

## **2-(2'-pyridyl)-4,6-diphenylphosphinine *versus* 2-(2'-pyridyl)-4,6-diphenylpyridine: An evaluation of their coordination chemistry towards Rh(I)**

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**Supplementary Material**

### General Remarks:

All manipulations were carried out under an argon atmosphere, using modified Schlenk techniques or in a MBraun dry box unless otherwise stated. All glassware was dried prior to use by heating under vacuum. All common solvents and chemicals were commercially available.  $[\text{Rh}(\text{cod})_2]\text{BF}_4$  and  $\text{NH}_3$  were purchased from STREM and Linde, respectively. 2-(2'-pyridyl)-4,6-diphenylphosphinine (**1**) was prepared according to the literature.<sup>[1]</sup> The solvents were taken from custom-made solvent purification columns filled with  $\text{Al}_2\text{O}_3$ . The elemental analyses were performed on a Perkin Elmer 2400, Series II CHNSO Analyzer within the Department of Chemical Engineering and Chemistry (TU/e). MALDI-TOF MS spectra were obtained using a Voyager-DE<sup>TM</sup> PRO Bio spectrometry<sup>TM</sup> Workstation (Applied Biosystems) time-of-flight mass spectrometer reflector.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra were recorded on a Varian Mercury 200 or 400 spectrometer and all chemical shifts are reported relative to the residual proton resonance in the deuterated solvents or referred to an 85% aqueous solution of  $\text{H}_3\text{PO}_4$ , respectively.

**Synthesis of 2-(2'-pyridyl)-4,6-diphenylpyridine (2):** Ligand **2** was prepared according to a modified literature-procedure. 2-(2'-pyridyl)-4,6-diphenylpyrylium tetrafluoroborate<sup>[1]</sup> (1.2 g, 3.0 mmol) was suspended in Me-THF (20 mL) and heated to  $T = 60^\circ\text{C}$ . A light stream of  $\text{NH}_3$  was bubbled through the reaction mixture for  $t = 30$  min and a yellow-orange suspension was formed. The solid was filtered off and MeOH (20 mL) was added to the yellow filtrate. An off-white solid was formed immediately, which was filtered off, washed with MeOH and dried under vacuum. Yield: 0.8 g (2.6 mmol, 87%). The analytical data of **2** are identical with those reported in literature.<sup>[2]</sup>

**Synthesis of  $[\text{Rh}(\text{cod})(\mathbf{1})]\text{BF}_4$  (3):**  $[\text{Rh}(\text{cod})_2]\text{BF}_4$  (37.3 mg, 0.092 mmol) and 2-(2'-pyridyl)-4,6-diphenylphosphinine (**1**) (30 mg, 0.092 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (2.0 mL). The dark red solution was stirred for 1h. Subsequently,  $\text{Et}_2\text{O}$  (6.0 mL) was added until a solid precipitated. The solution was decanted and the solid was dried under vacuum. Complex **3** was obtained as an orange-brown powder (37.6 mg, 0.06 mmol, 66%). Orange crystals of **3** suitable for X-ray diffraction and elemental analysis were obtained by slow crystallization from a mixture of  $[\text{Rh}(\text{cod})_2]\text{BF}_4$  (25 mg, 0.0615 mmol) and **1** (20 mg, 0.0615 mmol) in THF/ $\text{CH}_2\text{Cl}_2$  (2.0 mL) after filtration over Celite.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 2.26 (m, 4H,  $(\text{CH}_2)_{\text{COD}}$ ), 2.55 (m, 4H,  $(\text{CH}_2)_{\text{COD}}$ ), 5.31 (m, 4H,  $(\text{CH})_{\text{COD}}$ ), 7.50-7.70 (m, 10H), 7.74 (d, 2H,  $J_{\text{H-H}} = 8$  Hz), 8.17 (m, 2H), 8.26 (d, 1H,  $J_{\text{H-H}} = 8$  Hz), 8.57 (dd, 1H,  $J_{\text{H-P}} = 16$  Hz,

$J_{H-H} = 4$  Hz);  $^{19}\text{F}$  NMR (376.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -149.7;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 175.5 (d,  $J_{P-Rh} = 188.6$  Hz).  $^{13}\text{C}$  NMR (50.3 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 29.7 ( $(\text{CH}_2)_{\text{cod}}$ ), 107.5, 107.6 ( $(\text{CH})_{\text{cod}}$ ), 120.8 (d,  $J = 13.5$  Hz), 126.9, 127.6, 127.7, 127.9, 128.7, 129.3, 129.4, 129.6, 131.8 (d,  $J = 13.0$  Hz), 139.0 (m), 140.4, 141.5, 143.4, 151.7, 158.2 (m). MALDI-TOF (m/z): 575 [ $\text{M}^+ - \text{BF}_4 + \text{K}$ ], 536 [ $\text{M}^+ - \text{BF}_4$ ]. Anal. Calcd for  $\text{C}_{30}\text{H}_{28}\text{BF}_4\text{NPRh}$  ( $M = 623.24$  g/mol): C: 57.82; H: 4.53; N: 2.25. Found: C: 57.43; H: 4.48. N: 2.18.

**Synthesis of  $[\text{Rh}(\text{cod})_2]\text{BF}_4$  (**4**):**  $[\text{Rh}(\text{cod})_2]\text{BF}_4$  (26.3 mg, 0.065 mmol) and 2-(2'-pyridyl)-4,6-diphenylpyridine (**2**) (20 mg, 0.065 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (1.0 mL). The orange-red solution was stirred for 1h. Subsequently,  $\text{Et}_2\text{O}$  (5 mL) was added until a yellow solid precipitated. The solution was decanted and the solid was dried under vacuum. Complex **4** was obtained as an orange powder (37.6 mg, 0.06 mmol, 66%). Orange crystals of **4** suitable for X-ray diffraction and elemental analysis were obtained by slow diffusion of pentane into a mixture of  $[\text{Rh}(\text{cod})_2]\text{BF}_4$  (26.3 mg, 0.065 mmol) and **2** (20 mg, 0.065 mmol) in THF/ $\text{CH}_2\text{Cl}_2$  (2.0 mL) after filtration over Celite.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm) = 1.82 (d, b,  $J_{H-H} = 7.2$  Hz, 4H,  $(\text{CH}_2)_{\text{COD}}$ ), 2.27 (b, 4H,  $(\text{CH}_2)_{\text{COD}}$ ), 3.79 (b, 4H,  $(\text{CH})_{\text{COD}}$ ), 7.63 (m, 6H), 7.79 (m, 2H), 7.88 (s, 1H, cent. pyridine- $\text{H}_\beta$ ), 7.93 (m, 4H), 8.26 (t,  $J_{H-H} = 7.6$  Hz, 1H), 8.48 (d,  $J_{H-H} = 8.2$  Hz, 1H), 8.53 (s, 1H, cent. pyridine- $\text{H}_\beta$ ).  $^{19}\text{F}$  NMR ( $\text{CD}_2\text{Cl}_2$ ),  $\delta$  (ppm) = -152.6.  $^{13}\text{C}$  NMR (50.3 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 29.7, 29.9 ( $(\text{CH}_2)_{\text{cod}}$ ), 84.6 (m,  $(\text{CH})_{\text{cod}}$ ), 118.8, 124.1, 126.8, 127.4, 128.6, 128.9, 129.2, 129.7, 130.9, 131.2, 135.4, 138.4, 140.7, 148.2, 153.3, 156.4, 164.2. Anal. Calcd for  $\text{C}_{30}\text{H}_{28}\text{BF}_4\text{N}_2\text{Rh}$  ( $M = 606.27$  g/mol): C: 59.43; H: 4.66; N: 4.62. Found: C: 59.24; H: 4.48. N: 4.38.

### X-ray crystal structure determinations

X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator,  $\lambda = 0.71073$  Å) at a temperature of 150(2) K. Data were integrated with the HKL2000<sup>[3]</sup> (compound **3**) or EVAL15<sup>[4]</sup> software (compound **4**) and corrected for absorption using SADABS<sup>[5]</sup>. The structures were solved with Direct Methods using the programs SIR-97<sup>[6]</sup> (compound **3**) and SHELXS-97<sup>[7]</sup> (compound **4**). Least-squares refinement was performed with SHELXL-97<sup>[7]</sup> on  $F^2$  of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference-Fourier maps. Hydrogen atoms at the double bonds of the *cod* ligands were refined freely with isotropic displacement parameters; all other hydrogen atoms were refined as rigid groups. Drawings, structure calculations and checking for higher symmetry were performed

with the PLATON software<sup>[8]</sup>.

**Compound 3:** [C<sub>30</sub>H<sub>28</sub>NPRh]BF<sub>4</sub> · 0.4(CH<sub>2</sub>Cl<sub>2</sub>), Fw = 657.19, orange plate, 0.21x0.12x0.02 mm<sup>3</sup>, triclinic, P  $\bar{1}$  (no. 2), a = 9.7987(2), b = 10.3575(2), c = 14.5382(3) Å, α = 84.8750(6), β = 85.4051(6), γ = 71.0572(8)°, V = 1387.95(5) Å<sup>3</sup>, Z = 2, D<sub>calc</sub> = 1.573 g/cm<sup>3</sup>, μ = 0.80 mm<sup>-1</sup>. 21889 Reflections were measured up to a resolution of (sin θ/λ)<sub>max</sub> = 0.65 Å<sup>-1</sup> of which 6367 were unique (R<sub>int</sub> = 0.044) and 5109 observed [I > 2σ(I)]. The CH<sub>2</sub>Cl<sub>2</sub> molecule was located close to an inversion center and refined with partial occupancy. Absorption correction range: 0.88-0.98. 377 Parameters were refined with one restraint. R1/wR2 [I > 2σ(I)]: 0.0396/0.0872, R1/wR2 [all refl.]: 0.0586/0.0949. S = 1.047. Δρ<sub>min/max</sub> = -0.47/1.03 eÅ<sup>3</sup>.

**Compound 4:** [C<sub>39</sub>H<sub>28</sub>N<sub>2</sub>Rh]BF<sub>4</sub>, Fw = 606.26, orange needle, 0.54x0.18x0.06 mm<sup>3</sup>, monoclinic, P2<sub>1</sub>/c (no. 14), a = 7.4699(7), b = 13.7427(12), c = 24.527(2) Å, β = 100.250(5)°, V = 2477.7(4) Å<sup>3</sup>, Z = 4, D<sub>calc</sub> = 1.625 g/cm<sup>3</sup>, μ = 0.74 mm<sup>-1</sup>. 61166 Reflections were measured up to a resolution of (sin θ/λ)<sub>max</sub> = 0.65 Å<sup>-1</sup> of which 5685 were unique (R<sub>int</sub> = 0.034) and 4994 observed [I > 2σ(I)]. Absorption correction range: 0.75-0.98. 359 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0232/0.0550, R1/wR2 [all refl.]: 0.0286/0.0574. S = 1.060. Δρ<sub>min/max</sub> = -0.43/0.75 eÅ<sup>3</sup>.

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