1322 *Inorg. Chem.* **2010**, *49*, 1322–1324
DOI: 10.1021/ic902378h

Inorganic Chemistry
Communication

Fc-Fc Electronic Interaction through Equatorial Pathways of a Diruthenium Core

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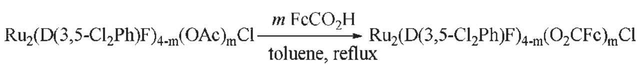
Received December 1, 2009

Diruthenium compounds bearing one (**3**) and two (**4**) ferrocene carboxylate ligands were prepared and characterized, and the electronic coupling between two equatorially adjacent Fc centers in compound **4** is significant, but weaker than those between Fc centers placed on the opposite axial sites.

The discovery of ferrocene by Pauson and Kealy in 1951 marks the beginning of modern organometallic chemistry.[1] Today, ferrocene still plays important roles in many different disciplines, including polymer materials, antitumor drugs, and asymmetric catalysis.[2] Because of the robustness of its 1 e$^-$ oxidation couple, ferrocene has been used extensively as a reporter group for gauging the degree of charge delocalization across a molecular fragment (X) through the study of mixed valency in the Fc-X-Fc assembly.[3] Early efforts from our laboratory resulted in the isolation of the *trans*-$Ru_2(DMBA)_4(C_{2n}Fc)_2$ type compounds with $n = 1-4$ (DMBA = *N*,*N*′-dimethylbenzamidinate) and demonstration of strong electronic couplings between two Fc centers situated in the opposite *axial positions* over distances up to 28 Å.[4,5] Described in this communication is the recent effort in exploring the electronic coupling between two Fc centers placed in the adjacent *equatorial sites* on the basis of structural, voltammetric, and spectroscopic studies. It is worth mentioning that the $M_2(O_2CFc)_4$ type compounds have been reported with M as Cu, Mo and Ru,[6,7] and equatorial Fc-Fc interaction was inferred from the voltammetric data of the latter compound.

Scheme 1. Preparation of Diruthenium Fc-Carboxylate Compounds



$$Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-m}(OAc)_mCl \xrightarrow[\text{toluene, reflux}]{m\ FcCO_2H} Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4-m}(O_2CFc)_mCl$$

1 ($m = 1$) or **2** ($m = 2$) **3** ($m = 1$) or **4** ($m = 2$)

The incorporation of Fc-bearing ligands in the equatorial positions of diruthenium moiety builds on the availability of the $Ru_2(DArF)_{4-m}(OAc)_m$ (m = 1 and 2, DArF is *N,N*′-diarylformamidinate) type compounds, which have been developed in the laboratories of Cotton,[8] Jiménez-Aparicio,[9] and Ren,[10−12] and played a pivotal role in the exploration of peripheral covalent chemistry.[13] As shown in Scheme 1, reactions between ferrocenylcarboxylic acid and either $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(OAc)Cl$ (**1**, D(3,5-Cl_2Ph)F is *N,N*′-di(3,5-dichlorophenyl)-formamidinate)[12] or $Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(OAc)_2Cl$ (**2**) under reflux resulted in $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(O_2CFc)Cl$ (**3**) or $Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(O_2CFc)_2Cl$ (**4**), respectively.[14] Both new compounds were analyzed satisfactorily and have an $S = 3/2$ ground state on the basis of their room-temperature magnetic moments (see the Supporting Information for more details).

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(14) Compound **1** (0.433 mmol) and ferrocene carboxylic acid (0.456 mmol) were refluxed in toluene with an acetic acid scrubbing apparatus for 36 h. The recrystallization of crude product in THF/hexanes (1:9) resulted in pure compound **3** as deep red crystals in 43% yield. Compound **2** (0.217 mmol) and ferrocene carboxylic acid (0.456 mmol) were refluxed in toluene with an acetic acid scrubbing apparatus for 36 h. Silica column purification of crude product with ethyl acetate/hexanes (v/v, 1:7 to 1:1) resulted in pure compound **4** as red crystals in 56% yield.

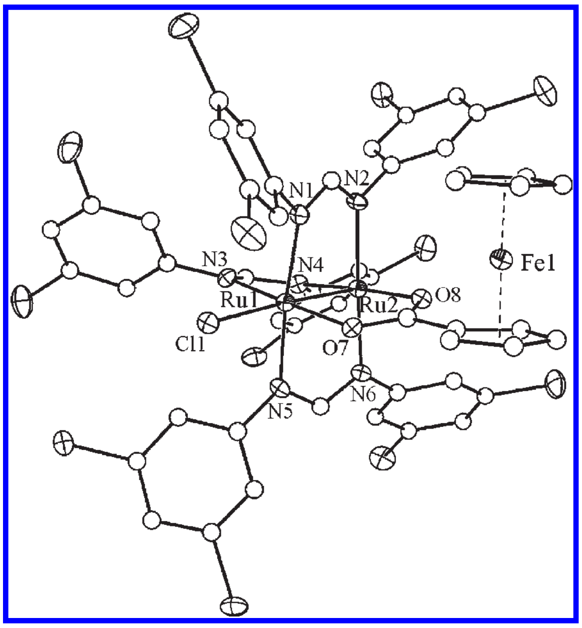


Figure 1. Structural plot of compound **3**. Selected bond lengths (Å): Ru1−Ru2, 2.3141(8); Ru1−Cl1, 2.408(2); Ru1−N_{av}, 2.09; Ru2−N_{av}., 2.04; Ru1−O7, 2.075(4); and Ru2−O8, 2.042(5).

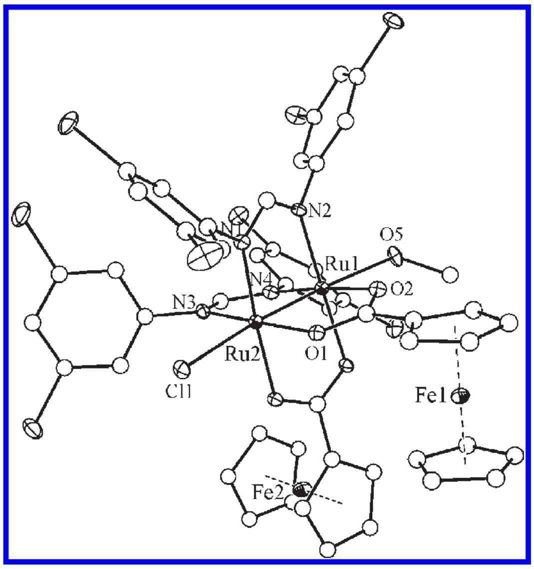


Figure 2. Structural plot of **4**·MeOH. Selected bond lengths (Å): Ru1−Ru2, 2.3169(5); Ru2−Cl1, 2.463(1); Ru1−N_{av}, 2.04; Ru2−N_{av}., 2.05; Ru1−O2, 2.051(3); Ru1−O4, 2.052(3); Ru1−O5, 2.310(4); Ru2−O1, 2.071(3); and Ru2−O3, 2.065(3). Fe1---Fe2, 7.46 Å.

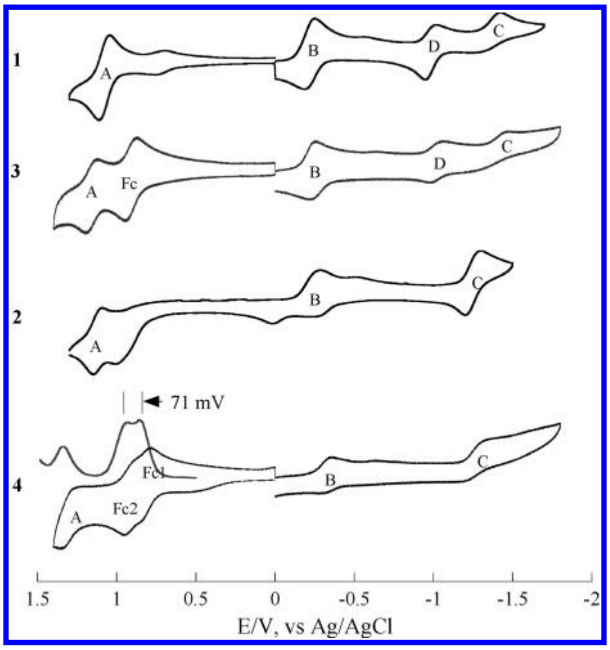
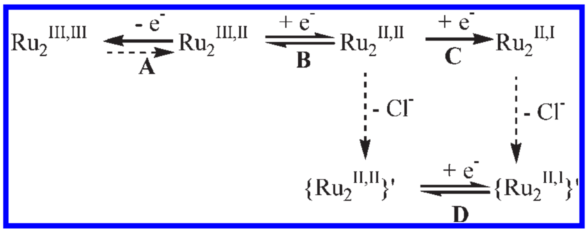


Figure 3. Cyclic voltammograms of compounds **1**−**4** recorded in THF with a scan rate of 100 mV/s.

Scheme 2. Assignments of Observed Ru_2-Based Redox Couples



The most definitive confirmation of the incorporation of the ferrocenyl-carboxylate ligand came from the single crystal X-ray diffraction studies of compounds **3** and **4**,[15] and structural plots of these compounds are shown in Figures 1 and 2, respectively. The coordination sphere of the Ru_2 core in **3** is very similar to that of **1** with comparable Ru−Ru distances (2.322 Å in **1** and 2.314 Å in **3**) and Ru−N and Ru−O bond lengths.[12] Compound **4** adopts the *cis*-(2,2) ligand arrangement that was found for its precursor **2**, and the similarity in bond lengths and angles around the Ru_2 is also noticed between two compounds.[12] When being crystallized from CH_3OH/*o*-$C_6H_4Cl_2$, compound **4** contains a methanol axial ligand at the Ru1 center and hence should be formulated as (**4**·MeOH) in the lattice. Clearly, the substitution of acetate by ferrocene carboxylate causes a very minimal structural change in the Ru_2 coordination sphere.

Similar to the prior study of the *trans*-$Ru_2(DMBA)_4(C_{2n}Fc)_2$ type compounds,[4,5] possible electronic coupling between two Fc centers in **4** was first examined with voltammetric method. The CVs of compounds **3** and **4** and their precursors **1** and **2** are shown in Figure 3, and the resemblance between the CVs of **3** and **4** and those of respective precursors is obvious. As designated in Scheme 2, compound **1** exhibits a 1 e^- oxidation (**A**) and two 1e^- reductions (**B** and **C**) and a couple related to the degradation product (**D**).[12] While the cathodic CV segment of **3** is nearly identical to that of **1**, a well-defined Fc oxidation wave can be identified in the anodic segment. The Ru_2-center oxidation (**A**) in **3** is shifted to a more positive potential than that of **1** due to the positive charge gained upon the oxidation of Fc center.

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(15) Single crystals of compounds **3** and **4** were grown from hexanes/CH_2Cl_2 and CH_3OH/*o*-dichlorobenzene solutions, respectively. X-ray diffraction data for **3** and **4** were collected on a Rigaku Rapid II image plate diffractometer using Cu Kα radiation (λ = 1.54184 Å) at 150 K. The structures were solved using the structure solution program PATTY in DIRDIF99 and refined using SHELX-07. Crystal data for **3**·$2CH_2Cl_2$: $C_{52}H_{34}Cl_{17}FeN_6O_2Ru_2$, fw = 1635.58, triclinic, $P\bar{1}$, a = 11.0193(7), b = 13.281(1), c = 23.350(1) Å, α = 92.43(7), β = 101.54(5), γ = 114.35(5)°, V = 3020.1(4) Å^3, Z = 2, D_{cacl} = 1.798 g cm^{-3}, $R1$ = 0.063, $wR2$ = 0.167. Crystal data for (**4**·CH_3OH)·CH_3OH: $C_{50}H_{40}Cl_9Fe_2N_4O_6Ru_2$, fw = 1635.58, triclinic, $P2_1/c$, a = 11.8533(4), b = 20.6367(6), c = 21.9307(5) Å, β = 90.15(2)°, V = 5364.5(3) Å^3, Z = 4, D_{cacl} = 1.765 g cm^{-3}, $R1$ = 0.051, $wR2$ = 0.138.

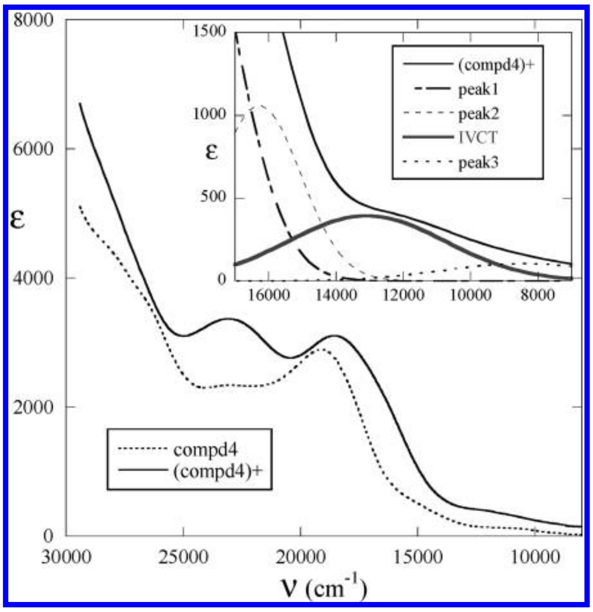

Figure 4. Vis-NIR spectra of compounds **4** and **4**$^+$ recorded in THF. The Gaussian deconvolution of the latter is shown as the insert.

Comparison of the CVs of **2** and **4** revealed very similar characteristics in the cathodic region. Noteworthy in the anodic region of compound **4** is a pair of closely spaced but clearly resolved 1e$^-$ oxidations that is absent in the CV of **2**, which is assigned as the consecutive oxidations of Fc centers. The pairwise appearance is indicative of an electronic coupling between two Fc centers in the mixed valent state ([Fc-Fc]$^+$).[3,5] The potential difference within the pair, ΔE, is about 71 mV from the differential pulse voltammogram of **4** (shown in Figure 3), which is substantially smaller than the ΔEs determined for *trans*-$Ru_2(DMBA)_4(C_{2n}Fc)_2$ ($\geq$200 mV).[4]

In addition to the Fc-Fc coupling, ΔE depends upon a number of factors including ion pairing, which for the oxidation of neutral species has been shown to reduce ΔE to a significant degree.[3] Hence, direct spectroscopic evidence for the Fc-Fc coupling in **4** is desired. The vis-near-infrared (vis-NIR) spectrum of **4** (Figure 4) features an intense peak at 523 nm (19120 cm^{-1}), a weak peak at 434 nm (23040 cm^{-1}), and a very weak shoulder at about 870 nm (11500 cm^{-1}). Treating compound **4** with 1.2 equiv of $AgBF_4$ in THF resulted in significant spectral changes: The peak at 523 nm is red-shifted to 539 nm (18550 cm^{-1}), while the peak at 434 nm is greatly intensified. The most interesting change, however, is the appearance of a broad shoulder around 840 nm (11900 cm^{-1}), which is assigned as the intervalence charge transfer transition (IVCT) of the [Fc-Fc]$^+$ ion. Gaussian deconvolution of the spectrum of [**4**]$^+$ (insert of Figure 4) yielded two peaks in the red-NIR region: The IVCT band with $\nu_{\max}$ and $\Delta\nu_{1/2}$ as 13100 and 5500 cm^{-1}, respectively, and peak 3 that corresponds approximately to the very weak shoulder observed in compound **4**. The measured $\Delta\nu_{1/2}$ is identical to that predicted by the Hush model [$\Delta\nu_{1/2}(\text{calc}) = (2310\nu_{\max})^{1/2} = 5{,}501$ cm^{-1}],[16] indicating that [**4**]$^+$ is best described as a Robin−Day class II mixed valent species.[17]

Inference of Fc-Fc coupling was made in the earlier study of $[Ru_2(O_2CFc)_4]^+$ based on CV and DPV evidence, but the nature of mixed valency was not elaborated.[7] With both the detectable ΔE and designation of class II mixed valency of **4**$^+$, the present study demonstrates unambiguously that the electronic coupling exists between two adjacent equatorial sites of a Ru_2 core, albeit weak. It is unclear whether the coupling occurs through space (Fe---Fe distance is about 7.46 Å) or through the covalent linkage (two Fc centers are separated by six bonds in **4**). It is quite possible that the electronic coupling across a diruthenium paddlewheel species is *anisotropic*: It is sustained over an extended distance (up to 28 Å) along the axial direction as in the case of *trans*-$Ru_2(DMBA)_4(C_{2n}Fc)_2$,[4] but strongly attenuated along the equatorial direction(s) as in the cases of **4** and *cis*-Ru_2-(*D*mAni*F*)$_2$(DMBA-4-C_2Fc)$_2$(C_2Ph)$_2$ reported earlier.[11]

The research of diruthenium compounds supported by either *O*,*O*′- or *N*,*N*′-bidentate bridge have experienced a rejuvenation in recent years with new developments including the generation of novel Ru−Ru≡N species,[18] new magnetic materials,[19] oxidation catalysis,[20] and molecular wires and devices.[21] Elaboration of the transmission of electronic couplings in diruthenium species is fundamentally important to these new endeavors, and further studies related to this work are being pursued in our laboratory.

Acknowledgment. We thank the National Science Foundation (Grant CHE 0715404) and Purdue Research Foundation for support.

Note Added after ASAP Publication. This article was released on December 28, 2009, with an author's name misspelled. The correct version was posted on January 8, 2010.

Supporting Information Available: Detailed syntheses and characterization of compounds **3** and **4** and X-ray crystallographic details (CIF) of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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