

## Supporting Information for

“Fc-Fc Electronic Interaction through Equatorial Pathways of A Diruthenium Core”

(revised)

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Ferrocene carboxylic acid was purchased from Alfa Inorganics, Beverly, MA. Potassium carbonate, toluene and silver nitrate were purchased from Mallinckrodt Baker, Phillipsburg, NJ. Tetrahydrofuran was purchased from Sigma Aldrich, St. Louis, MO. Silver tetrafluoroborate was purchased from Strem Chemicals, Newburyport, MA.  $\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3(\text{O}_2\text{CFc})\text{Cl}$  and  $\text{cis-Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_2(\text{O}_2\text{CFc})_2\text{Cl}$  were prepared as previously described.<sup>1</sup> Vis-NIR spectra in THF were obtained with a JASCO V-670 spectrophotometer. Magnetic susceptibilities were measured at room temperature using a Johnson Matthey Mark-I Magnetic Susceptibility Balance. Elemental analysis was performed by Atlantic Microlab, Norcross, GA. Cyclic voltammograms were recorded in 0.2 M (*n*-Bu)<sub>4</sub>NPF<sub>6</sub> solution (THF, N<sub>2</sub>-degassed) on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode and a Ag/AgCl reference electrode. The concentration of diruthenium species is always 1.0 mM. The ferrocenium/ferrocene couple was observed at 0.58 V (vs. Ag/AgCl) at the experimental conditions.

**Preparation of  $\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3(\text{O}_2\text{CFc})\text{Cl}$  (3).** A 100 mL round bottomed flask was charged with **1** (0.558 g, 0.429 mmol), ferrocene carboxylic acid (0.105 g, 0.456 mmol) and toluene (80 mL). The flask was mounted with a Soxhlet extractor containing a thimble that is charged with potassium carbonate covered by sand, which served as the scrubber for acetic acid.

The solution was allowed to reflux via a sand-filled heating pad and the progress was monitored with TLC (EtOAc/hexanes, 1:7), which indicated the complete consumption of **1** after about 36 h. After the solvent removal on rotavap, the residue was recrystallized from THF/hexanes (1:9) to afford 0.241 g of purple crystalline materials (43.0% based on Ru). Data for **3**:  $R_f = 0.37$  (EtOAc/hexanes, 1:7). ESI-MS ( $m/z$ , based on  $^{101}\text{Ru}$ ): 1430  $[\text{M} - \text{Cl}]^+$ . Anal. for  $\text{C}_{54}\text{H}_{38}\text{Cl}_{13}\text{N}_6\text{O}_3\text{Ru}_2\text{Fe}$  (**3**·THF), Found(calcd.): C, 42.1(42.2); H, 2.38(2.49); N, 5.48(5.46). Vis,  $\lambda_{\text{max}}(\text{nm}, \epsilon (\text{M}^{-1} \text{cm}^{-1}))$ : 517 (6,395).  $\chi_{\text{mol}}(\text{corrected}) = 5.68 \times 10^{-3} \text{ emu}$ ,  $\mu_{\text{eff}} = 3.68 \text{ BM}$ . Cyclic voltammogram [ $E_{1/2}/\text{V}$ ,  $\Delta E_p/\text{V}$ ,  $i_{\text{backward}}/i_{\text{forward}}$ ]: **A**, 1.160, 0.080, -0.260; **B**, -0.239, 0.039, -0.700;  $E_{\text{pc}}(\text{C})$ , -1.470; **D**, -1.015, 0.087, -0.643.

**Preparation of cis-Ru<sub>2</sub>(D(3,5-Cl<sub>2</sub>Ph)F)<sub>2</sub>(O<sub>2</sub>CFc)<sub>2</sub>Cl (**4**)**. This compound was prepared from 0.222 g (0.217 mmol) Ru<sub>2</sub>(D(3,5-Cl<sub>2</sub>Ph)F)<sub>2</sub>(OAc)<sub>2</sub>Cl and 0.102 g (0.443 mmol) FcCOOH using the same setup as that of **3**, and the reaction also completed in about 36 h. The crude reaction product was purified on silica gel column using ethyl acetate/hexanes (v/v, 1:7 to 1:1), which afforded 0.124g deep red crystals (55.9% based on Ru). Data for **4**:  $R_f = 0.55$  (EtOAc/hexanes, 1:2). ESI-MS ( $m/z$ , based on  $^{101}\text{Ru}$ ): 1327  $[\text{M} - \text{Cl}]^+$ . Anal. for  $\text{C}_{53}\text{H}_{47}\text{Cl}_9\text{N}_4\text{O}_8\text{Ru}_2\text{Fe}_2$ , (**4**·0.5hexane·4H<sub>2</sub>O) Found(calcd.): C, 43.0(42.4); H, 3.75(3.16); N, 3.65(3.73). Vis,  $\lambda_{\text{max}}(\text{nm}, \epsilon(\text{M}^{-1} \text{cm}^{-1}))$ : 524 (4,100).  $\chi_{\text{mol}}(\text{corrected}) = 6.09 \times 10^{-3} \text{ emu}$ ,  $\mu_{\text{eff}} = 3.81 \text{ BM}$ . Cyclic voltammogram [ $E_{1/2}/\text{V}$ ,  $\Delta E_p/\text{V}$ ,  $i_{\text{backward}}/i_{\text{forward}}$ ]:  $E_{\text{pa}}(\text{A})$ , 1.350; **B**, -0.312, 0.085, -0.874;  $E_{\text{pc}}(\text{C})$ , -1.361.

**Table S1.** Selected bond lengths (Å) and angles (°) for compounds **3** and **4**.

<b>3</b>		<b>4</b>	
Ru1 - Ru2	2.3141(8)	Ru1 - Ru2	2.3169(5)
Ru1 - Cl1	2.4078(18)	Ru1 - O5	2.310(4)
Ru1 - O7	2.075(4)	Ru1 - O4	2.052(3)
Ru1 - N1	2.092(6)	Ru1 - O2	2.051(3)
Ru1 - N3	2.075(6)	Ru1 - N2	2.048(4)
Ru1 - N5	2.097(6)	Ru1 - N4	2.034(4)
Ru2 - O8	2.042(5)	Ru2 - Cl1	2.4628(13)
Ru2 - N2	2.052(6)	Ru2 - O3	2.065(3)
Ru2 - N4	2.031(6)	Ru2 - O1	2.071(3)
Ru2 - N6	2.035(6)	Ru2 - N1	2.052(4)
O7 - C8	1.278(9)	Ru2 - N3	2.048(4)
O8 - C8	1.284(8)	O5 - C49	1.484(13)
C8 - C81	1.460(10)	O4 - C12	1.268(7)
		O3 - C12	1.276(6)
		C12 - C13	1.471(7)
		O2 - C1	1.266(6)
		O1 - C1	1.271(6)
		C1 - C2	1.460(7)
Ru2 - Ru1 - Cl1		Ru1 - O5 - C49	120.4(5)
		Ru1 - Ru2 - Cl1	174.01(3)
		Ru2 - Ru1 - O5	168.82(11)

**References:**

- (1) Chen, W.-Z.; Ren, T. *Inorg. Chem.* **2006**, *45*, 8156.