Synthesis, Structural and Spectroscopic Properties of Cyanido-bridged Mixed-valence Compound [Fe-NC-Ru-CN-Fe]

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Table S1. Crystallographic Data and Details of Structure Determination for Compounds **1**, **2** **4**, *trans*-$Ru^{II}(Meopy)_4(CN)_2$ and $[CpFe^{III}(dppe)Br](PF_6)$

Compound	**1**·$7H_2O$	2(**2**·CH_3CN·$0.5NH_4PF_6$)	**4**	*trans*-$Ru^{II}(Meopy)_4(CN)_2$	$[CpFe^{III}(dppe)Br](PF_6)$
CCDC	2233237	2233238	2233234	2233235	2233236
Chemical formula	$C_{84}H_{92}F_{12}Fe_2N_6O_7P_6Ru$	$C_{172}H_{166}F_{42}Fe_4N_{15}P_{15}Ru_2$	$C_{88}H_{86}F_{12}Fe_2N_6O_4P_6Ru$	$C_{26}H_{28}N_6O_4$ Ru	$C_{31}H_{29}BrF_6$ FeP_3
Formula weight	1924.22	4131.28	1918.21	589.61	744.21
Colour and Habit	red prism	red prism	red prism	red prism	red prism
Crystal Size / mm	0.47×0.33×0.04	0.38×0.32×0.12	0.20×0.10×0.09	0.61×0.13×0.05	0.41×0.31×0.18
T / K	293	293	293	293	293
Crystal system	tetragonal	monoclinic	triclinic	triclinic	monoclinic
Space group	$P4/n$	$C2/c$	P-1	P-1	$P2_1/n$
a / Å	30.879(4)	34.313(9)	11.243(16)	10.373(3)	13.129(5)
b /Å	30.879(4)	14.540(4)	13.466(17)	15.745(4)	12.844(4)
c / Å	20.440(4)	38.850(11)	15.947(19)	17.176(5)	18.599(6)
α / deg	90	90.00	90.274(9)	96.368(2)	90.00
β / deg	90	110.278(5)	107.892(14)	105.641(4	96.680(5)
γ / deg	90	90.00	111.689(9)	100.922(2)	90.00
V / Å^3	19490(6)	18182(8)	2116(5)	2613.3(12)	3114.9(18)
Z	8	4	1	4	4
ρ_{calcd}(g/cm^3)	1.312	1.509	1.505	1.499	1.587
λ (Mo K_α, Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ(Mo K_α, mm^{-1})	0.618	0.702	0.709	0.643	1.978
Completeness	99.8%	99.7%	98.8%	99.0%	99.4%
F(000)	7904	8392	982	1208	1500

h, k, l, range	-36≤h≤36, -36≤k≤30, -24≤l≤24	-40≤h≤40, -17≤k≤12, -46≤l≤46	-14≤h≤14, -17≤k≤17, -20≤l≤20	-13≤h≤13, -20≤k≤20, -22≤l≤22	16≤h≤16, -15≤k≤16, -24≤l≤24
θ range / deg	2.20-25.00	2.11-25.00	2.71-27.29	2.09-27.50	2.56-27.44
R_{int}	0.0765	0.0579	0.0511	0.0355	0.0603
Params/restraints/Data(obs.)	1225/575/17137	1230/534/15966	538/0/5854	667/0/11902	379/0/7065
GOF	1.035	1.088	1.049	1.073	1.046
R_1, $_\omega R_2$ (I >2 σ(I))	0.0758, 0.1921	0.0998, 0.2731	0.0742, 0.1921	0.0381, 0.0789	0.0481, 0.1209
R_1, $_\omega R_2$ (all data)	0.1365, 0.2522	0.1181 0.2945	0.1019, 0.2199	0.0517, 0.0915	0.0616, 0.1299

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

Table S2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds **1**, **2** **4**, *trans*-$Ru^{II}(meopy)_4(CN)_2$ and $[CpFe^{III}(dppe)Br](PF_6)$

	1·7H_2O	2(**2**·CH_3CN·0.5NH_4PF_6)	**4**	*trans*-$Ru^{II}(Meopy)_4(CN)_2$		$[CpFe^{III}(dppe)Br](PF_6)$
Ru1-C1	1.997(7)	2.048(7)	2.069(5)	2.055(3)	Fe1- C27	2.084(3)
Ru1-C2	2.036(7)	2.004(7)	2.069(5)	2.058(3)	Fe1 -C28	2.127(3)
Ru1-N3	2.098(6)	2.097(6)	2.146(4)	2.097(2)	Fe1-C29	2.152(3)
Ru1-N4	2.092(6)	2.105(6)	2.143(5)	2.105(2)	Fe1 -C30	2.155(3)
Ru1-N5	2.091(6)	2.095(6)	2.146(4)	2.101(2)	Fe1-C31	2.131(3)
Ru1-N6	2.102(6)	2.105(6)	2.143(5)	2.105(2)	Fe1-P1	2.2727(12)
C1≡N1	1.185(8)	1.174(9)	1.168(7)	1.160(4)	Fe1-P2	2.2823(10)
C2≡N2	1.173(8)	1.171(9)	1.168(7)	1.149(4)	Fe1-Br1	2.3649(9)
Fe1-N1	1.896(6)	1.914(6)	1.958(5)		P1-Fe1-Br1	90.90(3)
Fe2-N2	1.911(5)	1.889(5)	1.958(5)		P2-Fe1-Br1	95.99(3)
Fe1-P1	2.239(2)	2.204(2)	2.212(3)		P1-Fe1-P2	82.91(3)
Fe1-P2	2.251(2)	2.217(2)	2.212(3)			
Fe2-P3	2.218(2)	2.254(2)	2.212(3)			
Fe2-P4	2.224(2)	2.265(2)	2.212(3)			
Fe1-C23	2.101(10)	2.101(8)	2.111(5)			
Fe1-C24	2.114(10)	2.097(8)	2.090(6)			
Fe1-C25	2.145(10)	2.061(7)	2.105(6)			
Fe1-C26	2.096(9)	2.080(7)	2.122(6)			
Fe1-C27	2.044(8)	2.099(8)	2.122(6)			
Fe2-C54	2.101(8)	2.118(7)	2.111(5)			
Fe2-C55	2.081(7)	2.075(7)	2.090(6)			
Fe2-C56	2.053(8)	2.088(7)	2.105(6)			
Fe2-C57	2.100(8)	2.153(8)	2.122(6)			
Fe2-C58	2.102(8)	2.161(7)	2.122(6)			
C1-Ru1-C2	177.7(3)	178.2(3)	180.0	178.79(11)		
N1≡C1-Ru1	174.1(6)	173.9(6)	175.0(4)	177.8(3)		
N2≡C2-Ru1	179.3(6)	174.8(6)	175.0(4)	178.4(3)		

C1≡N1-Fe1	172.5(6)	172.3(6)	168.7(4)
C2≡N2-Fe2	173.8(5)	174.8(6)	168.7(4)
N1-Fe1-P1	89.68(18)	90.93(18)	93.03(14)
N1-Fe1-P2	93.49(19)	88.41(18)	87.87(13)
P1-Fe1-P2	84.83(8)	84.49(8)	84.89(8)
N2-Fe2-P3	93.36(18)	93.50(18)	93.03(14)
N2-Fe2-P4	93.6(2)	89.50(18)	87.87(13)
P3-Fe2-P4	84.34(8)	83.64(8)	84.89(8)
Fe1···Ru1	5.052	5.110	5.155
Fe2···Ru1	5.112	5.047	5.155
Fe1···Fe2	10.142	10.153	10.311

Table S3 Cyanide Stretching Frequencies, Electronic Absorption Spectra and Cyclic-Voltammetry Data for Compound **1-5** and Related Precursors.

Compound	ν_{CN} (cm^{-1})	ν_{max}, cm^{-1} (ε, $dm^3\ mol^{-1}\ cm^{-1}$)	*P*(V)/CH_3CN	*P*(V)/CH_2Cl_2
trans-$Ru^{II}(py)_4(CN)_2$	2058	40000 (20938), 27027 (28914)	0.92	
trans-$Ru^{II}(MeOpy)_4(CN)_2$	2056	27933 (17192)	0.54	
[$CpFe^{III}$(dppe)(CH_3CN)]Br		360(852), 458(634)		
1	2068	18657 (604)	0.33, 0.45	0.34, 0.47
2	2089, 2020	21505 (1297), 11641 (2357).		
3	2023	465 (21505), 760 (13158)		
4	2061	21367 (876), 18939 (745)	0.17, 0.33	0.30, 0.46
5	2084, 2010	21505 (1211), 19084 (983),9268 (2265)		

Figure S1. Molecular structure of compound *trans*-$Ru^{II}(MeOpy)_4(CN)_2$ (hydrogen atoms have been removed for clarity).

Figure S2 Molecular structure of $[CpFe^{III}(dppe)Br](PF_6)$. (hydrogen atoms have been removed for clarity).

Figure S3 Cyclic voltammogram of compound *trans*-$Ru(py)_4(CN)_2$ in a 0.10 M acetonitrile solution of $[Bu_4N][PF_6]$ at a scan rate of 100 mV s^{-1}.

Figure S4 Cyclic voltammogram of compound *trans*-Ru(meopy)$_4$(CN)$_2$ in a 0.10 M acetonitrile solution of [Bu$_4$N][PF$_6$] at a scan rate of 100 mV s^{-1}.

Figure S5 Cyclic voltammogram of compound **1** in a 0.10 M dichloromethane solution of [Bu$_4$N][PF$_6$] at a scan rate of 100 mV s^{-1}.

Figure S6 Cyclic voltammogram of compound **4** in a 0.10 M dichloromethane solution of $[Bu_4N][PF_6]$ at a scan rate of 100 mV s^{-1}.

Figure S7. IR spectra of compound *trans*-$Ru(py)_4(CN)_2$ in solid-state samples at room temperature. (KBr pellet)

Figure S8. IR spectra of compound *trans*-$Ru(meopy)_4(CN)_2$ in solid-state samples at room

temperature. (KBr pellet)

Figure S9. Electronic absorption spectra of compounds *trans*-$Ru(py)_4(CN)_2$ and *trans*-$Ru(Meopy)_4(CN)_2$ in CH_3CN solution at room temperature.