# Supporting Information

# Synthesis, Structural and Metal-to-Metal Charge Transfer Properties of Cyanide-Bridged Compound [$Fe^{II/III}$-NC-$Ru^{II}$-CN-$Fe^{II/III}$]

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## EXPERIMENTAL SECTION

### Materials and syntheses

All manipulations were performed under argon atmosphere with the use of standard Schlenk techniques unless otherwise stated. Dichloromethane was dried by distillation over calcium hydride and diethyl-ether was dried by distillation over sodium wire under argon atmosphere. Methanol was dried by distillation over magnesium under argon atmosphere and acetone was dried by anhydrous $Na_2SO_4$. $Ru^{II}(DMSO)_4Cl_2$[1,2] (DMSO = dimethyl sulfoxide) was prepared according to the literature procedures. All other reagents were available commercially and used without further purification

### *trans*-$Ru^{II}(^{tbu}py)_4(CN)_2$

A mixture of $Ru^{II}Cl_2(DMSO)_4$ (1000 mg, 2.065 mmol) and 4-tert-butylpyridine (10 ml) was stirred magnetically and heated to 130 °C for 30 min. After cooling to room temperature, KCN (1342 mg, 20.65 mmol) in 6 ml of water was added. After refluxing for 3 h, the organic layer was separated from the mixed solution by extract. After hexane (100 ml) was added to the organic

layer, large amount of yellow solid appeared. A yellow precipitate was isolated by filtration and washed with water, 2-propanol and ethyl ether, respectively. After drying in air, the desired yellow product (1088 mg, 67%) was obtained. Anal. Calcd for $C_{38}H_{60}N_6O_4Ru$: C, 59.58; H, 7.89; N, 10.97%. Found: C, 59.76; H, 7.54; N, 10.92%. IR ($\nu_{CN}$, KBr pellet, $cm^{-1}$): 2058 (s). UV-vis ($CH_3CN$), $\lambda_{max}$, nm ($\varepsilon$, $dm^3\ mol^{-1}\ cm^{-1}$): 248 (11652), 374 (22651). MS, m/z: 694.2 $[M+H]^+$.

**X-Ray structure determination.** The single crystal data of complexes **1-3** and *trans*-Ru($^{tbu}$py)$_4$(CN)$_2$ were all collected on a Saturn724+ diffractometer equipped with graphite-monochromatic Mo $K_\alpha$ ($\lambda$ = 0.71073 Å) radiation using an $\omega$-scan mode at 123 K. Data reduction, scaling and absorption corrections were performed using CrystalClear (Rigaku Inc., 2016). A Multi-scan absorption correction was performed using RIGAKU/MSC(2004), CrystalClear Version 1.3.6. All the structures were solved by the ShelXL-2016/4[3-5]structure solution program using direct methods and refined by full matrix least squares minimisation on $F^2$ using version 2018/3 of ShelXL 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. The $R$ values are defined as ${}_\omega R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and ${}_\omega R_2 = [\Sigma[_\omega(F_o^2 - F_c^2)^2]/\Sigma[_\omega(F_o^2)^2]]^{1/2}$. The detailed crystal data for complexes **1-3** and *trans*-Ru($^{tbu}$py)$_4$(CN)$_2$ were summarized in Table S1, and selected bond lengths and angles are presented in Table S2.

CCDC- 1989021 *trans*-Ru($^{tbu}$py)$_4$(CN)$_2$, CCDC- 1989022 **(1)**, CCDC-1989024**(2)**, CCDC-1989023 **(3)** contain the supplementary crystallographic data, related bond lengths and angles for this paper.

**Table S1**. Crystallographic Data and Details of Structure Determination for Complexes **1-3** and *trans*-Ru($^{tbu}$py)$_4$(CN)$_2$

| Complex | **1**·4$CH_2Cl_2$ | **2**·$C_3H_6O$ | **3**·3$C_3H_6O$·4$CH_3CN$ | *trans*-Ru($^{tbu}$py)$_4$(CN)$_2$·4$H_2O$ |
|---|---|---|---|---|
| CCDC NO. | 1989022 | 1989024 | 1989023 | 1989021 |
| Chemical formula | $C_{104}H_{118}Cl_8F_{12}Fe_2N_6P_6Ru$ | $C_{103}H_{116}F_{18}Fe_2N_6OP_7Ru$ | $C_{117}H_{140}F_{24}Fe_2N_{10}O_3P_8Ru$ | $C_{38}H_{60}N_6O_4Ru$ |
| Formula weight | 2362.23 | 2225.57 | 2650.91 | 765.99 |
| Colour and Habit | Red prism | Red prism | Brown prism | Orange prism |
| Crystal Size / mm | 0.48×0.37×0.11 | 0.51×0.33×0.18 | 0.49×0.38×0.23 | 0.31×0.15×0.14 |
| $T$ / K | 123 | 123 | 123 | 123 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic | Trigonal |
| Space group | $P2_1/c$ | $P2_1/n$ | $Pbca$ | $R$-3 |
| $a$ / Å | 13.838(3) | 13.0216(17) | 28.530(6) | 25.887(8) |
| $b$ /Å | 30.951(8) | 32.214(5) | 26.984(5) | 25.887(8) |
| $c$ / Å | 25.870(7) | 27.028(4) | 34.406(7) | 15.915(6) |
| $\alpha$ / deg | 90.00 | 90.00 | 90.00 | 90.00 |
| $\beta$ / deg | 96.100(6) | 98.184(3) | 90.00 | 90.00 |
| $\gamma$ / deg | 90.00 | 90.00 | 90.00 | 120.00 |
| $V$ / Å$^3$ | 11017(5) | 11222(3) | 26487(9) | 9236(6) |
| $Z$ | 4 | 4 | 8 | 9 |
| $\rho_{calcd}$(g/cm$^3$) | 1.424 | 1.317 | 1.330 | 1.239 |
| $\lambda$ (Mo K$_\alpha$, Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| $\mu$(Mo K$_\alpha$, mm$^{-1}$) | 0.745 | 0.568 | 0.509 | 0.428 |
| Completeness | 99.6% | 99.6% | 99.4% | 97.9% |
| $F$(000) | 4856 | 4588 | 10944 | 3654 |
| $h$, $k$, $l$, range | -16≤$h$≤15, -36≤$k$≤36, -30≤$l$≤28 | -15≤$h$≤14, -38≤$k$≤37, -32≤$l$≤32 | -35≤$h$≤37, -31≤$k$≤35, -44≤$l$≤44 | -33≤$h$≤33, -33≤$k$≤33, -20≤$l$≤20 |
| $\theta$ range / deg | 2.15-25.00 | 2.24-25.00 | 2.05-25.00 | 2.72-27.45 |
| Independent reflections | 19340 | 19681 | 30180 | 4608 |
| Reflections collected | 77510 | 78718 | 201480 | 36819 |
| $R_{int}$ | 0.0706 | 0.0409 | 0.0946 | 0.0663 |
| Params/restraints/ Data(obs.) | 1180/38/ 19340 | 1504/982/ 19681 | 1360/327/30180 | 331/8/4608 |
| GOF | 1.097 | 1.048 | 1.038 | 1.066 |
| $R_1$, $_\omega R_2$ ($I$ >2 $\sigma$($I$)) | 0.0646, 0.1458 | 0.0644, 0.1782 | 0.0841, 0.2228 | 0.0376, 0.1016 |
| $R_1$, $_\omega R_2$ (all data) | 0.0832, 0.1598 | 0.0738, 0.1886 | 0.1038, 0.244 | 0.0389, 0.1035 |

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $_\omega R_2 = [\Sigma[_\omega(F_o^2 - F_c^2)^2]/\Sigma[_\omega(F_o^2)^2]]^{1/2}$.

**Table S2.** Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **1-3**

| | **1** | **2** | **3** | *trans*-Ru($^{tbu}$py)$_4$(CN)$_2$ |
|---|---|---|---|---|
| Ru1-C1 | 2.036(4) | 2.050(4) | 2.038(4) | 2.061(2) |
| Ru1-C2 | 2.042(4) | 1.988(4) | 2.014(4) | |
| Ru1-N3 | 2.107(4) | 2.111(3) | 2.106(4) | 2.103(2) |
| Ru1-N4 | 2.091(3) | 2.093(3) | 2.115(3) | 2.110(2) |
| Ru1-N5 | 2.097(4) | 2.100(4) | 2.112(3) | |
| Ru1-N6 | 2.105(4) | 2.112(3) | 2.102(3) | |
| C1≡N1 | 1.161(5) | 1.171(5) | 1.155(5) | 1.149(3) |
| C2≡N2 | 1.157(5) | 1.176(5) | 1.174(5) | |
| Fe1-N1 | 1.937(4) | 1.913(3) | 1.908(4) | |
| Fe2-N2 | 1.931(4) | 1.886(3) | 1.896(3) | |
| Fe1-P1 | 2.197(1) | 2.203(1) | 2.282(2) | |
| Fe1-P2 | 2.204(1) | 2.207(1) | 2.283(2) | |
| Fe2-P3 | 2.196(1) | 2.247(1) | 2.266(1) | |
| Fe2-P4 | 2.204(1) | 2.250 (1) | 2.272(1) | |
| C1-Ru1-C2 | 178.6(2) | 177.4(2) | 176.3(2) | 180.0 |
| N1≡C1-Ru1 | 176.0(4) | 178.8(4) | 174.0(4) | 179.9(2) |
| N2≡C2-Ru1 | 176.7(4) | 174.7(4) | 175.8(4) | |
| C1≡N1-Fe1 | 173.7(4) | 174.9(4) | 167.0(4) | |
| C2≡N2-Fe2 | 173.8(4) | 176.0(3) | 172.8(3) | |
| Fe1···Ru1 | 5.121 | 5.135 | 5.047 | |
| Fe2···Ru1 | 5.116 | 5.049 | 5.068 | |
| Fe1···Fe2 | 10.228 | 10.162 | 10.019 | |

**Table S3** Cyanide Stretching Frequencies, Electronic Absorption Spectra and Cyclic-Voltammetry Data for Complex **1-3** and Related Precursors.

| Compound | $\nu_{CN}$ (cm$^{-1}$) | $\lambda_{max}$, nm ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) | $P$(V)/$CH_3CN$ | $P$(V)/$CH_2Cl_2$ |
|---|---|---|---|---|
| *trans*-Ru($^{tbu}$py)$_4$(CN)$_2$ | 2058 | 248 (11652), 374 (22651) | 0.62 | |
| **1** | 2071 | 476 (1214) | 0.31, 0.45 | 0.29, 0.45 |
| **2** | 2068, 2011 | 465 (1468), 957 (2381) | | |
| **3** | 2018 | 468 (1980), 780 (5573) | | |

**Table S4. Mössbauer Parameters for Complexes 1-3**

| Compound | IS (mm s$^{-1}$) | QS (mm s$^{-1}$) | |
|---|---|---|---|
| **1** (298K) | 0.371 | 2.013 | |
| **2**(298K) | 0.364 | 1.932 | 34.3% |
| | 0.395 | 0.736 | 65.7% |

| | | | |
|---|---|---|---|
| **3**(298K) | 0.517 | 1.205 | |
| **3**(10K) | 0.349 | 0.853 | |

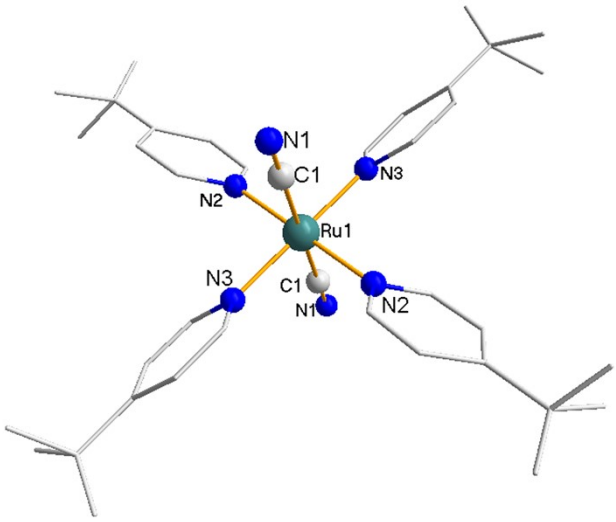


**Figure S1.** Molecular structure of *trans*-Ru($^{tbu}$py)$_4$(CN)$_2$, hydrogen atoms and solvent molecules have been removed for clarity.

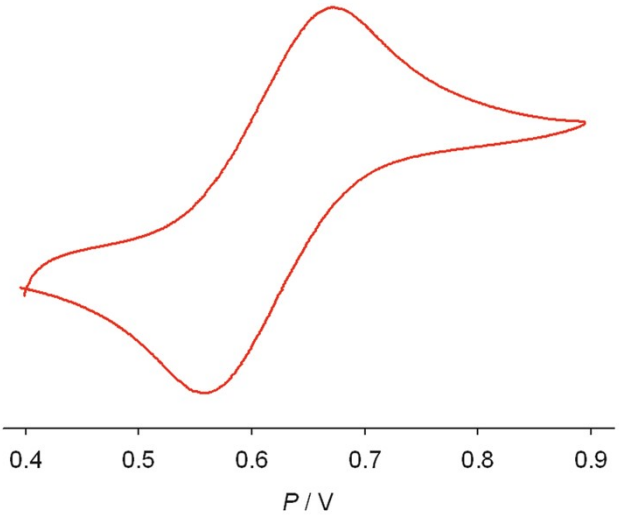


**Figure S2.** Cyclic voltammogram of *trans*-Ru($^{tbu}$py)$_4$(CN)$_2$ in a 0.10 M acetonitrile solution of [$Bu_4N$][$PF_6$] at a scan rate of 100 mV $s^{-1}$.

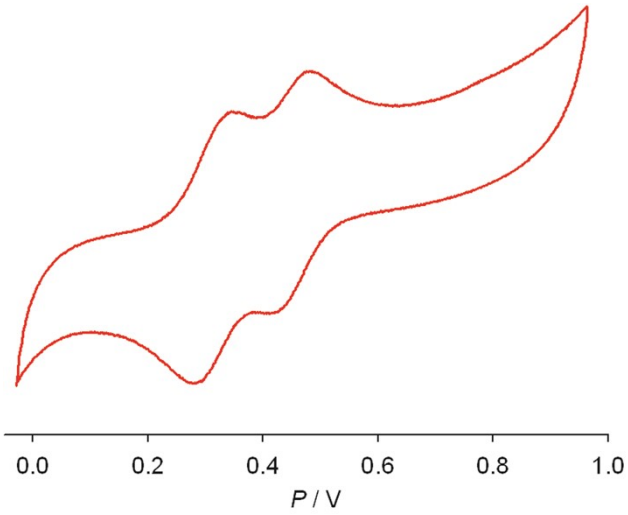


**Figure S3.** Cyclic voltammogram of complex **1** in a 0.10 M acetonitrile solution of $[Bu_4N][PF_6]$ at a scan rate of 100 mV $s^{-1}$.

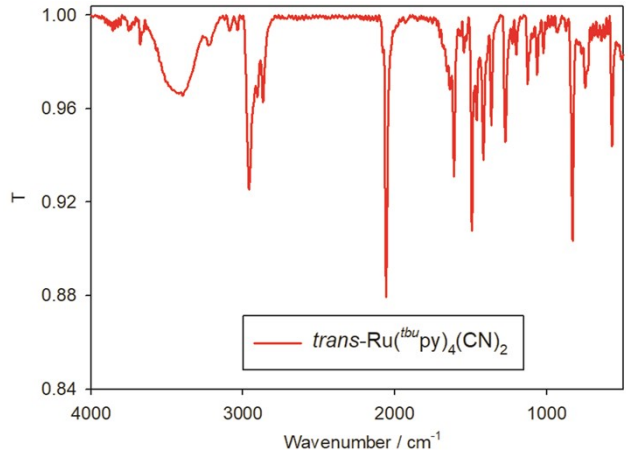


**Figure S4**. IR spectra of complex *trans*-Ru($^t$bupy)$_4$(CN)$_2$ in solid-state samples at room temperature. (KBr pellet)

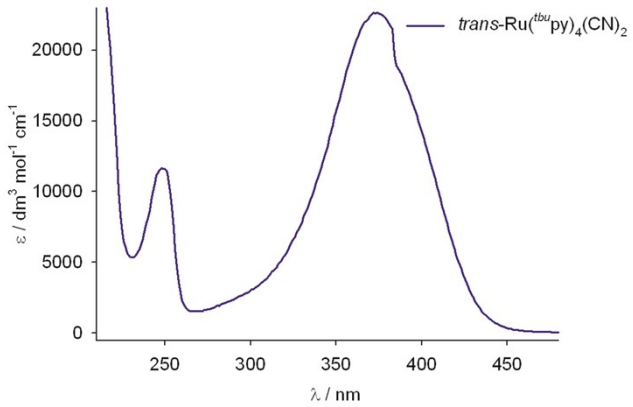


**Figure S5.** Electronic absorption spectra of *trans*-Ru($^t$bupy)$_4$(CN)$_2$ in $CH_3CN$ solution at room

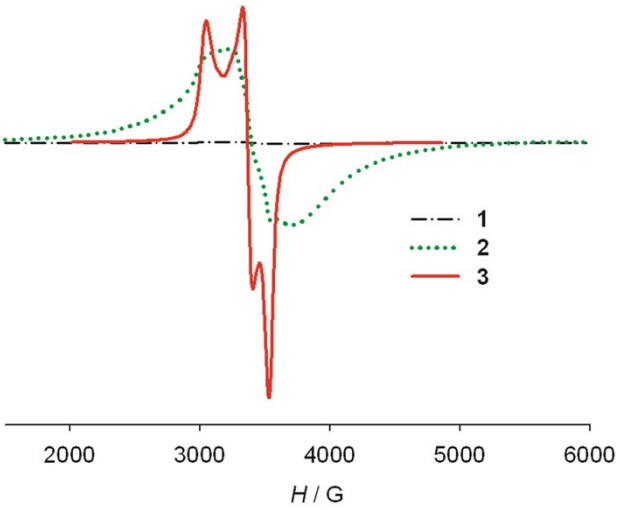


**Figure S6.** EPR spectra of complexes **1-3** in polycrystalline sample at 298K.

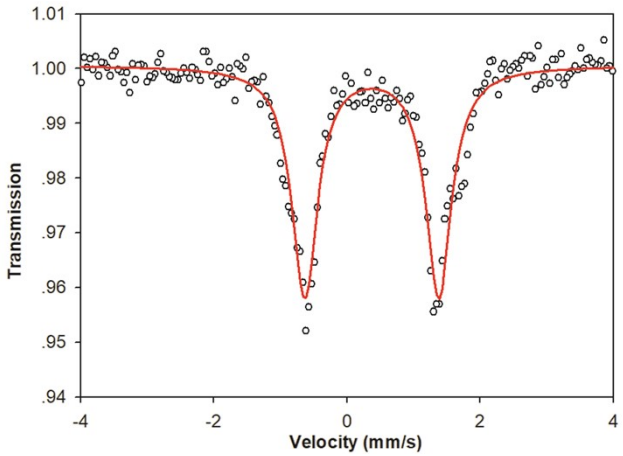


**Figure S7**. Zero field Mössbauer spectra of **1** at 298 K. The solid line represents a best fit. (IS = 0.371 mm/s, QS = 2.013 mm/s)

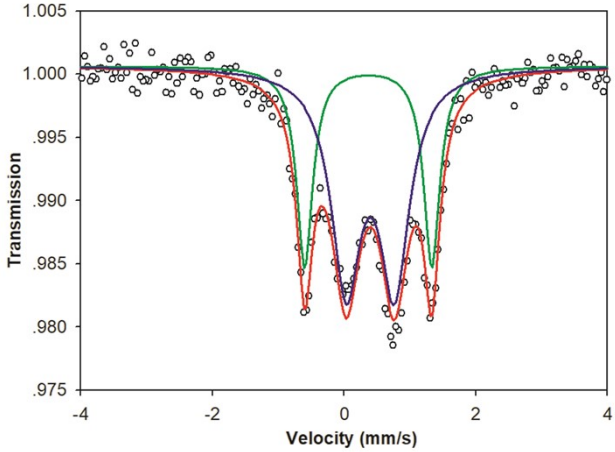


**Figure S8**. Zero field Mössbauer spectra of **2** at 298 K. The red line represents the sum of contributions for all types of Fe in the sample; the blue line is the simulated contribution of low-

spin $Fe^{III}$ (IS = 0.395 mm/s, QS = 0.736 mm/s); the green line is the simulated contribution of low-spin $Fe^{II}$ (IS = 0.364 mm/s, QS = 1.932 mm/s).

Reference


(1) Canard, G.; Piguet, C. *Inorg. Chem.* **2007**, *46*, 3511.

(2) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, *0*, 204.

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(4) Sheldrick, G. M. In *Program for X-ray Crystal Structure Refinement*; University of Göttingen: Germany 2016.

(5) Sheldrick, G. M. *Acta Crystallogr. Sect. C-Struct. Chem.* **2015**, *71*, 3.