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Supporting information for article:

Studies of κ^2 - and κ^3 -tripyridylamine complexes of ruthenium and π -stacking by pyridyls

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S1. Syntheses

All manipulations, except where noted, were performed under an atmosphere of dry nitrogen. All commercially available reagents were purchased from Aldrich Chemical Company. $[\text{CyRuCl}_2]_2$ was prepared as in the literature. ^1H NMR spectra were recorded on a GE-QE 300 MHz instrument and an Agilent DD2 400 MHz instrument. Elemental Analyses were performed by Atlantic Microlab, Norcross, GA.

S2. Synthesis of tri(2-pyridyl)amine, (2-py)₃N.

The synthesis is adapted from the method of Crabtree and Mosny.(Mosny & Crabtree, 1996) Owing to the extreme toxicity of 2-bromopyridine, all manipulations were performed in a fume hood. Di-(2-pyridyl)amine, (9.03 g, 52.8 mmol), fresh 2-bromopyridine, (25.00 g, 158.2 mmol), copper powder, (0.15 g, 2.4 mmol), potassium bromide, (0.10 g, 0.8 mmol), sodium carbonate, (5.00 g, 60.2 mmol), and 20 mL of dry mesitylene were combined in a 250 mL round-bottomed flask. The flask was purged with nitrogen and was then fitted with a condenser and heated at reflux under nitrogen for 24 hours. The reaction mixture was then cooled, and 100 mL of methylene chloride was added, whereupon most of the solid found at the end of the heating dissolved. The mixture was then filtered through a short column of silica and eluted with ethyl acetate. The volatile components of the combined filtrate and eluate were removed on a rotary evaporator. Addition of 50 mL of hexanes to the resulting yellow oil yielded pale yellow crystals, which were then collected by filtration and recrystallized from hot ethanol to give very pale-yellow needles of pure (2-py)₃N. Yield: 7.90 g (31.9 mmol, 61%). The ^1H NMR of this (2-py)₃N matched closely that previously reported by Crabtree and Mosny.(Mosny & Crabtree, 1996)

S3. Preparation of *cis*- $\text{RuCl}_2(\kappa^2\text{-(2-py)}_3\text{N})_2\cdot\text{CHCl}_3$, (**1a**).

In a 250 mL round-bottomed flask fitted with a reflux condenser $[\text{CyRuCl}_2]_2$, (0.172 g, 0.281 mmol), (2-py)₃N, (1.000 g, 4.03 mmol) and a stirring bar were combined. The flask was purged with N₂ before 25 mL of dry diglyme was added via cannula. The mixture was refluxed for 6 hours, during which time a red-brown precipitate was observed to form. The reaction mixture was then cooled and opened to the air. The diglyme was removed by rotary evaporation, and the residue was washed with 3 x 50 mL of heptane. The solid residue of **1** was then recrystallized from CHCl₃/hexane to give **1a** as

red-orange needles. Yield: 0.4099 g, (0.521 mmol, 92%). ^1H NMR (CD_2Cl_2): as per **1b** but with a resonance at 7.33 (s, 1H, CHCl_3). Anal. Calcd. for $\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{N}_8\text{Ru}_1\cdot\text{C}_1\text{H}_1\text{Cl}_3$: C, 47.26; H, 3.20; N, 14.22%. Found: C, 47.26; H, 3.25; N, 14.16%.

S4. Preparation of $\text{cis-RuCl}_2(\kappa^2\text{-(2-py)}_3\text{N})_2\cdot 2\text{CH}_2\text{Cl}_2$, (**1b**).

Recrystallization of **1a** from methylene chloride yielded red-orange plates of **1b**. ^1H NMR (CD_2Cl_2 , 400 MHz), *most resonances have unresolved or barely resolved 3J coupling ~ 1 Hz that are not reported*: δ 9.93 (d, $J = 5.7$ Hz, 2H), 8.20 (d, $J = 6.0$ Hz, 2H), 7.98 (d, $J = 5.0$ Hz, 2H), 7.79 (td, $J = 7.7$ Hz, 2H), 7.62 (d, $J = 7.7$ Hz, 2H), [overlapped 7.34 (t, $J \sim 6.0$ Hz, 2H), 7.32 (dd, $J \sim 8.5, \sim 7.0, 1.8$ Hz, 2H)], 7.18 (d, $J = 7.7$ Hz, 2H), 7.04 (t, $J = 7.7, 1.8$ Hz, 2H), 6.78 (dd, $J = 6.8, 5.0$ Hz, 2H), 6.73 (d, $J = 8.5$ Hz, 2H), 6.29 (dd, $J = 7.0, 6.0$ Hz, 2H), 5.33 (s, 4H CH_2Cl_2), 5.32 (t CDHCl_2). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 159.69, 158.07, 157.01(w), 155.33(w), 155.17(w), 146.99, 137.76, 135.98, 133.81, 124.08, 123.42, 122.00, 121.95, 117.33, 109.37, 54.38, 54.11, 53.84, 53.57, 53.30 (solvent). Crystals of **1b** were shown by X-ray diffraction to contain two methylene chloride solvates per ruthenium complex.

S5. Preparation of $[\text{RuCl}(\kappa^2\text{-(2-py)}_3\text{N})(\kappa^3\text{-(2-py)}_3\text{N})]\text{SbF}_6\cdot\text{CH}_2\text{Cl}_2$, (**2a**).

A 50 mL round-bottomed flask was charged with **1a** (0.0690 g, 0.088 mmol), 30 mL of freshly distilled CH_2Cl_2 and a stirring bar. The flask was purged with nitrogen before a solution of AgSbF_6 (0.0355 g, 0.103 mmol) in CH_2Cl_2 (5.0 mL) was added dropwise to the flask. The mixture was allowed to stir for 30 minutes, then opened to the air and filtered through a Celite plug. The filtrate was reduced in volume by rotary evaporation and the residue was recrystallized from CH_2Cl_2 /heptane to give yellow crystals of (**2a**). Yield: 0.0608 g, (0.064 mmol, 73%). ^1H NMR (CD_2Cl_2) *most resonances have unresolved or barely resolved 3J coupling ~ 1 Hz that are not reported*: δ 8.79 (d, 2H), 8.53 (d, 1H), 8.06 (d, 1H), 8.00-7.80 (m, 10H), 7.63 (d, 1H), 7.35 (m, 2H), 7.25 (dd, 1H), 7.17 (d, 1H), 7.10 (m, 3H), 6.97 (m, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2 , 400 MHz) δ 159.09, 157.68, 157.30, 156.97(2), 156.56, 154.34, 154.10(2), 148.12, 139.29(2), 138.83, 138.17(2), 126.65, 125.91, 125.70(2), 124.79(2), 123.11(2), 123.09(2), 121.10, 117.49, 54.38, 54.11, 53.84, 53.57, 53.30 (solvent) [owing to slow relaxation the intensities are approximate, one additional resonance is superimposed.]

Anal. Calcd. for $\text{C}_{30}\text{H}_{24}\text{Cl}_1\text{F}_6\text{N}_8\text{Ru}_1\text{Sb}_1\cdot\text{C}_1\text{H}_2\text{Cl}_2$: C, 39.04; H, 2.75; N, 11.75%. Found: C, 39.10; H, 2.81; N, 11.59%.

S6. Preparation of [RuCl(κ^2 -(2-py)₃N)(κ^3 -(2-py)₃N)]SbF₆·CHCl₃, (2b).

Recrystallization of **2a** from chloroform yielded **2b** as yellow crystals that diffracted better than those of **2a**.

S7. Preparation of [Ru(κ^3 -(2-py)₃N)₂][SbF₆]₂, (3).

A 50 mL round-bottomed flask was charged with **2a** (0.0820 g, 0.086 mmol), 25 mL of dry CH₂Cl₂ and a stirring bar. The flask was purged with N₂ before a solution of AgSbF₆ (0.040 g, 0.116 mmol) in CH₂Cl₂ (5.0 mL) was added dropwise to the yellow solution. An immediate color change was observed, from yellow to canary yellow, and the formation of a precipitate. The mixture was allowed to stir at room temperature for 15 minutes before the flask was opened to the air and the mixture filtered. The solid collected was washed with 4 x 20 mL of CH₂Cl₂, redissolved in the minimum volume of acetone and filtered through a Celite plug. The filtrate was reduced in volume and the yellow product was recrystallized in acetone/CH₂Cl₂ to give **3** as yellow crystals. Yield: 0.0625 g (0.059 mmol, 68%). ¹H NMR (acetone-d₆, 20°C): δ 8.36 (dd J = 7.6, ~1Hz, 6H); 8.27 (dt J = 7.6, ~1Hz, 6H); 8.03 (dd J = 5.6, ~1Hz, 6H); 7.47 (ddd, J = 7.6, 5.6, ~1 Hz 6H). ¹³C NMR (101 MHz acetone-d₆, 20°C): δ 206.19 solvent, 158.04, 156.14, 141.87, 127.59, 126.85, 29.84 (m) solvent. Anal. Calcd. For C₃₀H₂₄N₈Ru₁Sb₂F₁₂: C, 33.70; H, 2.26; N, 10.43%. Found: C, 33.73; H, 2.29; N, 10.43%.

S8. Preparation of [CyRuCl(κ^2 -(2-py)₃N)]SbF₆, (4).

A 50 mL round-bottomed flask was charged with 0.3146 g (1.27 mmol) of (2-py)₃N, 25 mL of freshly distilled CH₂Cl₂ and a stirring bar. A solution of [CyRuCl₂]₂ (0.1294 g, 0.211 mmol) in CH₂Cl₂ (5.0 mL) was added dropwise with stirring. The reaction was then stirred for a further 18 hours, and to the resulting yellow solution was added heptane, leading to a yellow precipitate. The reaction mixture was centrifuged, and the solids were washed with decanting with heptane (5 x 20 mL). The resulting solid was then dissolved in acetone and stirred with excess NaSbF₆ (0.5000 g, 1.93 mmol) for ten minutes. The acetone was then removed by rotary evaporation, and the residue extracted up in CH₂Cl₂. The mixture was then filtered through a Celite plug and the CH₂Cl₂ was removed by rotary evaporation to give **4**. Yield: 0.3025 g, (0.401 mmol, 95%). The ¹H NMR spectrum (CD₂Cl₂) was identical to that reported by Crabtree and Mosny. (Mosny *et al.*, 1995)

S9. Preparation of Ru(2,2'-bipy)₂Cl₂, 5.

In a 25 mL 3-neck round-bottomed flask, 0.172 g of [CyRuCl₂]₂ (0.281 mmol) and 2,2'-bipy (0.977g, 5.12 mmol) were dissolved in 5 mL diglyme. The flask was purged with N₂ and the initially yellow-orange solution was heated to reflux. After 1 h, the solution had turned deep red-purple and showed some suspended material. After 2.5 h of reflux, the flask was cooled to 80°C, the mixture filtered and the purple solid collected was washed with hexanes (2 x 30 mL), to give **5**. Yield 0.246 g (0.506 mmol, 90.0%). Anal. Calcd. For C₂₀H₁₆Cl₂N₄Ru: C, 49.60; H, 3.33; N, 11.57%. Found: C, 49.28; H, 3.32; N, 11.32%. The UV-Vis, IR and ¹H NMR spectra were all comparable to a commercial sample of *cis*-Ru(2,2'-bipy)₂Cl₂.