

Note

# Cyclometalated platinum complexes: High-yield synthesis, characterization, and a crystal structure

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## Abstract

The one-pot reaction of  $K_2PtCl_4$  and various 2-arylpyridines,  $HC^{\wedge}N$ , in a 3:1 (v/v) mixture of 2-ethoxyethanol and  $H_2O$  at 80 °C for 16 h affords cyclometalated platinum complexes,  $Pt(C^{\wedge}N)(HC^{\wedge}N)(Cl)$ , in high yield. These have been fully characterized and, in one case, the X-ray structure has been determined.

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## 1. Introduction

Cyclometalated complexes are important in catalysis [1] and polymerization processes; iridium [2] and platinum [3,4] examples have attracted attention as phosphors for organic light-emitting diodes (OLEDs), and platinum species have potential medicinal applications due to their cytotoxic [5] and luminescence properties. The synthesis [3] and use in OLEDs [4] of phosphorescent complexes with general structure  $Pt(C^{\wedge}N)(O^{\wedge}O)$ , where  $C^{\wedge}N$  is a cyclometalated ligand such as 2-phenylpyridinato-N,  $C^{2'}$  (ppy) and  $O^{\wedge}O$  is a  $\beta$ -diketonate, were recently reported. The  $Pt(C^{\wedge}N)(O^{\wedge}O)$  species of Ref. [3] were obtained from intermediate Pt complexes reported, without characterizing data, to be

$[Pt(C^{\wedge}N)(\mu-Cl)_2]$  dimers, which were themselves obtained from the reaction of  $K_2PtCl_4$  and  $HC^{\wedge}N$  [3,6]. Here we show that the products of  $K_2PtCl_4$  and  $HC^{\wedge}N$  ( $C^{\wedge}N =$  ppy, 2-(2,4-difluorophenyl)pyridine (4,6-dfppy), 2-benzo[b]thiophen-2-yl-pyridine (btp), and 1-phenylisoquinoline (piq)} under the conditions of Ref. [3] are, in fact, mononuclear species of the type  $Pt(C^{\wedge}N)(HC^{\wedge}N)(Cl)$ .

## 2. Experimental

### 2.1. General

$K_2PtCl_4$  (Strem) and Hppy and 2-ethoxyethanol (Aldrich) were used without further purification. H-4,6-dfppy, Hbtp, and Hpiq were prepared via the Suzuki coupling reactions of commercial available boronic acids with 2-bromopyridine or 1-chloroisoquinoline.

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## 2.2. *Pt(ppy)(Hppy)(Cl)* (**1**)

$K_2PtCl_4$  (3.0 g, 7.2 mmol) and 2-phenylpyridine (2.80 g, 18.1 mmol) in a 3:1 (v/v) mixture of 2-ethoxyethanol (75 mL) and  $H_2O$  (25 mL) were heated at 80 °C for 16 h under nitrogen atmosphere. The reaction mixture was allowed to cool down to room temperature and concentrated under reduced pressure.  $Et_2O$  was added to the resulting residue and a yellow solid was formed. The solid was collected by vacuum filtration. The solid was dissolved in  $CH_2Cl_2$  and washed with  $H_2O$ . The organic solvent was removed under reduced pressure. The residue was re-dissolved in minimal amount of  $CH_2Cl_2$  and MeOH (~50 times in volume) was added. The mixture was stirred at room temperature overnight. A yellow solid was collected by vacuum filtration and washed with MeOH. The product was dried under vacuum to give a bright yellow solid (3.04 g, 77.3%), data for which were consistent with the literature [7–9].

## 2.3. *Pt(4,6-dfppy)(H-4',6'-dfppy)(Cl)* (**2**)

$K_2PtCl_4$  (2.0 g, 4.8 mmol) and 2-(2,4-difluorophenyl)pyridine (2.54 g, 12.0 mmol) in a 3:1 (v/v) mixture of 2-ethoxyethanol (54 mL) and  $H_2O$  (18 mL) were heated at 80 °C for 16 h under  $N_2$  atmosphere. The reaction mixture was allowed to cool down to room temperature and concentrated under reduced pressure.  $H_2O$  was added and the resulting yellow precipitate was collected by vacuum filtration and washed with  $H_2O$  and hexanes to give a yellow solid (2.57 g, 87%).  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$ ): 9.60 (d,  $J = 5.8$  Hz, 1H), 9.19 (d,  $J = 5.2$  Hz, 1H), 8.41 (dd,  $J = 14.8, 8.5$  Hz, 1H), 7.96 (t,  $J = 7.7$  Hz, 1H), 7.89 (d,  $J = 8.2$  Hz, 1H), 7.77 (t,  $J = 7.7$  Hz, 1H), 7.65 (d,  $J = 8.0$  Hz, 1H), 7.44 (t,  $J = 6.0$  Hz, 1H), 7.09 (t,  $J = 6.0$  Hz, 1H), 6.87 (m, 1H), 6.73 (m, 1H), 6.47 (m, 1H), 5.62 (d,  $J = 8.8$  Hz, 1H). HRMS-FAB ( $m/z$ ):  $[M]^+$ , calc. for  $C_{22}H_{13}ClN_2PtF_4$ , 610.03302; found, 610.03414. Anal. Calc. for  $C_{22}H_{13}ClN_2PtF_4$ : C, 43.18; H, 2.14; N, 4.58. Found: C, 43.20; H, 2.20; N, 4.51%.

## 2.4. *Pt(btp)(Hbtp)(Cl)* (**3**)

$K_2PtCl_4$  (2.0 g, 4.8 mmol) and 2-benzo[b]thiophen-2-yl-pyridine (2.3 g, 12.0 mmol) in a 3:1 (v/v) mixture of 2-ethoxyethanol (54 mL) and  $H_2O$  (18 mL) were heated at 80 °C for 16 h under  $N_2$  atmosphere. The reaction was allowed to cool down to room temperature and concentrated under reduced pressure.  $H_2O$  was added and the resulting brown precipitate was collected by vacuum filtration, and washed with  $H_2O$ , methanol, and hexanes to give a brown solid (3.0 g, 95.4%).  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$ ): 9.56 (br s, 1H), 9.36 (br s, 1H),

7.15–8.14 (m, 12H), 6.98 (br s, 1H), 6.88 (br s, 1H), 6.11 (d,  $J = 6.6$  Hz, 1H). HRMS-ESI ( $m/z$ ):  $[M - Cl]^+$  calcd for  $C_{26}H_{17}N_2S_2Pt$ , 616.04755; found, 616.0526. Anal. Calc. for  $C_{26}H_{17}ClN_2PtS_2$ : C, 47.89; H, 2.63; N, 4.30. Found: C, 48.03; H, 2.55; N, 4.16%.

## 2.5. *Pt(piq)(Hpiq)(Cl)* (**4**)

$K_2PtCl_4$  (1.67 g, 4.0 mmol) and 1-phenyl-isoquinoline (2.06 g, 10.0 mmol) in a 3:1 (v/v) mixture of 2-ethoxyethanol (51 mL) and  $H_2O$  (17 mL) were heated at 80 °C for 16 h under  $N_2$  atmosphere. The reaction was allowed to cool down to room temperature and concentrated under reduced pressure. The resulting orange brown precipitate was collected by vacuum filtration and washed with  $H_2O$  and hexanes to give an orange-brown solid (2.20 g, 85.6%). The analytically pure product was recrystallized from  $CH_2Cl_2$ .  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 9.53 (d,  $J = 6.3$  Hz, 1H), 9.03 (d,  $J = 6.3$  Hz, 1H), 8.72 (d,  $J = 8.5$  Hz, 1H), 8.15–8.19 (m, 1H), 7.97 (d,  $J = 8.2$  Hz, 1H), 7.91–7.94 (m, 1H), 7.66–7.85 (m, 5H), 7.54–7.62 (m, 2H), 7.43–7.51 (m, 2H), 7.31–7.38 (m, 2H), 7.19–7.25 (m, 1H), 7.03–7.09 (m, 1H), 6.87 (td,  $J = 7.7, 1.4$  Hz, 1H), 6.37 (dd,  $J = 7.7, 1.1$  Hz, 1H). HRMS-ESI ( $m/z$ ):  $[M - Cl]^+$  calcd for  $C_{30}H_{21}N_2Pt$ , 604.13471; found, 604.1371. Anal. Calc. for  $C_{30}H_{21}ClN_2Pt$ : C, 56.30; H, 3.31; N, 4.38. Found: C, 56.27; H, 3.33; N, 4.34%.

## 2.6. *Pt(piq)(acac)*

A mixture of **4** (1.0 g, 1.6 mmol), 2,4-pentanedione (0.34 g, 3.4 mmol), and  $Na_2CO_3$  (1.65 g, 15.6 mmol) in 20 mL of 2-ethoxyethanol was heated at 100 °C overnight under  $N_2$  atmosphere. The reaction was allowed to cool down to room temperature and  $H_2O$  was added. The mixture was extracted with  $CH_2Cl_2$ . The organic layer was washed with  $H_2O$  and dried over anhydrous  $MgSO_4$ . The organic solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane as eluting solvent) to give an orange brown solid (0.50 g, 64.2%).  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$ ): 8.93 (d,  $J = 6.6$  Hz, 1H), 8.85 (d,  $J = 8.5$  Hz, 1H), 8.07 (dd,  $J = 8.0, 1.4$  Hz, 1H), 7.59–7.82 (m, 4H), 7.40 (d,  $J = 6.3$  Hz, 1H), 7.23 (td,  $J = 7.1, 1.4$  Hz, 1H), 7.15 (td,  $J = 7.1, 1.4$  Hz, 1H), 5.47 (s, 1H), 2.010 (s, 3H), 2.005 (s, 3H).  $^{13}C\{^1H\}$  NMR (75 MHz,  $CDCl_3$ ,  $\delta$ ): 185.76, 184.00, 168.44, 146.09, 141.43, 139.10, 137.25, 131.01, 130.45, 129.25, 128.41, 128.09, 127.36, 126.10, 125.80, 123.14, 119.44, 102.49, 28.43, 27.26. HRMS-EI ( $m/z$ ):  $[M]^+$  calcd for  $C_{20}H_{17}NO_2Pt$ , 498.09071; found, 498.09022. Anal. Calc. for  $C_{20}H_{17}NO_2Pt$ : C, 48.19; H, 3.44; N, 2.81. Found: C, 48.13; H, 3.36; N, 2.71%. *Pt(ppy)(acac)* (0.35 g, 84.3%) was obtained from **1** under analogous conditions.

### 2.7. Crystallography

We studied a red prism ( $0.15 \times 0.10 \times 0.10$  mm) of **4** ( $C_{30}H_{21}N_2ClPt$ , fw = 640.03) which was obtained by recrystallization from  $CH_2Cl_2/MeOH$  using a SMART 1000 CCD diffractometer ( $\lambda(Mo\ K\alpha) = 0.71073$  Å, graphite monochromator,  $\omega$ -scans) at 120 K. The crystal was found to belong to the triclinic space group  $P\bar{1}$ , with  $a = 10.1817(17)$  Å,  $b = 10.2249(17)$  Å,  $c = 12.054(2)$  Å,  $\alpha = 89.539(3)^\circ$ ,  $\beta = 71.474(3)^\circ$ ,  $\gamma = 72.195(3)^\circ$ ,  $V = 1127.4(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{calc} = 1.885$  g cm<sup>-3</sup>,  $F(000) = 620$ , and  $\mu = 6.365$  mm<sup>-1</sup>. Data (10,992 reflections, 5317 independent reflections,  $R_{int} = 0.0286$ ) were collected in the  $\theta$  range  $1.79$ – $28.00^\circ$  ( $-13 \leq h \leq 13$ ,  $-13 \leq k \leq 13$ ,  $-15 \leq l \leq 15$ ). Refinement (307 parameters) converged to give  $GOF(F^2) = 0.995$ ,  $R_1(F) = 0.0310$  (for 4560 data with  $I > 2\sigma(I)$ ), and  $wR_2(F^2) = 0.0724$  (all data), with residual electron density maxima and minima of 1.519 and  $-1.016$  e Å<sup>-3</sup>, respectively. SAINT Plus [10], SADABS [11], and SHELXTL-97 [12] software packages were used.

### 3. Results and discussion

The reaction of  $K_2PtCl_4$  with Hppy, H-4,6-dfppy, Hbtp, and Hpiq in 1:2.5 mole ratio in 3:1 (v/v) 2-ethoxyethanol/ $H_2O$  at  $80^\circ C$  for 16 h gives products **1–4**, respectively (Fig. 1) in high yield. NMR data, high-resolution mass spectrometry, elemental analysis, and the crystal structure determination of **4** indicate that these species have the general formula  $Pt(C^{\wedge}N)(HC^{\wedge}N)(Cl)$ . **2–4** are new compounds (although the products of the reaction of H-4,6-dfppy and Hbtp with  $K_2PtCl_4$  under conditions identical to ours have previously been reported, without characterizing data, to be  $[Pt(C^{\wedge}N)(\mu-Cl)]_2$  dimers [3], as has the product of Hppy and  $K_2PtCl_4$ ). **1** has previously been characterized as a significant side-product of the reaction of 1:1  $K_2PtCl_4$  and Hppy (1:1 dioxane/water; 72 h at room temperature; 72 h at reflux) to give  $[Pt(ppy)(\mu-Cl)]_2$  [7]; it has also been obtained in 59% yield from the reaction of  $Pt(COD)Cl_2$  with excess Hppy in the presence of NaOAc in 95% ethanol [8], in 40% yield from the reaction of  $[Et_4N]^+[Pt(NH_3)Cl_3]^-$  and Hppy in water [5], and

as a minor side-product in a synthesis of  $[Bu_4N]^+[Pt(ppy)Cl_2]^-$  [9].

Complexes **1–4** can be used as starting materials for  $Pt(C^{\wedge}N)(O^{\wedge}O)$  species (as can the species claimed as  $[Pt(C^{\wedge}N)(\mu-Cl)]_2$  in reference 3).  $Pt(ppy)(acac)$  is obtained in 84% yield from **1** using a modification of the conditions reported in reference 3, and the new compound  $Pt(piq)(acac)$  is obtained in 64% yield from **4**.

An X-ray structure of **4** (Fig. 2) provides further support for its formulation as  $Pt(C^{\wedge}N)(HC^{\wedge}N)(Cl)$ . The bond lengths and angles around the platinum atom are similar to those in the structure of **1** [5a,9]; the Pt–Cl bonds are significantly elongated as a consequence of the *trans* effect of the C(1) atom. The chelating piq ligand in **4** is less planar (mean deviation 0.189 Å) than the ppy ligand of **1**, presumably due to steric repulsion between the closest hydrogen atoms (attached to C(5) and C(9)). The shortest intermolecular contacts are

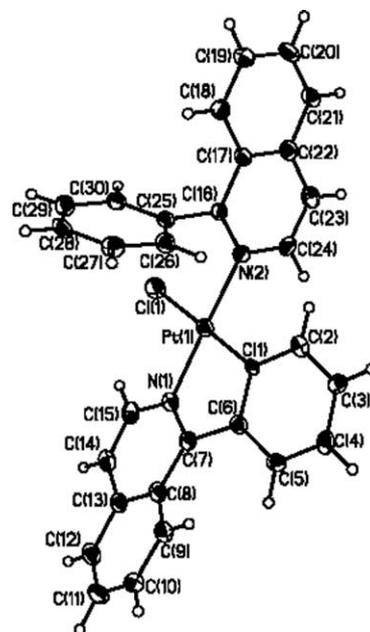


Fig. 2. ORTEP view (50%) of **4**. Selected parameters (Å, °): Pt(1)–C(1) 2.001(4), Pt(1)–N(1) 2.025(4), Pt(1)–N(2) 2.026(4), Pt(1)–Cl(1) 2.4084(12), C(1)–Pt(1)–N(2) 95.94(15), N(1)–Pt(1)–N(2) 177.01(14), C(1)–Pt(1)–Cl(1) 175.23(12), N(1)–Pt(1)–Cl(1) 96.91(11), N(2)–Pt(1)–Cl(1) 86.00(10).

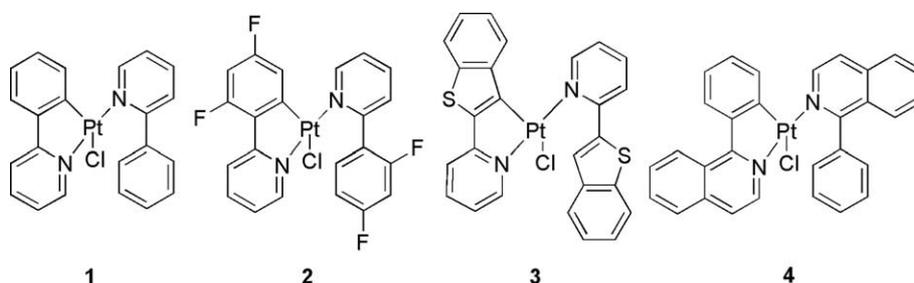


Fig. 1. Structures of complexes **1–4**.

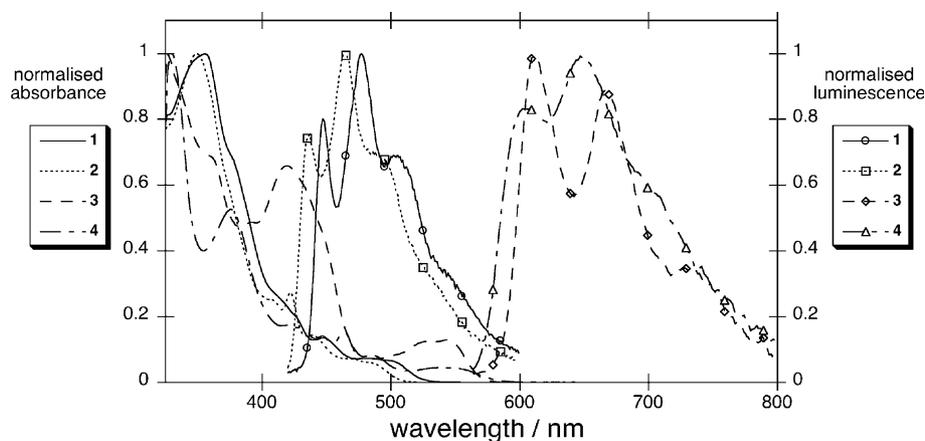


Fig. 3. Comparison of UV-vis. absorption and luminescence spectra for **1–4** in  $\text{CH}_2\text{Cl}_2$ .

3.301(6) Å (C(12)–C(15)) and 3.192(6) Å (C(4)–C(15)). There are also weak intermolecular C–H... $\pi$  interactions (2.47 Å between H(28a) and the centroid of the C(1)–C(6) ring).

We have also recorded UV-vis. absorption and luminescence spectra for **1–4**; these are compared in Fig. 3.

#### 4. Supplementary information

Crystallographic data for **4** have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 269303 for complex **4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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