## New N<sup>C</sup>N-coordinated Pd(II) and Pt(II) complexes of a tridentate N-heterocyclic carbene ligand featuring a 6-membered central ring: synthesis, structures and luminescence

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## **Supplementary Information**

## **Experimental section**

**General experimental methods:** All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Diethyl ether was distilled from sodium–benzophenone and CH<sub>3</sub>CN was distilled from CaH<sub>2</sub>. <sup>1</sup>H NMR spectra were recorded at 400.13 MHz and <sup>13</sup>C NMR spectra were recorded at 100.61 MHz in CD<sub>3</sub>CN. Proligand N,N'-bis(2-pyridyl)-tetrahydropyrimidinium hexafluorophosphate L·HPF<sub>6</sub> (1) was prepared according to a slightly modified procedure described in the literature. Other reagents were obtained from commercial suppliers and used as received. Infra-red spectra were measured using Tensor 27 (ATR diamond) Bruker spectrometer. IR data are reported in cm<sup>-1</sup> of characteristic bands. Samples for elemental analyses were prepared by recrystallization by slow diffusion of diethylether into acetonitrile solutions of compounds 2a and 2b, the obtained crystals were then dried overnight under high vacuum and sent to the "centre de microanalyse" at Gif-sur-Yvette (CNRS).

UV-visible absorption spectra were recorded for solutions in dichloromethane contained within 1 cm pathlength quartz cuvettes using a Biotek Instruments XS spectrometer. Luminescence spectra were recorded using a FluoroMax-2 spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier tube. Samples for low-temperature measurements were contained within 4 mm o.d. tubes held within a quartz Dewar. Spectra were corrected for the wavelength dependence of the detector and emission grating. The luminescence lifetimes of the Pt(II) complex in the solid at 298 K and in butyronitrile at 77 K were measured by time-correlated single-photon counting (TCSPC), following excitation with a laser diode at 405 nm. The longer lifetime of the Pd(II) complex in butyronitrile at 77 K was obtained by multichannel scaling, following excitation with a microsecond pulsed xenon flashlamp. In both cases, the emitted light was detected at 90° using a Peltier-cooled R928 photomultiplier tube after passage through a monochromator.

Synthesis of complex [Pd(N^C^N)Cl][PF<sub>6</sub>] (2a): Na<sub>2</sub>PdCl<sub>4</sub> (63 mg; 0.182 mmol) and the proligand L·HPF<sub>6</sub> (1) (70 mg; 0.182 mmol) in a mixture of methanol (25 mL) and water (5 mL) were stirred at reflux temperature with the exclusion of light for 24 hours. Then the solvent volume was reduced to approximately 10 mL under vacuum, this caused precipitation of beige microcrystalline solid, which was filtered through a sintered glass and washed with two more portions of water (10 mL each). The microcrystalline solid was then dissolved in acetonitrile and recrystallized by slow addition of diethyl ether (20 mg; 0.035 mmol). Yield: 19%. Anal. calcd. (%) for C<sub>14</sub>H<sub>14</sub>ClF<sub>6</sub>N<sub>4</sub>PPd (525,13 g.mol<sup>-1</sup>): C 32.02, H 2.69; N 10.67; found: C 32.43, H 2.35; N 10.43. <sup>1</sup>H NMR (400.13 MHz, CD<sub>3</sub>CN):  $\delta$  = 8.56 (d, 2H, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz, H<sub>a</sub>, *py*), 8,18 ddd, 2H, <sup>3</sup>J<sub>H-H</sub> = 12.0 Hz, <sup>3</sup>J<sub>H-H</sub> = 4.0 Hz, H<sub>β</sub>, *py*, H<sub>a</sub>  $\Box$   $\Box$  7,40 (ddd, 2H, <sup>3</sup>J<sub>H-H</sub> = 12.0 Hz, <sup>3</sup>J<sub>H-H</sub> = 4.0 Hz, H<sub>β</sub>, *py*, H<sub>a</sub>  $\Box$   $\Box$  7,40 (ddd, 2H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, -*CH*<sub>2</sub>) ppm. <sup>13</sup>C {<sup>1</sup>H} NMR (75.45 MHz, CD<sub>3</sub>CN):  $\delta$  = 19.6 (-*CH*<sub>2</sub>), 42.9 (-N*CH*<sub>2</sub>), 113.5 (*Py*), 123.9 (*Py*), 144.7 (*Py*) 151.4 (*Py*) ppm. IR (ATR): v = 3055, 1641, 1607, 1576, 1438, 1446, 1273, 1217, 1069, 1028, 1167, 822, 752, 694, 635, 515, 325, 270, 222, 206 cm<sup>-1</sup>.

## Synthesis of complex [Pt(N^CN^)Cl][PF<sub>6</sub>] (2b):

This compound was prepared using the procedure for **2a** using  $K_2PtCl_4$  (125 mg; 0.301 mmol) instead of  $Na_2PdCl_4$  and the proligand (113 mg; 0.290 mmol). **2b** was obtained as a yellow/orange microcrystalline acetonitrile solvate solid (27 mg; 0.035 mmol). Yield: 15%. Anal. calcd. (%) for  $C_{14}H_{14}ClF_6N_4PPt \cdot CH_3CN$  (654,85 g.mol<sup>-1</sup>): C 29.35, H 2.62; N 10.69; found: C 29.44, H 3.13; N 10.20.

<sup>1</sup>H NMR (400.13 MHz, CD<sub>3</sub>CN):  $\delta = 8.72$  (d, 2 H,  ${}^{3}J_{\text{H-H}} = 8.0$  Hz,  ${}^{3}J_{\text{H-Pt}} \approx 50$  Hz *py*, H<sub> $\alpha$ </sub>), 8,21  $\Box$ ddd, 2H,  ${}^{3}J_{\text{H-H}} = 11.0$  Hz,  ${}^{3}J_{\text{H-H}} = 5.0$  Hz, *py*, H<sub> $\beta$ </sub> $\Box \Box 7,44$  (ddd, 2H,  ${}^{3}J_{\text{H-H}} = 8.0$  Hz,  ${}^{3}J_{\text{H-H}} = 4.0$  Hz, *py*, H<sub> $\gamma$ </sub>) 7,34  $\Box$ d, 2H,  ${}^{3}J_{\text{H-H}} = 8.0$  Hz, *py*, H<sub> $\beta$ </sub> $\Box \Box 3,76$   $\Box$ t, 4H,  ${}^{3}J_{\text{H-H}} = 8.0$  Hz, N-*CH*<sub>2</sub> $\Box$ , 2,48 (q, 2H,  ${}^{3}J_{\text{H-H}} = 8.0$  Hz, *-CH*<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75.45 MHz, CD<sub>3</sub>CN):  $\delta = 19.9$  (*-CH*<sub>2</sub>), 42.2 (-N*CH*<sub>2</sub>), 113.7 (*Py*), 123.6 (*Py*), 144.9 (*Py*) 150.7 (*Py*) ppm. IR (ATR): v = 3055, 1641, 1607, 1576, 1438, 1446, 1273, 1217, 1069, 1028, 1167, 822, 752, 694, 635, 515, 325, 270, 222, 206 cm<sup>-1</sup>.



Figure S1: <sup>1</sup>H NMR of the proligand N,N'-bis(2-pyridyl)-tetrahydropyrimidinium hexafluorophosphate  $L \cdot HPF_6$  (1) in CD<sub>3</sub>CN.



Figure S2: <sup>1</sup>H NMR of complex [Pd(N^C^N)Cl][PF<sub>6</sub>] (2a) in CD<sub>3</sub>CN.





**Figure S4:** <sup>1</sup>H NMR of complex [Pt(N^C^N)Cl][PF<sub>6</sub>] (**2b**) in CD<sub>3</sub>CN.



Figure S5: <sup>13</sup>C NMR of complex [PtLCl][PF<sub>6</sub>] (2b) in CD<sub>3</sub>CN.



**Figure S6:** UV-visible absorption spectra of proligand **1** (black line) and its Pd(II) (**2a**, red line) and Pt(II) (**2b**, blue line) complexes in acetonitrile at 298 K. The dashed line shows the low-energy part of the spectrum of **2b** on an arbitrarily expanded *y*-scale to highlight the weaker low-energy bands observed for this complex.



**Figure S7:** Photograph of a solid sample of complex [PtLCl][PF<sub>6</sub>] (**2b**) under ambient light (a) and under UV irradiation ( $\lambda_{exc} = 365$  nm) in the dark (b).