Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis, characterization and solution behavior of a systematic series of pentapyridyl-supported Ru^{II} complexes: Comparison to bimetallic analogs

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Modified preparation of **2**. A mixture of Py_5Me_2 (561.7 mg, 1.266 mmol) and $RuCl_3 \cdot 3H_2O$ (351.8 mg, 1.345 mmol) was refluxed in 120 mL of ethanol under N_2 for 24 hours. After cooling the mixture to room temperature, the solvent was removed and water was added to the residue. The mixture was filtered over a fine frit, and to the yellow filtrate was added excess NH_4PF_6. The resulting dark yellow precipitate was collected and washed with water. Yield: 473.8 mg (52%).

Modified preparation of **3**. To 412.7 mg of **1** (0.5692 mmol) in 300 mL of ultrapure water was added excess $AgPF_6$. The mixture was refluxed in air for 3 hours and filtered hot over celite to remove unreacted **1**. The filtrate was concentrated with a rotary evaporator and the crude product was washed with cold water prior to recrystallization in a mixture of water and acetone to give yellow crystals. Yield: 215.5 mg (44%).

Figure S1. NMR spectrum of $[Ru(Py_5Me_2)(N_3)](PF_6)$ (**1**) in CD_3CN.

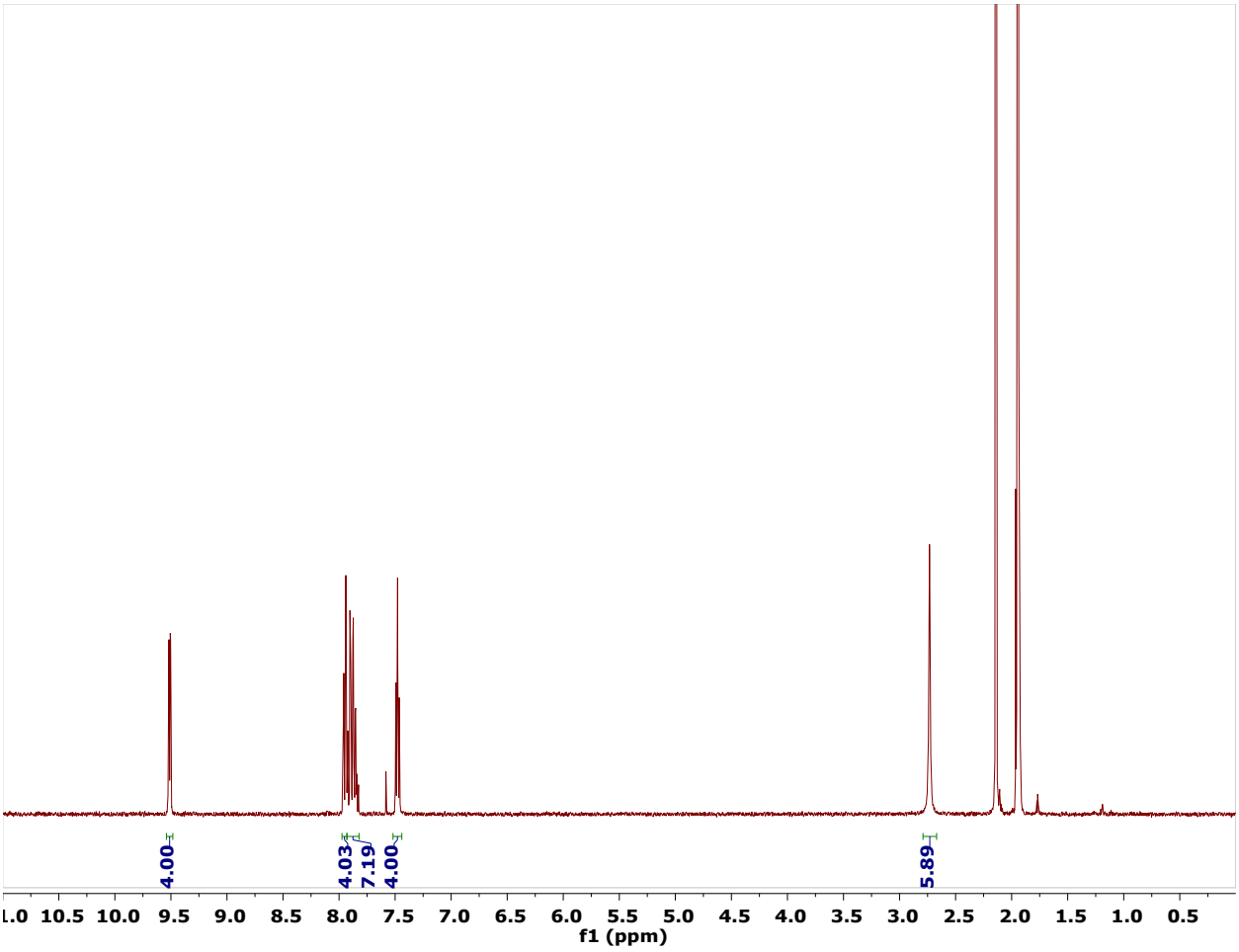


Figure S2. NMR spectrum of $[Ru(Py_5Me_2)(MeCN)](PF_6)_2$ (**4**) in CD_3CN.

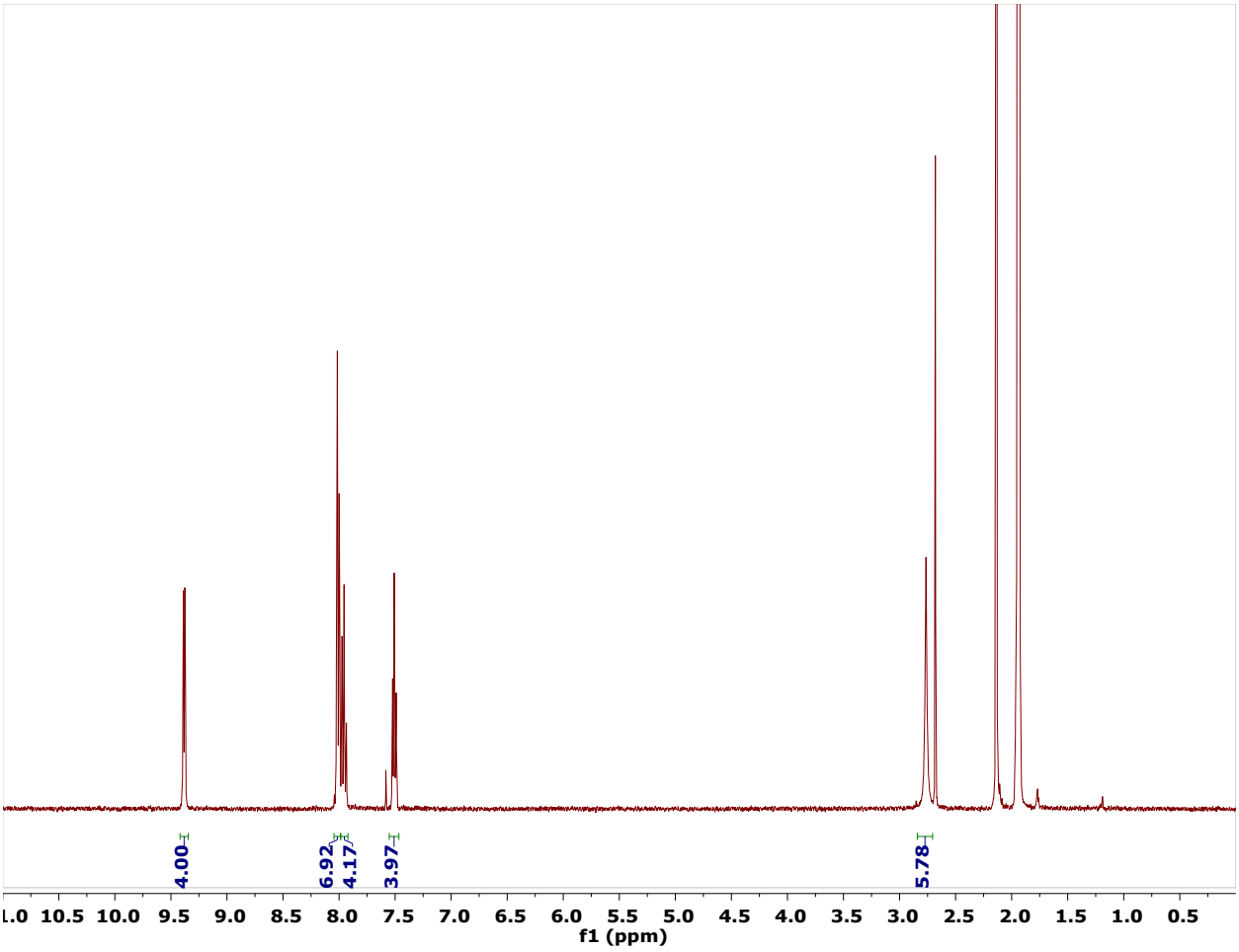
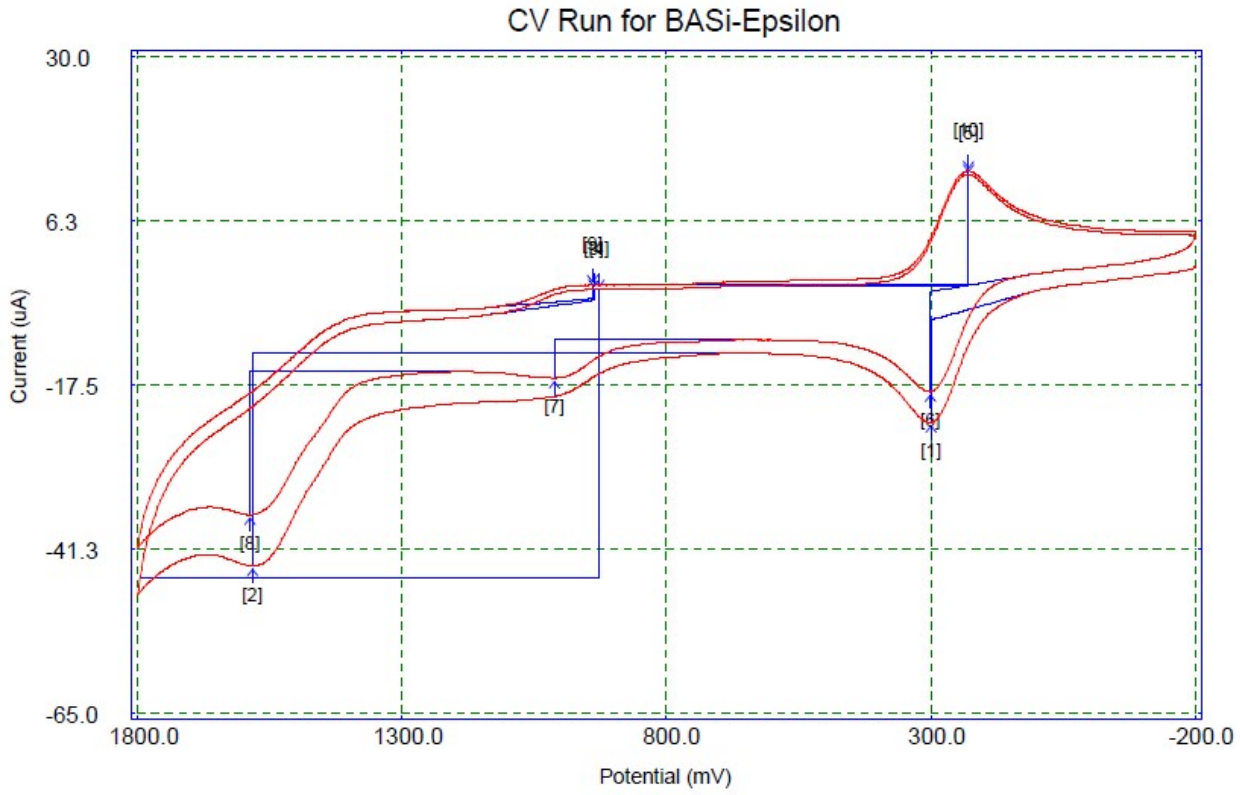


Figure S3. CV raw data for $[Ru(Py_5Me_2)(N_3)](PF_6)$ (**1**) in CH_3CN.



Peak Data:

peak [1] @ 300 [mV], 14.7860 (uA), 9.7211 (uC)

peak [2] @ 1582 [mV], 30.7866 (uA), 75.7944 (uC)

peak [3] @ 937 [mV], 1.4740 (uA), 1.9424 (uC)

peak [4] @ 928 [mV], 41.6449 (uA), 273.5188 (uC)

peak [5] @ 229 [mV], 16.2051 (uA), 11.6376 (uC)

peak [6] @ 301 [mV], 14.4381 (uA), 9.1390 (uC)

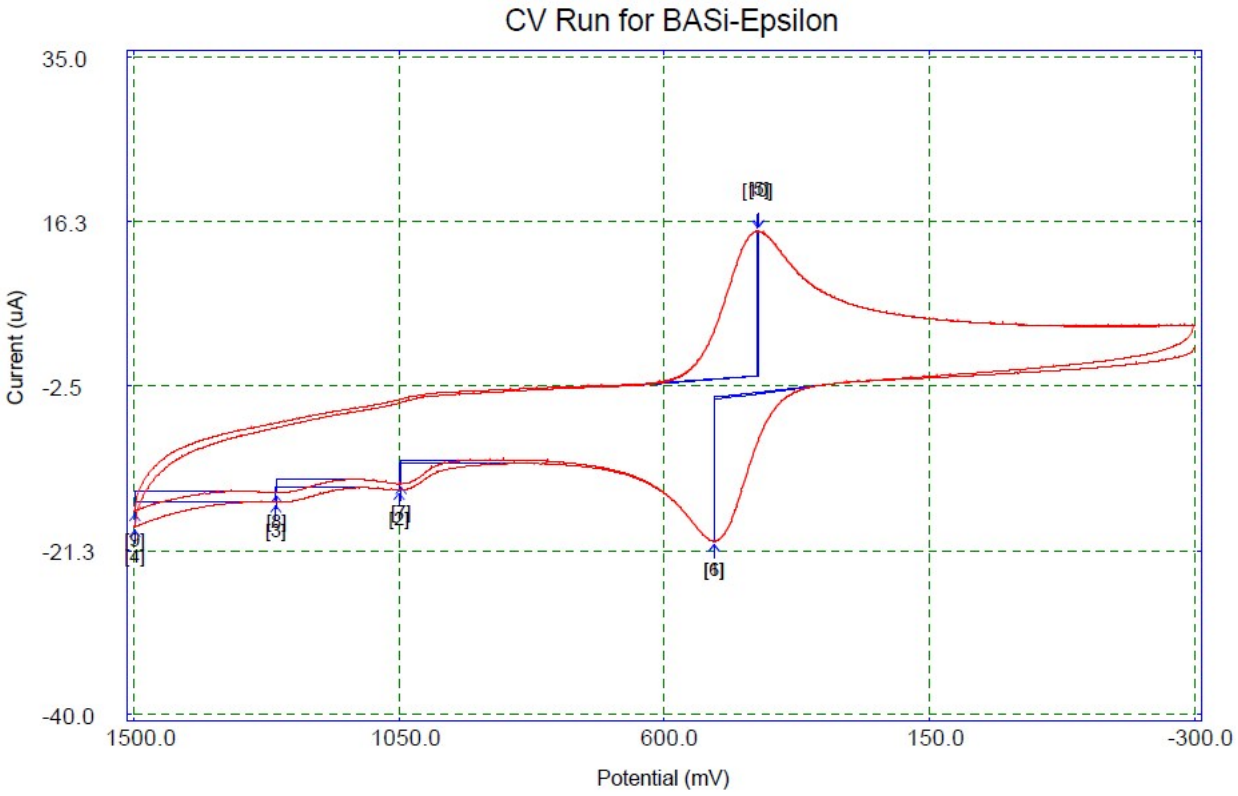
peak [7] @ 1012 [mV], 5.5482 (uA), 5.3944 (uC)

peak [8] @ 1587 [mV], 20.7156 (uA), 25.0665 (uC)

peak [9] @ 940 [mV], 2.0447 (uA), 2.2861 (uC)

peak [10] @ 229 [mV], 16.5133 (uA), 14.0487 (uC)

Figure S4. CV raw data for $[Ru(Py_5Me_2)(Cl)](PF_6)$ (**2**) in CH_3CN.



Peak Data:

peak [1] @ 516 [mV], 16.1440 (uA), 10.3923 (uC)

peak [2] @ 1050 [mV], 3.0030 (uA), 1.8449 (uC)

peak [3] @ 1259 [mV], 1.6815 (uA), 1.1315 (uC)

peak [4] @ 1499 [mV], 2.6276 (uA), 1.7675 (uC)

peak [5] @ 440 [mV], 16.4492 (uA), 10.5065 (uC)

peak [6] @ 515 [mV], 16.4523 (uA), 10.5221 (uC)

peak [7] @ 1047 [mV], 2.7192 (uA), 1.2835 (uC)

peak [8] @ 1258 [mV], 1.4893 (uA), 0.9050 (uC)

peak [9] @ 1499 [mV], 2.1027 (uA), 1.2066 (uC)

peak [10] @ 442 [mV], 16.5286 (uA), 10.7109 (uC)

Crystal Structure Tables

	1	**3**	**4**
Compound	$[Ru(Py_5Me_2)(N_3)](PF_6)$	$[Ru(Py_5Me_2)(OH_2)](PF_6)_2 \cdot 2H_2O$	$[Ru(Py_5Me_2)(MeCN)](PF_6)_2$
Empirical formula	$C_{29}H_{25}F_6N_8PRu$	$C_{29}H_{31}F_{12}N_5O_3P_2Ru$	$C_{31}H_{28}F_{12}N_6P_2Ru$
Formula weight	731.61	888.60	875.60
Temperature/K	100.01	100.0	100.0
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.805(4)	11.563(4)	11.443(4)
b/Å	12.202(4)	12.841(5)	12.524(4)
c/Å	12.256(5)	13.303(5)	13.131(5)
α/°	94.78(1)	82.41(1)	110.34(2)
β/°	99.50(1)	65.52(1)	108.48(1)
γ/°	106.99(2)	64.36(2)	90.75(1)
Volume/Å^3	1369.6(9)	1618(1)	1657(1)
Z	2	2	2
ρ_{calc}g/cm^3	1.774	1.824	1.755
μ/mm^{-1}	0.710	0.695	0.672
F(000)	736.0	892.0	876.0
Crystal size/mm^3	0.22 × 0.05 × 0.05	0.409 × 0.237 × 0.044	0.095 × 0.051 × 0.01
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.402 to 52.808	3.37 to 55.026	3.502 to 52.888
Index ranges	$-12 \le h \le 12$, $-15 \le k \le 15$, $-15 \le l \le 15$	$-14 \le h \le 15$, $-16 \le k \le 16$, $-17 \le l \le 17$	$-14 \le h \le 14$, $-15 \le k \le 15$, $-16 \le l \le 16$
Reflections collected	20179	32212	29045
Independent reflections	5604 [R_{int} = 0.0785, R_{sigma} = 0.0802]	7421 [R_{int} = 0.0734, R_{sigma} = 0.0777]	6829 [R_{int} = 0.0626, R_{sigma} = 0.0639]
Data/restraints/parameters	5604/0/408	7421/104/543	6829/0/472
Goodness-of-fit on F^2	1.022	1.024	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0546, wR_2 = 0.1213	R_1 = 0.0472, wR_2 = 0.1168	R_1 = 0.0391, wR_2 = 0.0860
Final R indexes [all data]	R_1 = 0.0776, wR_2 = 0.1303	R_1 = 0.0795, wR_2 = 0.1250	R_1 = 0.0608, wR_2 = 0.0906
Largest diff. peak/hole / e Å^{-3}	1.17/–0.47	0.81/–0.58	0.60/–0.97

Calculation of Thermodynamic Parameters

K_{eq} for CD_3CN substitution from **3**. A known concentration of **3** in CD_3CN was used for NMR analysis. The peak integration values corresponding to $[Ru(Py_5Me_2)(OH_2)]^{2+}$, $[Ru(Py_5Me_2)(CD_3CN)]^{2+}$ and H_2O were respectively normalized and used in the following equation:

$$K_{eq} = \frac{[[Ru^{II}(Py_5Me_2)(CD_3CN)]^{2+}][H_2O]}{[[Ru^{II}(Py_5Me_2)(H_2O)]^{2+}]}$$

K_{eq} for cross reaction in **1** and **2**. K values were calculated according to the formula $K = e^{F(\Delta E)/RT}$ as described in the reference.[1] Signs of the $E_{1/2}$ values were flipped to account for oxidations; hence, $\Delta E = -E_{1/2}$ (Ru–X) + $E_{1/2}$ (Ru–MeCN).

References

1 S. W. Feldberg and L. Jeftic, *J. Phys. Chem.*, 1972, **76**, 2439–2446.