-30] and **XX** [31-34].

Incorporation of heteroaromatic groups such as pyridyl and bipyridyl group into polyaromatic systems opens the possibility for them to act as ligands [22, 26-36].

The synthesis of a pyridyl-centered polyphenylene ligands such as 3,4,5,6-tetraphenylbipyridine and 7,10-di(phenyl/aryl)-9-(2-pyridyl)-8-azafluoranthene and their coordination

chemistry, particularly with rhodium, molybdenum and palladium have been reported [35, 36].

Thus, it is of interest to explore the chemistry of this pyridyl azafluoranthene ligand (**2**) with Pt to devise synthetic routes to complexes of the type [(C<sup>^</sup>N<sup>^</sup>N)PtX] and [(C<sup>^</sup>N<sup>^</sup>N)Pt(L')]PF<sub>6</sub>, where X = halide or trifluoroacetate or acetylidy; L' = PPh<sub>3</sub> or DMAP. Here we report the studies carried out to synthesize such complexes.



**Figure 3 Molecular structures of ligands XII-XX**

### 2. Methodology

All the experiments were carried out in an inert atmosphere (nitrogen or argon). Elemental analyses were carried out on a Carlo Erba 1006 automatic analyzer. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer fitted with a universal ATR sampling accessory. Electrospray mass spectra were obtained on a Micromass LCT electrospray mass spectrometer. MALDI-TOF mass spectra were recorded on a Waters MALDI-QTOF Premier spectrometer using  $\alpha$ -cyano-4-hydroxy cinnamic acid matrix. Accurate mass spectra were referenced against Leucine Enkephalin. NMR spectra were recorded on a Bruker DPX 400/600 spectrometer (operating frequencies for <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C are 400/600, 376.5, and 100/151 MHz, respectively). <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. <sup>31</sup>P NMR spectra were recorded at 161 MHz and were standardized with respect to 85% phosphoric acid. 7,9-Diphenyl-8H-cyclopenta[*h*]acenaphthylen-8-one (**1**) and 7,10-di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafluoranthene (**2**) were prepared according to literature procedures [11, 36].

**7,10-Di(4-*tert*-butylphenyl)-9-(2-pyridyl)-8-azafuoranthene (2)**

Data for **(2)**:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 8.53 (br, m, 1H,  $^3\text{J}(\text{HH})$  4.0 Hz,  $\text{H}^{10}$ ), 7.93 (d, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^1$ ), 7.92 (d, 2H,  $^3\text{J}(\text{HH})$  8.5 Hz,  $\text{H}^4$ ), 7.87 (d, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^1$ ), 7.74 (d, 1H,  $^3\text{J}(\text{HH})$  7.0 Hz,  $\text{H}^3$ ), 7.64 (d, 2H,  $^3\text{J}(\text{HH})$  8.5 Hz,  $\text{H}^5$ ), 7.53-7.53 (m, 2H,  $\text{H}^2$  and  $\text{H}^8$ ), 7.47-7.44 (m, 3H,  $^3\text{J}(\text{HH})$  8.5 Hz,  $\text{H}^5$  and  $\text{H}^2$ ), 7.45 (d, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^7$ ), 7.35 (d, 2H,  $^3\text{J}(\text{HH})$  8.5 Hz,  $\text{H}^4$ ), 7.12 (m, 1H,  $\text{H}^9$ ), 7.04 (d, 1H,  $^3\text{J}(\text{HH})$  7.0 Hz,  $\text{H}^3$ ), 1.45 (s, 9H,  $\text{CMe}_3$ ) and 1.41 (s, 9H,  $\text{CMe}_3$ ).

**[(L)PtCl](3)**

A suspension of the ligand **(2)** (LH) (40 mg, 0.0734 mmol),  $[\text{PtCl}_2(\text{dmsO})_2]$  (31 mg, 0.0734 mmol) and triethylamine (27 mg, 0.27 mmol) in chloroform (8 mL) was refluxed for 24 h to give a red precipitate. The solution was concentrated (ca. 1.5 mL) and **(3)** was filtered off and washed with methanol (52 mg, 91%). Found: C, 61.00; H, 4.30; N 3.07, calcd. (%) for  $\text{C}_{40}\text{H}_{35}\text{ClN}_2\text{Pt}\cdot 0.2\text{CHCl}_3$ : C, 60.57; H, 4.45; N 3.52. IR (neat,  $\nu$ ,  $\text{cm}^{-1}$ ): 2966, 1583, 1419, 755, 820, 771, 745 and 671. ESI-MS (MeCN,  $m/z$ ): found: 779.2744; calcd. 779.2714 for  $\text{C}_{42}\text{H}_{38}\text{N}_3\text{Pt}$ ,  $[\text{M-Cl+MeCN}]^+$ .  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 9.36 (d, 1H,  $^3\text{J}(\text{HH})$  4.4 Hz,  $\text{H}^{10}$ ), 8.90 (d, 1H,  $^3\text{J}(\text{HH})$  7.2 Hz,  $\text{H}^3$ ), 8.27 (d, 1H,  $^3\text{J}(\text{HH})$  8.3 Hz,  $\text{H}^{13}$ ), 8.27 (d, 1H,  $^4\text{J}(\text{HH})$  2.0 Hz,  $\text{H}^{11}$ ), 8.03 (d, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^1$ ), 8.01 (d, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^1$ ), 7.78 (t, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^2$ ), 7.76 (d, 2H,  $^3\text{J}(\text{HH})$  8.5 Hz,  $\text{H}^5$ ), 7.49 (dt, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $^4\text{J}(\text{HH})$  1.5 Hz,  $\text{H}^8$ ), 7.43 (d, 2H,  $^3\text{J}(\text{HH})$  8.5 Hz,  $\text{H}^4$ ), 7.42 (m, 1H,  $\text{H}^2$  overlap with  $\text{H}^4$ ), 7.35 (m, 1H,  $^3\text{J}(\text{HH})$  5.0 Hz,  $^4\text{J}(\text{HH})$  1.5 Hz,  $\text{H}^9$ ), 7.25 (dd, 1H,  $^3\text{J}(\text{HH})$  8.5 Hz,  $^4\text{J}(\text{HH})$  2.0 Hz,  $\text{H}^{12}$ ), 6.85 (d, 1H,  $^3\text{J}(\text{HH})$  8.5 Hz,  $\text{H}^7$ ), 6.48 (d, 1H,  $^3\text{J}(\text{HH})$  7.5 Hz,  $\text{H}^3$ ), 1.54 (s, 9H,  $\text{CMe}_3$ ) and 1.44 (s, 9H,  $\text{CMe}_3$ ).  $^{13}\text{C-NMR}$  (151 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 148.5 ( $\text{C}^{10}$ ), 131.9 ( $\text{C}^{11}$ ), 137.5 ( $\text{C}^8$ ), 129.7 ( $\text{C}^1$  or  $\text{C}^1$ ), 128.4 ( $\text{C}^1$  or  $\text{C}^1$ ), 128.6 (2C,  $\text{C}^{4\&4'}$ ), 127.8 ( $\text{C}^2$ ), 128.1 ( $\text{C}^2$ ), 127.6 (2C,  $\text{C}^{5\&5'}$ ), 126.5 ( $\text{C}^{13}$ ), 126.1 ( $\text{C}^3$ ), 125.8 ( $\text{C}^3$ ), 126.0 ( $\text{C}^7$ ), 126.0 ( $\text{C}^9$ ), 120.4 ( $\text{C}^{12}$ ), 31.4 ( $\text{CMe}_3$ ) and 31.3 ( $\text{CMe}_3$ ).

**[( $\eta^3$ -methallyl)Pt(2)]PF<sub>6</sub>(4)**

The ligand **(2)** (10.5 mg, 0.019 mmol) and  $[(\eta^3\text{-metallyl})\text{Pt}(\mu\text{-Cl})_2]$  (5.5 mg, 0.0096 mmol) and  $\text{NH}_4\text{PF}_6$  (7 mg, 0.04 mmol) were dissolved in a mixture of chloroform (1 mL) and methanol (0.5 mL). The reaction mixture was heated at 50 °C for 4 h. The resulting dark solution was concentrated to a low volume and methanol was added to yield **(4)** as a yellow solid (14 mg, 78%). Found: C, 55.80; H, 4.50; N 3.05, calcd. (%) for  $\text{C}_{44}\text{H}_{43}\text{F}_6\text{N}_2\text{PPT}$ : C, 56.23; H, 4.61; N 2.98. IR (neat,  $\nu$ ,  $\text{cm}^{-1}$ ): 2958, 1559, 1421, 1267, 1116, 829, 776 and 739. Maldi (DCM,  $m/z$ ): found: 794.3080; calcd. 794.3074 for

$\text{C}_{44}\text{H}_{43}\text{N}_2\text{Pt}$ ,  $[\text{M-PF}_6]^+$ .  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 9.25 (d, 1H,  $^3\text{J}(\text{HH})$  5.0 Hz,  $^3\text{J}(\text{PtH})$  40 Hz,  $\text{H}^{10}$ ), 8.10 (d, 1H,  $^3\text{J}(\text{HH})$  8.1 Hz,  $\text{H}^1$  or  $\text{H}^1$ ), 8.03 (d, 1H,  $^3\text{J}(\text{HH})$  8.1 Hz,  $\text{H}^1$  or  $\text{H}^1$ ), 7.88-7.71 (m, 6H, Ar &  $\text{H}^8$ ), 7.69-7.61 (m, 2H), 7.59-7.48 (m, 4H, Ar), 7.20 (d, 1H,  $^3\text{J}(\text{HH})$  7.0 Hz,  $\text{H}^3$  or  $\text{H}^3$  or  $\text{H}^7$ ), 7.08 (d, 1H,  $^3\text{J}(\text{HH})$  7.0 Hz,  $\text{H}^3$  or  $\text{H}^3$  or  $\text{H}^7$ ), 6.85 (d, 1H,  $^3\text{J}(\text{HH})$  7.2 Hz,  $\text{H}^3$  or  $\text{H}^3$  or  $\text{H}^7$ ), 3.83 (s, 1H,  $^2\text{J}(\text{PtH})$  75 Hz, allyl-H), 2.87 (s, 1H,  $^2\text{J}(\text{PtH})$  75 Hz, allyl-H), 2.06 (s, 3H,  $^3\text{J}(\text{PtH})$  = 80 Hz, Me), 1.87 (s, 1H,  $^2\text{J}(\text{PtH})$  not resolved, allyl-H), 1.78 (s, 1H,  $^2\text{J}(\text{PtH})$  not resolved, satellite overlaps with other peaks, allyl-H), 1.58 (s, 9H,  $\text{CMe}_3$ ) and 1.55 (s, 9H,  $\text{CMe}_3$ ).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 156.6, 155.8, 154.4 ( $\text{C}^{10}$ ), 154.0, 153.7, 151.0, 148.8, 139.0, 138.6 ( $\text{C}^8$ ), 133.95, 133.9, 133.1, 132.18, 132.1, 131.9, 130.9 ( $\text{C}^1$  or  $\text{C}^1$ ), 129.33, 129.26 ( $\text{C}^1$  or  $\text{C}^1$ ), 129.2 ( $\text{C}^{\text{Ar}}$ ), 128.2 ( $\text{C}^{\text{Ar}}$ ), 128.1 ( $\text{C}^3$  or  $\text{C}^3$  or  $\text{C}^7$ ), 127.9, 127.5, 128.1 ( $\text{C}^{\text{Ar}}$ ), 127.4 ( $\text{C}^3$  or  $\text{C}^3$  or  $\text{C}^7$ ), 127.35 ( $\text{C}^{\text{Ar}}$ ), 126.0 ( $\text{C}^3$  or  $\text{C}^3$  or  $\text{C}^7$ ), 122.3, 47.7 ( $\text{CH}_2$ ), 43.3 ( $\text{CH}_2$ ), 34.8 ( $\text{CMe}_3$ ), 34.75 ( $\text{CMe}_3$ ), 31.0 ( $\text{CMe}_3$ ), 30.95 ( $\text{CMe}_3$ ) and 22.3 (Me).

**[(L)PtI] (5)**

A warm solution of **(3)** (15 mg, 0.019 mmol) in chloroform (2 mL) was added to a hot solution of NaI (20 mg, 0.13 mmol) in acetone (3 mL). The reaction mixture was heated at 45 °C for 18 h; the solvent was then removed, and the residue was extracted with chloroform (3 x 3 mL). The combined extract was concentrated, and methanol was added to give **(5)** as a dark red solid, (14 mg, 84%). Found: C, 55.05; H, 3.80; N 3.00, calcd. (%) for  $\text{C}_{40}\text{H}_{35}\text{IN}_2\text{Pt}$ : C, 55.50; H, 4.08; N 3.24. IR (neat,  $\nu$ ,  $\text{cm}^{-1}$ ): 2960, 2900, 2862, 1586, 1545, 1459, 1420, 1363, 1327, 1259, 1226, 1169, 1085, 1017, 820, 801, 775, 743, 730 and 667. Mass (MALDI-TOF,  $\text{CHCl}_3$ ): found: 865.1528; calcd. 865.1493 for  $\text{C}_{40}\text{H}_{35}\text{IN}_2\text{Pt}$ ,  $[\text{M}]^+$ .  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 9.75 (br, d, 1H,  $^3\text{J}(\text{HH})$  5.5 Hz,  $\text{H}^{10}$ ), 8.79 (d, 1H,  $^3\text{J}(\text{HH})$  7.0 Hz,  $\text{H}^3$ ), 8.55 (br, s 1H,  $^3\text{J}(\text{PtH})$  47 Hz,  $\text{H}^{11}$ ), 8.16 (d, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^{13}$ ), 7.97 (d, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^1$  or  $\text{H}^1$ ), 7.93 (d, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^1$  or  $\text{H}^1$ ), 7.74-7.66 (m, 3H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^5$  and  $\text{H}^2$ ), 7.47 (t, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^8$ ), 7.39-7.27 (m, 4H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^2$ ,  $\text{H}^9$  and  $\text{H}^4$ ), 7.15 (br, d, 1H,  $^3\text{J}(\text{HH})$  8.0 Hz,  $\text{H}^{12}$ ), 6.79 (d, 1H,  $^3\text{J}(\text{HH})$  8.5 Hz,  $\text{H}^7$ ), 6.41 (d, 1H,  $^3\text{J}(\text{HH})$  7.0 Hz,  $\text{H}^3$ ), 1.47 (s, 9H,  $\text{CMe}_3$ ) and 1.37 (s, 9H,  $\text{CMe}_3$ ).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 153.0 ( $\text{C}^{10}$ ), 139.9 ( $\text{C}^{11}$ ), 137.5 ( $\text{C}^8$ ), 129.9 ( $\text{C}^1$ ), 128.8 ( $\text{C}^1$ ), 128.75 (2C,  $\text{C}^{4\&4'}$ ), 128.3 ( $\text{C}^2$ ), 128.2 ( $\text{C}^2$ ), 127.7 (2C,  $\text{C}^{5\&5'}$ ), 126.9 ( $\text{C}^{13}$ ), 126.3 ( $\text{C}^3$ ), 126.2 (2C,  $\text{C}^7$  &  $\text{C}^9$ ), 125.9 ( $\text{C}^3$ ), 120.3 ( $\text{C}^{12}$ ), 31.5 ( $\text{CMe}_3$ ) and 31.3 ( $\text{CMe}_3$ ).

**[(L)PtO<sub>2</sub>CCF<sub>3</sub>] (6)**

A solution of silver trifluoroacetate ( $\text{AgO}_2\text{CCF}_3$ ) (4.3 mg, 0.019 mmol) in methanol (1 mL) was added to

a solution of **(3)** (15 mg, 0.019 mmol) in dichloromethane (3 mL) to give a red solution. Reaction mixture was stirred at room temperature for 20 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 **(6)** a red solid (13 mg, 79%). Found: C, 58.90; H, 3.90; N 2.95, calcd. (%) for  $C_{42}H_{35}F_3N_2O_2Pt$ : C, 59.22; H, 4.14; N 3.29. IR (neat,  $cm^{-1}$ ): 2961, 1696, 1588, 1548, 1474, 1404, 1362, 1329, 1262, 1137, 1021, 847, 821, 771, 728 and 670. Mass ( $m/z$ -MALDI-TOF,  $CH_2Cl_2$ ): found: 738.2452; calcd. 738.2448 for  $C_{40}H_{35}N_2Pt$ ,  $[M-O_2CCF_3]^+$ .  $^{19}F$  NMR (376.5 MHz,  $CDCl_3$ ): -74.5 (s) ppm.  $^1H$ -NMR (400 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 8.74 (br, d, 1H,  $^3J(HH)$  4.5 Hz,  $H^{10}$ ), 8.61 (d, 1H,  $^3J(HH)$  7.0 Hz,  $H^3$ ), 8.14 (d, 1H,  $^3J(HH)$  8.0 Hz,  $H^{13}$ ), 7.98 (d, 1H,  $^3J(HH)$  8.0 Hz,  $H^1$ ), 7.88 (d, 1H,  $^3J(HH)$  8.0 Hz,  $H^1$ ), 7.75 (d, 2H,  $^3J(HH)$  8.0 Hz,  $H^5$ ), 7.57 (t, 1H,  $^3J(HH)$  8.0 Hz,  $H^8$ ), 7.54-7.46 (m, 2H,  $H^2$  and  $H^9$ ), 7.41-7.32 (m, 3H,  $H^2$  and  $H^4$ ), 7.27-7.20 (m, 2H,  $H^{11}$  and  $H^{12}$ ), 6.75 (d, 1H,  $^3J(HH)$  8.0 Hz,  $H^7$ ), 6.42 (d, 1H,  $^3J(HH)$  7.5 Hz,  $H^3$ ), 1.54 (s, 9H,  $CMe_3$ ) and 1.38 (s, 9H,  $CMe_3$ ).  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 149.7 ( $C^{10}$ ), 138.4 ( $C^8$ ), 130.2 ( $C^1$ ), 129.7 ( $C^{11}$ ), 128.8 ( $C^1$ ), 128.8 (2C,  $C^4$ ), 128.7 ( $C^2$ ), 128.1 (1C,  $C^2$ ), 127.7 (2C,  $C^5$ ), 126.75 ( $C^{13}$ ), 126.7 ( $C^3$ ), 126.7 ( $C^9$ ), 126.6 ( $C^7$ ), 125.9 ( $C^3$ ), 120.9 ( $C^{12}$ ) 31.2 ( $CMe_3$ ) and 31.3 ( $CMe_3$ ).

#### **[(L)PtC≡CC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>](7)**

CuI (1 mg, 0.005 mmol) was added to a degassed solution containing **(3)** (19 mg, 0.024 mmol), 4-*tert*-butylphenyl acetylene (20 mg, 0.13 mmol) and triethylamine (0.5 mL) in dry dichloromethane (5 mL). The resulting dark red solution was stirred under nitrogen for 24 h. It was concentrated to a low volume and methanol was added to give **(7)** as a red solid (19 mg, 87%). IR (neat,  $cm^{-1}$ ): 2959, 2904, 2862, 2091, 1598, 1584, 1552, 1499, 1459, 1421, 1362, 1332, 1262, 1108, 1017, 827, 778 and 672. Mass ( $m/z$ -MALDI-TOF,  $CH_2Cl_2$ ): found: 895.3475; calcd. 895.3465 for  $C_{52}H_{48}N_2Pt$ ,  $[M]^+$ .  $^1H$ -NMR (400 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 9.40 (br, d, 1H,  $^3J(HH)$  5.0 Hz,  $H^{10}$ ), 8.86 (d, 1H,  $^3J(HH)$  7.5 Hz,  $H^3$ ), 8.27 (br, s 1H,  $^3J(PtH)$  65 Hz,  $H^{11}$ ), 8.25 (d, 1H,  $^3J(HH)$  8.0 Hz,  $H^{13}$ ), 8.03-7.97 (m, 2H,  $H^1$  and  $H^1$  overlapping), 7.78-7.70 (m, 3H,  $^3J(HH)$  8.0 Hz,  $H^5$  and  $H^2$ ), 7.58-7.51 (m, 3H,  $^3J(HH)$  8.0 Hz,  $H^{Ar}$  and  $H^8$ ), 7.43 (d, 2H,  $^3J(HH)$  8.0 Hz,  $H^4$ ), 7.39-7.31 (m, 4H,  $H^2$ ,  $H^9$  and  $H^{Ar}$ ), 7.23 (br, d, 1H,  $^3J(HH)$  8.0 Hz,  $H^{12}$ ), 6.83 (d, 1H,  $^3J(HH)$  8.5 Hz,  $H^7$ ), 6.45 (d, 1H,  $^3J(HH)$  7.5 Hz,  $H^3$ ), 1.54 (s, 9H,  $CMe_3$ ), 1.45 (s, 9H,  $CMe_3$ ) and 1.36 (s, 9H,  $CMe_3$ ).  $^{13}C$  NMR (101 MHz;  $CDCl_3$ ,  $\delta_c$ ): 151.2 ( $C^{10}$ ), 136.9 ( $C^8$ ), 135.1 ( $C^{11}$ ), 131.0 (2C,  $C^{Ar}$ ), 129.3 ( $C^1$  or  $C^1$ ), 128.3 (2C,  $C^{4&4'}$ ), 128.0 ( $C^1$  or  $C^1$ ), 127.7 ( $C^2$ ), 127.6 ( $C^2$ ), 127.1 (2C,  $C^{5&5'}$ ), 126.4 ( $C^{13}$ ), 126.1 ( $C^3$ ), 126.0

( $C^3$ ), 125.8 ( $C^9$ ), 125.5 ( $C^{12}$ ), 124.3 (2C,  $C^{Ar}$ ), 31.1 ( $CMe_3$ ), 30.92 ( $CMe_3$ ) and 30.89 (3C,  $CMe_3$ ).

#### **[(L)Pt(PPh<sub>3</sub>)]PF<sub>6</sub>(8)**

A solution of  $NH_4PF_6$  (10 mg, 0.06 mmol) in methanol (1 mL) was added to a solution of **(3)** (15 mg, 0.0193 mmol) and triphenylphosphine (7 mg, 0.026 mmol) in chloroform (2.5 mL) to give an orange solution. After 15 min, the solution was concentrated to give **(8)** as an orange solid (21 mg, 95%). Found: C, 59.03; H, 4.24; N 2.23, calcd. (%) for  $C_{58}H_{50}N_2P_2F_6Pt \cdot 0.25CHCl_3$ : C, 59.49; H, 4.33; N 2.38. IR (neat,  $\nu$ ,  $cm^{-1}$ ): 3006, 1586, 1554, 1420, 1276, 1261, 836, 764 and 750. ESI-MS (acetone,  $m/z$ ): found: 1000.3376; calcd. 1000.3359 for  $C_{58}H_{50}N_2P_2Pt$ ,  $[M-PF_6]^+$ .  $^{31}P$ -NMR (161.9 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 27.4 (s),  $^1J(PtP)$  = 4132 Hz ( $PPh_3$ ) and -143.2 (septet,  $PF_6^-$ ).  $^1H$ -NMR (400 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 8.91 (d, 1H,  $^3J(HH)$  7.0 Hz,  $H^3$ ), 8.30 (d, 1H,  $^3J(HH)$  8.5 Hz,  $H^{13}$ ), 8.13 (d, 1H,  $^3J(HH)$  8.0 Hz,  $H^1$ ), 8.11 (d, 1H,  $^3J(HH)$  8.0 Hz,  $H^1$ ), 7.94-7.86 (m, 5H, Ph), 7.84-7.77 (m, 3H,  $^3J(HH)$  8.0 Hz,  $H^5$  and  $H^2$ ), 7.70-7.60 (m, 4H,  $^3J(HH)$  7.5 Hz,  $^4J(HH)$  1.5 Hz, Ph and  $H^8$ ), 7.58-7.52 (m, 6H, Ph), 7.51-7.42 (m, 3H,  $^3J(HH)$  8.0 Hz,  $H^2$  &  $H^4$ ), 7.21 (dd, 1H,  $^3J(HH)$  8.5 Hz,  $^4J(HH)$  2.0 Hz,  $H^{12}$ ), 7.13-7.03 (m, 2H,  $^3J(HH)$  5.0, 8.5 Hz,  $H^7$  and  $H^9$ ), 6.87 (br, d, 1H,  $^3J(HH)$  5.0 Hz,  $H^{10}$ ), 6.77 (m, 1H,  $^4J(HH)$  2.0 Hz,  $^3J(PtH)$  50 Hz,  $H^{11}$ ), 6.54 (d, 1H,  $^3J(HH)$  7.5 Hz,  $H^3$ ), 1.54 (s, 9H,  $CMe_3$ ) and 0.81 (s, 9H,  $CMe_3$ ).  $^{13}C$ -NMR (151 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 150.7 ( $C^{10}$ ), 139.6 ( $C^8$ ), 137.2 ( $C^{11}$ ), 130.8 ( $C^1$ ), 129.7 ( $C^1$ ), 128.3 (2C,  $C^{4&4'}$ ), 128.2 ( $C^2$ ), 128.0 ( $C^2$ ), 127.9 (2C,  $C^{5&5'}$ ), 127.5 ( $C^{13}$ ), 127.4 ( $C^3$ ), 127.3 ( $C^7$ ), 126.7 ( $C^9$ ), 126.3 ( $C^3$ ), 121.3 ( $C^{12}$ ), 31.0 ( $CMe_3$ ), 30.0 ( $CMe_3$ ).

#### **[(L)Pt(DMAP)]PF<sub>6</sub>(9)**

A solution of  $NH_4PF_6$  (15 mg, 0.092 mmol) in methanol (1 mL) was added to a suspension containing **(3)** (15 mg, 0.0193 mmol) and 4-dimethylaminopyridine (10 mg, 0.082 mmol) in chloroform (3 mL). The reaction mixture was refluxed for 1 h to give an orange/red solution which was concentrated to give **(9)** as a red solid (18 mg, 93%). Found: C, 51.26; H, 4.11; N 4.87, calcd. (%) for  $C_{47}H_{45}N_4PF_6Pt \cdot 1.0CHCl_3$ : C, 51.23; H, 4.21; N 4.98. IR (neat,  $\nu$ ,  $cm^{-1}$ ): 2947, 1619, 1540, 1420, 1390, 1220, 838, 826 and 750. ESI-MS (acetone,  $m/z$ ): found: 860.3294; calcd. 860.3292 for  $C_{47}H_{45}N_4Pt$ ,  $[M-PF_6]^+$ .  $^1H$ -NMR (600 MHz,  $CDCl_3$ ,  $\delta$  in ppm): 8.87 (d, 1H,  $^3J(HH)$  7.3 Hz,  $H^3$ ), 8.40 (d, 2H,  $^3J(HH)$  7.3 Hz,  $H^{DMAP}$ ), 8.36 (d, 1H,  $^3J(HH)$  8.4 Hz,  $H^{13}$ ), 8.23 (br, d, 1H,  $^3J(HH)$  5.1 Hz,  $H^{10}$ ), 8.10 (d, 1H,  $^3J(HH)$  8.0 Hz,  $H^1$ ), 8.08 (d, 1H,  $^3J(HH)$  8.0 Hz,  $H^1$ ), 7.82 (t, 1H,  $^3J(HH)$  7.7 Hz,  $H^2$ , overlaps with  $H^5$ ), 7.81 (d, 2H,  $^3J(HH)$  8.4 Hz,  $H^5$ ), 7.78 (m, 1H,  $H^9$ ), 7.67 (m, 1H,  $^3J(HH)$  8.0 Hz,  $H^8$ ), 7.46-7.44

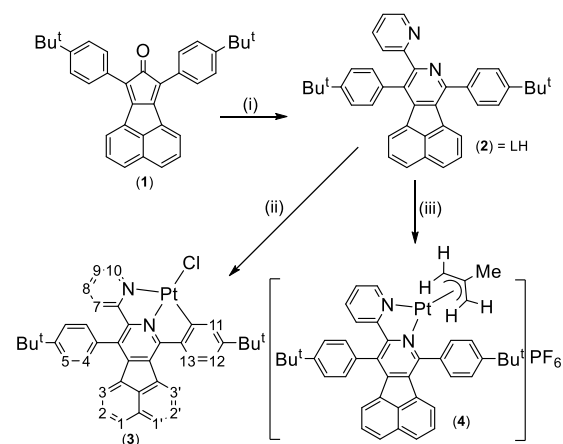
(m, 1H, H<sup>2</sup>, overlap with H<sup>4</sup>), 7.45 (d, 2H, <sup>3</sup>J(HH) 8.4 Hz, H<sup>4</sup>), 7.34 (dd, 1H, <sup>3</sup>J(HH) 8.8 Hz, <sup>4</sup>J(HH) 2.2 Hz, H<sup>12</sup>), 6.92 (d, 1H, <sup>3</sup>J(HH) 8.4 Hz, H<sup>7</sup>), 6.85 (d, 1H, <sup>4</sup>J(HH) 2.2 Hz, H<sup>11</sup>), 6.82 (d, 2H, <sup>3</sup>J(HH) 7.3 Hz, H<sup>DMAP</sup>), 6.53 (d, 1H, <sup>3</sup>J(HH) 7.3 Hz, H<sup>3</sup>), 3.25 (s, 6H, NMe<sub>2</sub>) 1.55 (s, 9H, CMe<sub>3</sub>) and 1.32 (s, 9H, CMe<sub>3</sub>). <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>, δ in ppm): 157.2, 154.6, 154.4, 153.8, 150.6 (C<sup>DMAP</sup>), 150.0 149.3 (C<sup>10</sup>), 145.8, 143.0, 139.1 (C<sup>8</sup>), 133.4, 132.1, 131.8 (C<sup>11</sup>), 130.5 (C<sup>1</sup>), 130.0, 129.9, 129.2 (C<sup>1</sup>), 128.3 (2C, C<sup>4&4'</sup>), 128.1 (C<sup>2</sup>), 128.1 (C<sup>2'</sup>), 127.7 (2C, C<sup>5&5'</sup>), 127.4, 127.7 (C<sup>9</sup>), 127.4 (C<sup>7</sup>), 127.3 (C<sup>3</sup>), 126.9 (C<sup>13</sup>), 126.2 (C<sup>3'</sup>), 122.1 (C<sup>12</sup>), 109.6 (C<sup>DMAP</sup>), 38.9 (NMe<sub>2</sub>), 31.5 (CMe<sub>3</sub>) and 31.3 (CMe<sub>3</sub>).

### 3. Results and Discussion

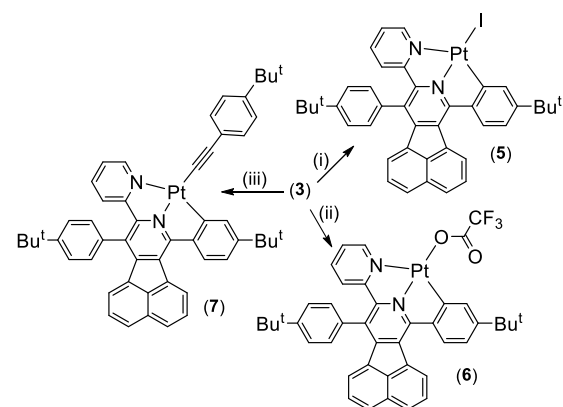
The ligand (2) was prepared by a Diels-Alder cycloaddition reaction between 2-cyanopyridine and (1) [11] (Scheme 1). Treatment of the ligand (LH) (2) with [PtCl<sub>2</sub>(dmsO)<sub>2</sub>] in the presence of NEt<sub>3</sub> in boiling chloroform yielded the cyclometallated square-planar Pt(II) complex [(L)PtCl] (3) as a red solid which contains an anionic tridentate (C<sup>^-</sup>N<sup>^-</sup>N<sup>^-</sup>) ligand. Characterizing data for metal complexes are given in the experimental section. All new complexes were characterized by a combination of elemental analysis, IR, Mass and NMR spectroscopy. Solubility of some metal complexes were poor in deuterated solvents and carbon-13 chemical shifts (δ<sub>C</sub>) were identified by <sup>13</sup>C-<sup>1</sup>H-COSY experiments. The <sup>1</sup>H and <sup>13</sup>C NMR data observed for H<sup>7</sup>, H<sup>8</sup>, H<sup>10</sup>, C<sup>7</sup>, C<sup>8</sup> and C<sup>10</sup> of the 2-pyridyl group of the complexes (3)-(8) are in good agreement with the values reported in the literature [35-37]. The platinum satellites were not resolved for most of the proton resonances due to poor solubility and overlapping of signals.

The elemental and mass spectral analyses of the complex [(L)PtCl] (3) confirmed the proposed structure with the composition C<sub>40</sub>H<sub>35</sub>ClN<sub>2</sub>Pt. In the <sup>1</sup>H NMR spectrum, the H<sup>10</sup> proton attached to carbon (C<sup>10</sup>) adjacent to nitrogen of the pyridyl group appeared at 9.36 ppm. It was deshielded by about 0.83 ppm upon coordination to Pt(II) centre when compared to the δ<sub>H</sub> value observed (8.53 ppm) for the same of the free ligand. Treatment of (2) with 0.5 equivalent of [(η<sup>3</sup>-methyl)Pt(μ-Cl)]<sub>2</sub> in dichloromethane and subsequent addition of NH<sub>4</sub>PF<sub>6</sub> in methanol resulted in the formation of the salt [(η<sup>3</sup>-methyl)Pt(2)]PF<sub>6</sub> (4) as a yellow solid in 78% yield. In this complex, the ligand is coordinated to the metal through both nitrogen donors as a bidentate ligand. Accurate mass spectral data showed a signal at 794.3080 for [M-PF<sub>6</sub>]<sup>+</sup>. The <sup>1</sup>H NMR spectrum of (4) displayed signals at 3.83, 2.87, 1.87 and 1.78 ppm for the four allyl protons.

Substitution reactions of (3) with anionic ligands were studied first (Scheme 2): the chloride ligand was replaced by an iodide by treating (3) with a large excess of NaI in a hot mixture of acetone and chloroform to give [(L)PtI] (5) as a dark red solid in 87% yield. The <sup>1</sup>H and <sup>13</sup>C NMR resonances observed for H<sup>10</sup> (9.75 ppm) and C<sup>10</sup> (153.0 ppm) indicate the relative deshielding effect exerted by the iodide ligand.



**Scheme 1.** Synthetic routes to (2)-(4). (i) 2-cyanopyridine; (ii) [PtCl<sub>2</sub>(dmsO)<sub>2</sub>]; (iii) 0.5 equiv. [(η<sup>3</sup>-methyl)Pt(μ-Cl)]<sub>2</sub>; and atom labelling used for the assignment of NMR data.



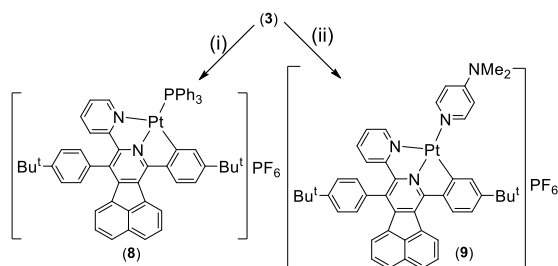
**Scheme 2.** Synthetic routes to complexes (5)-(7). (i) NaI; (ii) AgO<sub>2</sub>CCF<sub>3</sub>; (iii) HC≡CC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4

The chloride of (2) was replaced by trifluoroacetate ion to obtain [(L)PtO<sub>2</sub>CCF<sub>3</sub>] (6) as a red solid in 79% yield. Mass spectrum of (6) indicated an accurate mass value of 738.2452 for the [M-O<sub>2</sub>CCF<sub>3</sub>]<sup>+</sup> ion. The IR spectrum showed an IR band at 1696 cm<sup>-1</sup> for the C=O group. The <sup>19</sup>F NMR spectrum showed a singlet at -74.5 ppm for the fluorine nuclei of the CF<sub>3</sub> group.

Cyclometallated Pt(II) acetylides have shown interesting photophysical properties [27-29] and the complex (3) was converted into its acetylide [(L)PtC≡CC<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4] (7) in 87% yield as a red solid,

by reacting it with 4-*tert*-butylphenyl acetylene in the presence of triethylamine and catalytic amount of CuI in dry dichloromethane. Mass spectrum of (7) indicated an accurate mass value of 895.3475 for the molecular ion  $[M]^+$  with the composition  $C_{52}H_{48}N_2Pt$ . As expected, in the  $^1H$  NMR spectrum, the resonances of the aryl protons of (-C<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4) group appeared as an AB pattern at 7.55 (d) and 7.35 (d) ppm with  $^3J(HH) = 8.0$  Hz. The IR spectrum of (7) showed an IR band at 2091 cm<sup>-1</sup> for the acetylide ligand.

Substitution of the chloride ion by neutral ligands such as phosphine and 4-dimethylaminopyridine (DMAP) was studied (Scheme 3). Replacement of the labile chloride ligand of the complex (3) by triphenylphosphine afforded the salt (8) as an orange solid in 95% yield. The elemental and mass spectral analyses confirmed the proposed structure with the composition  $C_{58}H_{50}N_2P_2F_6Pt$ .  $^{31}P$ - $\{^1H\}$  NMR spectrum of (8) showed a singlet at 27.4 ppm with platinum satellites,  $^1J(PtP) = 4132$  Hz, for PPh<sub>3</sub> and a septet at -143.2 ppm for the PF<sub>6</sub><sup>-</sup> group. In the  $^1H$  NMR spectrum, H<sup>11</sup> was a multiplet at 6.77 ppm with coupling to H<sup>12</sup> and Pt;  $^4J(HH) = 2.0$  Hz and  $^3J(PtH) 50$  Hz.



**Scheme 3.** Synthetic routes to complexes (8)-(9).

(i) PPh<sub>3</sub>/NH<sub>4</sub>PF<sub>6</sub>; (ii) DMAP/NH<sub>4</sub>PF<sub>6</sub>

Replacement of the labile chloride ligand of (3) with 4-dimethylaminopyridine in the presence of NH<sub>4</sub>PF<sub>6</sub> resulted in the formation of the salt [(L)Pt(DMAP)]PF<sub>6</sub> (9). In its  $^1H$ -NMR spectrum, the methyl proton resonance of NMe<sub>2</sub> group appeared as a singlet at 3.25 ppm., H<sup>11</sup> appeared as a doublet at 6.85 ppm with  $^4J(HH) = 2.2$  Hz whilst the aryl protons of DMAP appeared as a AB-pattern at 8.40 and 6.82 ppm with  $^3J(HH) = 7.3$  Hz. The complexes (8) and (9) are more soluble in CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> when compared to complex (3).

#### 4. Conclusions

The ligand (2) was converted into a quite insoluble cyclometallated terdentate complex (3) with the terdentate C<sup>3</sup>N<sup>3</sup>N ligand. In complex [(η<sup>3</sup>-methylallyl)Pt(2)]PF<sub>6</sub> (4), the ligand (2) acts as a

bidentate ligand. The chloride (3) was converted into the corresponding iodide (5) trifluoroacetate (6) and acetylide (7). Introduction of a neutral ligand such as phosphine and DMAP generated more soluble salts of the type [(C<sup>3</sup>N<sup>3</sup>N)Pt(L')]PF<sub>6</sub> where L' = PPh<sub>3</sub>, DMAP.

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