# Dalton Transactions

## PAPER

# Tuning of the ionization potential of paddlewheel diruthenium(II, II) complexes with fluorine atoms on the benzoate ligands<sup>†</sup>

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A series of paddlewheel diruthenium(II, II) complexes with various fluorine-substituted benzoate ligands were isolated as THF adducts and structurally characterized: [Ru<sub>2</sub>(F<sub>2</sub>PhCO<sub>2</sub>)<sub>4</sub>(THF)<sub>2</sub>]  $(\mathbf{F}_{x}\mathbf{PhCO}_{2}^{-} = o$ -fluorobenzoate, o-**F**; *m*-fluorobenzoate, **m**-**F**; *p*-fluorobenzoate, **p**-**F**; 2,6-difluorobenzoate, **2,6-F**<sub>2</sub>; 3,4-difluorobenzoate, **3,4-F**<sub>2</sub>; 3,5-difluorobenzoate, **3,5-F**<sub>3</sub>; 2,3,4-trifluorobenzoate, 2,3,4-F<sub>3</sub>; 2,3,6-trifluorobenzoate, 2,3,6-F<sub>3</sub>; 2,4,5-trifluorobenzoate, 2,4,5-F<sub>3</sub>; 2,4,6-trifluorobenzoate, **2,4,6-F**<sub>3</sub>; 3,4,5-trifluorobenzoate, **3,4,5-F**<sub>3</sub>; 2,3,4,5-tetrafluorobenzoate, 2,3,4,5-F<sub>4</sub>; 2,3,5,6-tetrafluorobenzoate, 2,3,5,6-F<sub>4</sub>; pentafluorobenzoate, F<sub>5</sub>). By adding fluorine atoms on the benzoate ligands, it was possible to tune the redox potential  $(E_{1/2})$  for  $[Ru_2^{II,II}]/[Ru_2^{II,III}]^+$  over a wide range of potentials from -40 mV to 350 mV (vs. Ag/Ag<sup>+</sup> in THF). 2,3,6-F<sub>3</sub>, 2,3,4,5-F<sub>4</sub>, 2,3,5,6-F<sub>4</sub> and  $\mathbf{F}_{5}$  were relatively air-stable compounds even though they are  $[Ru_{7}^{II,II}]$  species. The redox potential in THF was dependent on an electronic effect rather than on a structural (steric) effect of the o-F atoms, although more than one substituent in the *m*- and *p*-positions shifted  $E_{1/2}$  to higher potentials in relation to the general Hammett equation. A quasi-Hammett parameter for an o-F atom ( $\sigma_{0}$ ) was estimated to be ~0.2, and a plot of  $E_{1/2}$  vs. a sum of Hammett parameters including  $\sigma_0$  was linear. In addition, the HOMO energy levels, which was calculated based on atomic coordinates of solid-state structures, as well as the redox potential were affected by adding F atoms. Nevertheless, a steric contribution stabilizing their static structures in the solid state was present in addition to the electronic effect. On the basis of the electronic effect, the redox potential of these complexes is correlated to the HOMO energy level, and the electronic effect of F atoms is the main factor controlling the ionization potential of the complexes with ligands free from the rotational constraint, *i.e.* complexes in solution.

#### Introduction

Paddlewheel complexes with metal–metal bonds have been extensively studied over the past four decades.<sup>1</sup> The most fascinating aspect of paddlewheel complexes is their rich electrochemistry: the complexes undergo both oxidation and reduction at the dimetal center with systematical changes in the metal–metal bond length in relation to the arrangement of electrons in the frontier orbitals  $\sigma \pi_2 \delta \delta^* \pi^* \sigma^*$  without considerable structural change. Among such paddlewheel dimetal complexes, a family of diruthenium complexes with bridging carboxylate ligands,<sup>2</sup> [Ru<sub>2</sub>(RCO<sub>2</sub>)<sub>4</sub>]<sup>n+</sup> (n = 0 or 1; abbreviated as [Ru<sub>2</sub>]<sup>n+</sup>), are interesting for studying the magnetic properties of their assemblies<sup>3-7</sup> and

for designing electronic modules in aggregated charge-transfer systems.<sup>8-12</sup> This is because the two oxidation states [Ru<sub>2</sub><sup>II,II</sup>] and  $[Ru_2^{II,III}]^+$ , which possess unpaired spins with  $S = 1^{13}$  and S = 3/2, respectively, in a degenerated orbital set of  $(\delta^* \pi^*)$ and considerably large zero-field splitting ( $D \approx +250$  cm<sup>-1</sup> and +60 cm<sup>-1</sup>, respectively), are relatively stable and can be isolated.<sup>1</sup> Recently, our group has focused on assemblies of [Ru211,11] with 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) and its derivatives to design a charge-transfer system with metal-organic frameworks (MOFs), where [Ru2<sup>II,II</sup>] and TCNQ are regarded as a one-electron (1-e<sup>-</sup>) donor (D) and acceptor (A), respectively. Although no interunit charge transfer occurs in a D<sub>2</sub>A two-dimensional assembly,  $[{Ru_2(O_2CCF_3)_4}_2(TCNQ)]$ ,<sup>8</sup> which is neutral, substitution with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF<sub>4</sub>) led to charge transfer forming TCNQF4<sup>--</sup> due to the higher electron affinity of TCNQF<sub>4</sub> than that of TCNQ.<sup>10</sup> In addition, this compound exhibited long-range antiferromagnetic ordering at a Néel temperature  $T_{\rm N}$  = 95 K owing to intralayer ferromagnetic ordering and interlayer antiferromagnetic ordering. These results clearly indicate that [Ru2<sup>II,II</sup>] complexes are capable of acting not only as a coordination-acceptor to form MOFs with TCNQ

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groups but also as charge-transfer insulators or 1-e<sup>-</sup> donors even in the same D<sub>2</sub>A system. In other words, tuning of the ionization potential  $(I_{\rm D})$  of  $[{\rm Ru_2}^{\rm II,II}]$  and the electron affinity  $(E_{\rm A})$  of the TCNQ unit makes it possible to design D/A MOFs with various electronic and spin states. For this strategy, [Ru<sub>2</sub><sup>II,II</sup>] complexes with benzoate ligands are good candidates for donor units, of which  $I_{\rm D}$ can be systematically tuned by adding substituents on the phenyl ring. A few of these complexes are charge-transfer magnets when combined with the appropriate TCNQ derivatives.<sup>12,14</sup> However, only a few examples of these [Ru211,11] complexes have been reported to date<sup>15-23</sup> likely because it is difficult to isolate and characterize them, and to the best of our knowledge, a systematic investigation of their electrochemistry to determine indirectly  $I_{\rm D}$ has never been done. Here, we introduce a series of [Ru2<sup>II,II</sup>] complexes with various fluorine-substituted benzoate ligands,  $[\operatorname{Ru}_2(\operatorname{F}_x\operatorname{PhCO}_2)_4(\operatorname{THF})_2]$   $(\operatorname{F}_x\operatorname{PhCO}_2^- = o$ -fluorobenzoate, o-F; mfluorobenzoate, m-F; p-fluorobenzoate, p-F; 2,6-difluorobenzoate, **2,6-F**<sub>2</sub>; 3,4-difluorobenzoate, **3,4-F**<sub>2</sub>; 3,5-difluorobenzoate, **3,5-F**<sub>2</sub>; 2,3,4-trifluorobenzoate, 2,3,4-F<sub>3</sub>; 2,3,6-trifluorobenzoate, 2,3,6-F<sub>3</sub>; 2,4,5-trifluorobenzoate, 2,4,5-F<sub>3</sub>; 2,4,6-trifluorobenzoate, 2,4,6-F<sub>3</sub>; 3,4,5-trifluorobenzoate, **3,4,5-F**<sub>3</sub>; 2,3,4,5-tetrafluorobenzoate, **2,3,4,5-F**<sub>4</sub>; 2,3,5,6-tetrafluorobenzoate, **2,3,5,6-F**<sub>4</sub>; pentafluorobenzoate, F<sub>5</sub>) (Chart 1).

#### Chart 1

Fluorine atoms on benzoic acid change its acidity, *i.e.*,  $pK_a$ , depending on the position on the ring and the number of substituents. The redox potentials of these complexes vary dramatically in relation to the  $pK_a$  of the F-substituted benzoate ligands. Interestingly, the collective law between the redox potential, and the  $pK_a$  of this series strongly depends on the moiety at the *o*-position (non-, mono-, and di-*o*-F), leading to a co-linear dependency with the *m*- and *p*-F groups in relation to non-, mono-, and di-*o*-substituted subgroups. Therefore, on the basis of a Hammett analysis, we were able to determine a Hammett constant for *o*-F,  $\sigma_o \approx 0.2$ , in this series. The present compounds encompass a wide range of redox potentials from -40 to 350 mV vs. Ag/Ag<sup>+</sup> in THF, giving an  $I_D$ -tunable series of a 1-e<sup>-</sup> donor [Ru<sub>2</sub><sup>II,II</sup>]. Furthermore, it was found that **2,3,6-F<sub>3</sub>**, **2,3,4,5-F<sub>4</sub>**,

**2,3,5,6-F**<sub>4</sub>, and **F**<sub>5</sub>, of which  $E_{1/2} > 300$  mV, were considerably stable even in air. Finally, molecular orbital (MO) calculations based on their crystal structures were performed to compare their HOMO energy levels with their redox potentials. In this paper, the syntheses, characterizations, and electrochemistry in comparison to energy levels of MOs of these complexes, which would afford us useful information to know their redox nature related to  $I_{\rm D}$ , are summarized.

#### Experimental

#### General procedures and materials

Except for **2,3,6-F**<sub>3</sub>, **2,3,4,5-F**<sub>4</sub>, **2,3,5,6-F**<sub>4</sub> and **F**<sub>5</sub>, all synthetic procedures were performed under anaerobic conditions using standard Schlenk techniques. All chemicals were purchased as reagent grade from commercial sources. THF, *n*-hexane, *N*,*N*-dimethylaniline (NDMA), and methanol were purchased from Wako Pure Chemical Industries, and except for methanol, dried and distilled with common drying agents under a nitrogen atmosphere before use.  $[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2]BF_4^{24}$  and  $[Ru_2^{II,III}(O_2CCH_3)_4CI]^{25}$  were prepared according to previously reported procedures.

# Syntheses of $[Ru_2^{II,II}(O_2CPh-o-F)_4(THF)_2]$ (o-F), $[Ru_2^{II,II}(O_2CPh-m-F)_4(THF)_2]$ (m-F), $[Ru_2^{II,II}(O_2CPh-p-F)_4(THF)_2]$ (p-F), $[Ru_2^{II,II}-(O_2CPh-2,6-F_2)_4(THF)_2]$ (2,6-F<sub>2</sub>), $[Ru_2^{II,II}(O_2CPh-3,4-F_2)_4(THF)_2]$ (3,4-F<sub>2</sub>), $[Ru_2^{II,II}(O_2CPh-3,5-F_2)_4(THF)_2]$ (3,5-F<sub>2</sub>), $[Ru_2^{II,II}(O_2CPh-2,3,4-F_3)_4(THF)_2]$ (2,3,4-F<sub>3</sub>), and $[Ru_2^{II,II}(O_2CPh-2,4,6-F_3)_4-(THF)_2]$ (2,4,6-F<sub>3</sub>)

The compounds were synthesized using a method based on a report by Furukawa and Kitagawa.<sup>22</sup> Only the procedure for o-F is described: [Ru<sub>2</sub><sup>II,III</sup>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(THF)<sub>2</sub>]BF<sub>4</sub> (335 mg, 0.5 mmol) and o-fluorobenzoic acid (280 mg, 2.0 mmol) were refluxed in 15 mL of NDMA for 12 h. After removal of the solvent in vacuo, the brown residue was washed with *n*-hexane (10 mL  $\times$  3) and dissolved in a minimum amount of THF. The red solution was filtered and then layered with *n*-hexane to obtain brown crystals of *o*-F after one week or more. Yield: 68%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>32</sub>F<sub>4</sub>O<sub>10</sub>Ru<sub>2</sub>: C 47.90, H 3.57. Found: C 47.80, H 3.57. IR (KBr):  $v(CO_2) = 1554$ , 1402 cm<sup>-1</sup>. For *m*-F, yield: 67%. Elemental analysis (%) calcd for  $C_{36}H_{32}F_4O_{10}Ru_2$ : C 47.90, H 3.57. Found: C 47.60, H 3.58. IR (KBr): v(CO<sub>2</sub>), 1558, 1396 cm<sup>-1</sup>. For *p*-**F**, yield: 68%. Elemental analysis (%) calcd for  $C_{36}H_{32}F_4O_{10}Ru_2$ : C 47.90, H 3.57. Found: C 47.91, H 3.78. IR (KBr): v(CO<sub>2</sub>) = 1554, 1407 cm<sup>-1</sup>. For  $2,6-F_2$ , yield: 63%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>28</sub>F<sub>8</sub>O<sub>10</sub>Ru<sub>2</sub>: C 44.36, H 2.90. Found: C 44.08, H 3.01. IR (KBr):  $v(CO_2) = 1570$ , 1406 cm<sup>-1</sup>. For **3,4-F<sub>2</sub>**, yield: 40%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>28</sub>F<sub>8</sub>O<sub>10</sub>Ru<sub>2</sub>: C 44.36, H 2.90. Found: C 44.32, H 2.84. IR (KBr):  $v(CO_2) = 1562$ , 1394 cm<sup>-1</sup>. For 3,5-F<sub>2</sub>, the reaction time should be taken for 14 h. Yield: 53%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>28</sub>F<sub>8</sub>O<sub>10</sub>Ru<sub>2</sub>: C 44.36, H 2.90. Found: C 44.36, H 3.16. IR (KBr):  $v(CO_2) = 1564$ , 1400 cm<sup>-1</sup>. For 2,3,4-F<sub>3</sub>, vield: 52%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>24</sub>F<sub>12</sub>O<sub>10</sub>Ru<sub>2</sub>: C 41.31, H 2.31. Found: C 41.39, H 2.45. IR (KBr): v(CO<sub>2</sub>) = 1571, 1400 cm<sup>-1</sup>. For **2,4,6-F**<sub>3</sub>, yield: 60%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>24</sub>F<sub>12</sub>O<sub>10</sub>Ru<sub>2</sub>: C 41.31, H 2.31. Found: C 41.40, H 2.52. IR (KBr):  $v(CO_2) = 1570$ , 1406 cm<sup>-1</sup>.



### Syntheses of $[Ru_2^{II,II}(O_2CPh-2,4,5-F_3)_4(THF)_2]$ (2,4,5-F<sub>3</sub>) and $[Ru_2^{II,II}(O_2CPh-3,4,5-F_3)_4(THF)_2]$ (3,4,5-F<sub>3</sub>)

These two compounds were synthesized step-by-step via a ligandsubstitution process involving  $[Ru_2^{II,III}]^+$ , followed by reduction to the final [Ru211,11] products.26 As a representative example, the procedure for **2,4,5-F**<sub>3</sub> is described: [Ru<sub>2</sub><sup>II,III</sup>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>Cl] (200 mg, 0.42 mmol) and 2,4,5-trifluorobenzoic acid (599 mg, 3.4 mmol) were refluxed in a 1:1 solution of MeOH-H<sub>2</sub>O (20 mL) for 12 h under aerobic conditions to give [Ru<sub>2</sub><sup>II,III</sup>(O<sub>2</sub>CPh-2,4,5-F<sub>3</sub>)<sub>4</sub>Cl]. The obtained red precipitate was collected by filtration, washed with water, and dried in vacuo. Without further purification, a solution of the crude product and Zn powder (52 mg, 0.80 mmol) in THF (10 mL) was stirred for 24 h under a nitrogen atmosphere. During this time, most of the solid dissolved. The reddish-colored solution was filtered, and the filtrate was layered with *n*-hexane to obtain brown crystals of 2,4,5-F<sub>3</sub> after one week or more. Yield: 45%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>24</sub>F<sub>12</sub>O<sub>10</sub>Ru<sub>2</sub>: C 41.31, H 2.31. Found: C 41.27, H 2.37. IR (KBr): v(CO<sub>2</sub>) = 1573, 1386 cm<sup>-1</sup>. For **3,4,5-F**<sub>3</sub>, yield: 60%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>24</sub>F<sub>12</sub>O<sub>10</sub>Ru<sub>2</sub>: C 41.31, H 2.31. Found: C 41.11, H 2.41. IR (KBr):  $v(CO_2) = 1529$ , 1415 cm<sup>-1</sup>.

#### Syntheses of $[Ru_2^{II,II}(O_2CPh-2,3,6-F_3)_4(THF)_2]$ (2,3,6-F<sub>3</sub>), $[Ru_2^{II,II}(O_2CPh-2,3,4,5-F_4)_4(THF)_2]$ (2,3,4,5-F<sub>4</sub>), $[Ru_2^{II,II}(O_2CPh-2,3,5,6-F_4)_4(THF)_2]$ (2,3,5,6-F<sub>4</sub>), and $[Ru_2^{II,II}(O_2CPh-F_5)_4(THF)_2]$ (F<sub>5</sub>)

For these compounds, the first part of the syntheses, i.e., the ligand-substitution process of [Ru2<sup>II,III</sup>(O2CCH3)4Cl], was performed under anaerobic conditions similar to the above method. However, the reduction of the Ru center occurred at the same time as the ligand substitution. As a representative example, the procedure for  $2,3,6-F_3$  is described:  $[Ru_2^{II,III}(O_2CCH_3)_4CI]$ (474 mg, 1.0 mmol) and 2,3,6-trifluorobenzoic acid (704 mg, 4.0 mmol) were refluxed in MeOH (100 mL) for 85 h under aerobic conditions. Then the solution was cooled to room temperature, and the solvent was evaporated under vacuum. After washing with degassed water and drying again, the residue was dissolved in a minimal amount of THF under a nitrogen atmosphere. The reddish-colored solution was filtered and then layered with nhexane to obtain brown crystals of 2,3,6-F<sub>3</sub> after one week or more. Yield: 56%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>24</sub>F<sub>12</sub>O<sub>10</sub>Ru<sub>2</sub>: C 41.31, H 2.31. Found: C 41.05, H 2.49. IR (KBr): v(CO<sub>2</sub>) = 1581, 1402 cm<sup>-1</sup>. For 2,3,4,5-F<sub>4</sub>, yield: 47%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>20</sub>F<sub>16</sub>O<sub>10</sub>Ru<sub>2</sub>: C 38.65, H 1.80. Found: C 38.69, H 2.01. IR (KBr):  $v(CO_2) = 1529$ , 1414 cm<sup>-1</sup>. For 2,3,5,6-F<sub>4</sub>, yield: 58%. Elemental analysis (%) calcd for C<sub>36</sub>H<sub>20</sub>F<sub>16</sub>O<sub>10</sub>Ru<sub>2</sub>: C 38.65, H 1.80. Found: C 38.54, H 1.88. IR (KBr): v(CO<sub>2</sub>) = 1589, 1398 cm<sup>-1</sup>. For F<sub>5</sub>, yield: 60%. ESI MS (MeOH) m/z: 1070.73  $[[Ru_2(F_5PhCO_2)_4]+Na]^+, 1220.62 [[Ru_2(F_5PhCO_2)_4]+Na+NaI]^+,$  $[[Ru_2(F_5PhCO_2)_4]+Na+2NaI]^+, 1520.41$   $[[Ru_2(F_5-$ 1370.52 PhCO<sub>2</sub>)<sub>4</sub>]+Na+3NaI]<sup>+</sup>, 1670.30 [[Ru<sub>2</sub>(F<sub>5</sub>PhCO<sub>2</sub>)<sub>4</sub>]+Na+4NaI]<sup>+</sup>. IR (KBr):  $v(CO_2) = 1596$ , 1400 cm<sup>-1</sup>.

#### Physical measurements

Infrared spectra were measured as KBr disks on a Jasco FT-IR 620 spectrophotometer. ESI MS was measured on a Bruker Daltonics APEXIII spectrometer. Magnetic susceptibility measurements

were conducted using a Quantum Design SQUID magnetometer (MPMS-XL or -5S) in the temperature range of 1.8-300 K, where the applied magnetic fields were 1 T for o-F and m-F and 0.1 T for the other complexes. Corrections for diamagnetism and for the samples wrapped in vinyl capsules were applied using Pascal's constants.<sup>27</sup> Cyclic voltammograms (CVs) were recorded in THF with tetra-*n*-butylammonium hexafluorophosphate n-Bu<sub>4</sub>N(PF<sub>6</sub>) (0.1 M) as supporting electrolyte under a nitrogen atmosphere using a BAS CV-50 W voltammetric analyzer. At the beginning of the measurements, CVs of the solvent with only supporting electrolyte were measured. To this solution were added the compounds ([Compound] =  $1 \times 10^{-3}$  M), and the CVs were acquired using a glassy carbon electrode as the working electrode, a Pt counter electrode, and an Ag/AgNO3 reference electrode. Finally, CV potentials were adjusted with the ferrocene/ferrocenium couple used as an internal standard (Fc/Fc<sup>+</sup> = 213 mV ( $\Delta E$  = 91 mV) in THF vs. Ag/Ag<sup>+</sup>).

#### Crystallographic analyses

Crystal data were collected on a Rigaku CCD diffractometer (Saturn 70 or VariMax) with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71070$  Å). The structures were solved using direct methods (SIR97).28 The non-hydrogen atoms were refined anisotropically, except for some disordered solvent atoms, which were refined isotropically. The hydrogen atoms were only introduced for non-disordered carbon atoms at fixed positions, because H atoms on disordered atoms seem to be not accurate in their position (in addition, electron density with less than 1e<sup>-</sup> is inconsequential for the accuracy of other atoms). The positiondisordered F atoms in o-F, m-F, and 3,4-F<sub>2</sub> and C atoms for THF in 3,5- $F_2$ , 3,4,5- $F_3$ , and  $F_5$  were first calculated with free occupancies to find subequal proportions of temperature factor between the possible two sites, and then adequate occupancies for the two sites, which come to 1, were determined to two places of decimals. Fullmatrix least-squares refinements on  $F^2$  converged with unweighted and weighted agreement factors of  $R1 = \Sigma ||F_0| - |F_c|| / \Sigma ||F_0|$  (I  $> 2.00\sigma(I)$  and all data), and  $wR2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}$ (all data), respectively. In some final analyses, relatively large residual electron densities remain around Ru centers, which are possibly due to satellite peaks of Ru atoms. A Sheldrick weighting scheme was used, where the f' and f' scattering factor values were refined in four places of decimals (the values were rounded in the CIF). All calculations were performed using the CrystalStructure crystallographic software package.<sup>29</sup> The crystal data and details of all compounds are summarized in Table 1.

#### **Computational details**

Molecular orbital (MO) calculations of the present complexes were carried out using the density functional theory (DFT) formalism with the unrestricted spin option, as implemented in the Gaussian03 software,<sup>30</sup> with the B3LYP (UB3LYP) exchange– correlation functional. The quasi-relativistic pseudo-potentials of the Ru atoms proposed by Hay and Wadt<sup>31</sup> with 16 valence electrons were employed, and LANL2TZ basis sets with polarization (LANL2TZ(f))<sup>32</sup> for Ru atoms and LANL2DZ basis sets with polarization and diffuse functions (LANL2DZpd)<sup>33</sup> for C, H, F and O atoms associated with the pseudo-potential

#### **Table 1** Crystallographic data of $[Ru_2(F_xPhCO_2)_4(THF)_2]$

	<i>o</i> -F	<i>m</i> -F	<i>p</i> -F	<b>2,6-F</b> <sub>2</sub>	3,4-F <sub>2</sub>	3,5-F <sub>2</sub>	2,3,4-F <sub>3</sub>
Formula	$C_{36}H_{32}O_{10}F_4Ru_2$	$C_{36}H_{32}O_{10}F_4Ru_2$	$C_{36}H_{32}O_{10}F_4Ru_2$	$C_{36}H_{28}O_{10}F_8Ru_2$	$C_{36}H_{28}O_{10}F_8Ru_2$	$C_{36}H_{28}O_{10}F_8Ru_2$	$C_{36}H_{24}O_{10}F_{12}Ru_2$
Formula weight	902.78 Manaalinia	902.78 Manaalinia	902.78 Manaalinia	974.74 Orth a sh a subia	974.74	974.74 Manaalinia	1046.70 Manaalinia
Space group	$C_2/c$	$P2_{n}$	$P_{2}/c$	P2.2.2	P2/c	N1000000000000000000000000000000000000	$P_{2}/c$
a/Å	19 188(7)	$\frac{1}{2}$	9.0627(19)	$12_{1}2_{1}2_{1}$ 12,4495(5)	9090(2)	10.634(3)	91898(5)
b/Å	9.225(3)	19.076(9)	17.772(3)	15.2218(7)	18.451(4)	10.835(3)	17.7022(9)
c/Å	20.991(8)	10.793(6)	11.225(2)	18.5927(8)	11.068(3)	15.883(5)	11.4563(9)
$\alpha/^{\circ}$	90	90	90	90	90	90	90
$\beta/^{\circ}$	111.679(5)	101.521(6)	109.466(2)	90	108.293(3)	95.196(4)	105.975(4)
$\gamma/^{\circ}$	90	90	90	90	90	90	90
$V/Å^3$	3453(2)	1746.0(16)	1704.6(6)	3523.4(3)	1762.5(7)	1822.4(9)	1791.74(19)
Z Crystal size/mm	$0.08 \times 0.05 \times$	$0.75 \times 0.08 \times$	$0.25 \times 0.20 \times$	$0.15 \times 0.13 \times$	$0.25 \times 0.10 \times$	$0.20 \times 0.15 \times$	$0.09 \times 0.04 \times$
	0.02	0.05	0.15	0.13	0.10	0.10	0.04
T/K	93(1)	93(1)	103(1)	93(1)	93(1)	93(1)	103(1)
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.737	1.717	1.759	1.837	1.837	1.776	1.940
F <sub>000</sub>	1808.00	904.00	904.00	1936.00	968.00	968.00	1032.00
$\lambda/A$	0.71070	0.71070	0.71070	0.71070	0.71070	0.71070	0.71070
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	9.553	9.446	9.676	9.593	9.588	9.273	9.659
Data measured	15156	14039	13003	28681	12930	14413	14298
data unique	4728	3978	3868	7908	3942	4151	4024
R <sub>int</sub>	0.066	0.088	0.023	0.01/	0.110	0.0729	0.018
No. of observations	3004	3978	3808	/908	3942	3/01	4024
$P_{L} = 2.00 \sigma(I)^{a}$	2/1	243	231	500 0.0107	207	204	265
$R_1 (I > 2.000(I))^{\alpha}$	0.0393	0.0449	0.0313	0.0197	0.0098	0.0331	0.0218
R (all reflections) <sup>b</sup>	0.0418	0.0000	0.0370	0.0200	0.0801	0.0891	0.0290
GOF	1 003	0.1070	1 019	1.066	1 009	1 019	1 113
Flack narameter		0.000		0.155(13)			
CCDC No.	766149	766148	766150	766142	766145	766146	766136
	236.F.	2 4 5-F.	246-F.	3 4 5-F.	2345-F	2356-F	
	2,3,0-Г <sub>3</sub>	2,4,3-13	2,4,0-13	<b>3,4,3-r</b> <sub>3</sub>	2,3,4,3-г4	2,3,3,0-F <sub>4</sub>	<b>F</b> 5
Formula	$C_{36}H_{24}O_{10}F_{12}Ru_2$	$C_{36}H_{24}O_{10}F_{12}Ru_2$	$C_{36}H_{24}O_{10}F_{12}Ru_2$	$C_{36}H_{24}O_{10}F_{12}Ru_2$	$C_{36}H_{20}O_{10}F_{16}Ru_2$	$C_{36}H_{20}O_{10}F_{16}Ru_2$	$C_{36}H_{16}O_{10}F_{20}Ru_2$
Formula weight	1046.70	1046.70	1046.70	1046.70	1118.66	1118.66	1190.62
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Iriclinic
Space group	$P_{2_1}/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	P1
a/A	9.0102(17)	9.25/2(16)	8./241(5)	8.882(3)	12.000(3)	8.8140(17)	10.838(4)
D/A	11.332(2) 16.766(2)	19.413(3) 10.1825(17)	12.0006(8)	17.855(4)	17.274(4) 17.522(4)	10.920(3) 12.077(2)	11./33(4)
c/A	10.700(5)	10.1855(17)	17.9403(8)	12.027(5)	17.525(4)	13.077(3)	13.317(3) 77.607(9)
β/°	100.046(2)	103 330(2)	101 429(2)	109 561(3)	107 667(4)	109 572(2)	81 127(11)
$\gamma / ^{\circ}$	90	90	90	90	90	90	86 496(10)
$V/Å^3$	1802.1(6)	1780 7(5)	1841 01(18)	1886 9(8)	3653 3(15)	1838 2(6)	1907.0(11)
Z	2	2	2	2	4	2	2
Crystal size/mm	$0.50 \times 0.20 \times$	$0.10 \times 0.08 \times$	$0.20 \times 0.10 \times$	$0.46 \times 0.05 \times$	$0.32 \times 0.13 \times$	$0.65 \times 0.12 \times$	$0.47 \times 0.15 \times$
	0.10	0.03	0.08	0.05	0.04	0.08	0.14
T/K	93(1)	93(1)	93(1)	193(1)	93(1)	93(1)	93(1)
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.929	1.952	1.888	1.842	2.034	2.021	2.073
$F_{000}$	1032.00	1032.00	1032.00	1032.00	2192.00	1096.00	1160.00
$\lambda/A$	0./10/0	0./10/0	0./10/0	0./10/0	0./10/0	0./10/0	0./10/0
$\mu(MO-K\alpha)/cm^{-1}$	9.603	9./18	9.400	9.172	9.697	9.035	9.501
Data measured	14200	14300	11977	13034	20009	15200	13000
	4048	4072	4133	4297	0.035	4129	0.0250
No. of observations	4048	4072	4135	4297	8194	4129	8337
No of variables	272	272	283	275	597	290	615
$R_{1}(I > 2 (0)\sigma(I))^{a}$	<i>212</i>	0.0471	0 0267	0.0389	0.0523	0.0620	0.0282
	0.0273	1104/1		0.0000	0.0020	0.0020	0.0202
R (all reflections) <sup><i>a</i></sup>	0.0273 0.0322	0.0471	0.0335	0.0482	0.0774	0.0676	0.0372
R (all reflections) <sup><i>a</i></sup> $wR_2$ (all reflections) <sup><i>b</i></sup>	0.0273 0.0322 0.0721	0.0622 0.1130	0.0335 0.0655	0.0482 0.1036	0.0774 0.1438	$0.0676 \\ 0.1644$	0.0372 0.0605
R (all reflections) <sup><i>a</i></sup> $wR_2$ (all reflections) <sup><i>b</i></sup> GOF	0.0273 0.0322 0.0721 0.970	0.0471 0.0622 0.1130 1.123	0.0335 0.0655 1.027	0.0482 0.1036 1.004	0.0774 0.1438 1.009	0.0676 0.1644 1.070	0.0372 0.0605 1.109
$R \text{ (all reflections)}^{a}$ $WR_2 \text{ (all reflections)}^{b}$ $GOF$ Flack parameter	0.0273 0.0322 0.0721 0.970	0.06471 0.0622 0.1130 1.123	0.0335 0.0655 1.027	0.0482 0.1036 1.004	0.0774 0.1438 1.009	0.0676 0.1644 1.070	0.0372 0.0605 1.109

were adopted. In the calculations, spin polarization with  $S_z = 1$  (spin multiplicity of 3) for all [Ru<sub>2</sub>] units was used. The atomic coordinates determined by using X-ray crystallography with those for [Ru<sub>2</sub>(PhCO<sub>2</sub>)<sub>4</sub>(THF)<sub>2</sub>] being taken from ref. 22 were used. In the case of disordered fluorine atoms on the benzoate groups, the fluorine atoms with major occupancy were used, and H atoms were added instead of vacant positions.

#### **Results and discussion**

The one-step synthetic method reported by Furukawa and Kitagawa,<sup>22</sup> in which ligand-substitution and reduction of the diruthenium center of [Ru2<sup>II,III</sup>(CH3CO2)4(THF)2]<sup>+</sup> occurring in N,N-dimethylaniline (NDMA), was used to synthesize most of the [Ru2<sup>II,II</sup>] complexes with mono-, di-, and tri-F-substituted benzoate ligands. However, in the cases of 2,4,5-F<sub>3</sub> and 3,4,5- $\mathbf{F}_{3}$ , the  $[\mathbf{R}\mathbf{u}_{2}^{II,II}]$  complexes reacted with 4,4'-methylenebis(N,Ndimethylaniline) (NDMA-me-NDMA), which formed from the oxidation of NDMA, to afford [Ru2<sup>II,II</sup>(FxPhCO2)4(NDMA-me-NDMA)<sub>2</sub>] even after several attempts to purify it with THF-nhexane for modifying from NDMA-me-NDMA to THF (2,4,5-F<sub>3</sub>-NDMA: CCDC-766139; 3,4,5-F<sub>3</sub>-NDMA: CCDC 766143; Table S1 and Fig. S1<sup>†</sup>). Therefore, a step-by-step procedure via the isolation of  $[Ru_2^{II,III}(F_xPhCO_2)_4Cl]$ , followed by reduction with Zn powder,<sup>26</sup> was used to prepare the THF-adducts of these complexes. Note that this procedure should be applicable to the preparation of other [Ru2<sup>II,II</sup>] compounds even if two steps are required. In the cases of 2,3,5,6-F<sub>4</sub> and F<sub>5</sub>, the NDMA method afforded only [Ru211,11(CH3CO2)4(THF)2] in high yield without substitution of the CH3CO2- ligands, which is formed from the reduction of the starting material. Interestingly, the ligandsubstituted [Ru2<sup>II,II</sup>] complexes for these species were obtained as methanol-adducts from the ligand-substitution reaction of [Ru<sub>2</sub><sup>II,III</sup>(CH<sub>3</sub>CO<sub>2</sub>)<sub>4</sub>Cl] with methanol in air, which were then modified to obtain the desired complexes by crystallizing in THF under an  $N_2$  atmosphere. Although complexes 2,3,6-F<sub>3</sub> and 2,3,4,5- $F_4$  could be synthesized by using the one-step reaction in NDMA, they were produced in low yield. However, they as well as 2,3,5,6- $F_4$ , and  $F_5$  could be prepared in high yield by using the aerobic reaction in MeOH. Even under aerobic conditions, which are usually disadvantageous for the syntheses of [Ru2<sup>II,II</sup>] species, the reduction of [Ru2<sup>II,III</sup>]+ occurred simultaneously with ligand substitution, indicating that fluorine atoms of 2,3,6-F<sub>3</sub>, 2,3,4,5-F<sub>4</sub>, 2,3,5,6-F<sub>4</sub>, and F<sub>5</sub> act as strong electron-withdrawing groups, stabilizing the  $[Ru_2^{II,II}]$  state in air (see electrochemistry).

All compounds were structurally characterized by using single crystal X-ray crystallography. Fig. 1 shows ORTEP drawings of o-F, 2,6-F<sub>2</sub>, 2,4,6-F<sub>3</sub>, 2,3,5,6-F<sub>4</sub>, and F<sub>5</sub> (the other complexes are shown in Fig. S2†), and the relevant bond lengths around the Ru centers are summarized in Table 2 together with those of several representative [Ru<sub>2</sub><sup>II,II</sup>],<sup>4b,15,1618-20,22,23</sup> and [Ru<sub>2</sub><sup>II,III</sup>]<sup>+</sup> complexes.<sup>20,34-36</sup> Except for 2,6-F<sub>2</sub> and 2,3,4,5-F<sub>4</sub>, the complexes have an inversion center on the midpoint of the Ru–Ru vector. Complex F<sub>5</sub> contains two structurally-independent units in a unit cell, which are very similar to each other (one of them was depicted in Fig. 1e), even if one of them has a disordering form in the part of THF moieties (Fig. S3†). The Ru–Ru bond lengths of complexes are in the range of 2.27–2.28 Å similar to those of previously reported [Ru<sub>2</sub><sup>II,III</sup>] compounds (see Table 2). However, the Ru–Ru bond length has



**Fig. 1** ORTEP drawings of (a) *o*-**F**, (b) **2,6-F**<sub>2</sub>, (c) **2,4,6-F**<sub>3</sub>, (d) **2,3,5,6-F**<sub>4</sub>, and (e) **F**<sub>5</sub> (one unit in an asymmetric set), where the dotted bonds for F atoms represent disordered atomic positions (50% probability thermal ellipsoids; symmetry operations (\*) -x-1/2, -y-1.5, -z+1 for *o*-**F**; -x+1, -y+1, -z for **2,4,6-F**<sub>2</sub>; -x+2, -y+2, -z+1 for **2,3,5,6-F**<sub>4</sub>; -x+2, -y+1, -z+1 for **F**<sub>5</sub>).

been shown to be scarcely dependent on the valence state of the Ru centers, although the formal Ru–Ru bond order is 2.5 for  $[Ru_2^{II,III}]^+$ and 2 for  $[Ru_2^{II,II}]$ . On the basis of the  $[Ru_2^{II,III}]^+$  complexes in Table 2, the Ru-Ru bond lengths are basically in the range of 2.25-2.29 Å. In other words, the bond length does not provide proof for the valence state of the compounds. The bonds that reflect the valence state of the Ru centers are the Ru-O(carboxylate) bonds (Ru– $O_{eq}$ ), of which one set of  $\delta$  frontier orbitals ( $[\delta\delta^*]_2$ ) made from the  $d_{x^2-y^2}$  and  $d_{xy}$  orbitals of the two Ru atoms mainly form the bond. Another set of  $\delta\delta^*$  orbitals is used for the Ru-Ru bond and an electron in this  $\delta^*$  orbital is directly related to the valence state of the metals (vide infra). The electron configurations of the valence states are  $\sigma^2 \pi_2^4 \delta^2 \delta^{*2} \pi^{*2} \sigma^{*0}$  for  $[Ru_2^{II,II}]$  (S = 1) and  $\sigma^2 \pi_2^4 \delta^2 \delta^{*1} \pi_2^{*2} \sigma^{*0}$  for  $[Ru_2^{II,III}]^+$  (S = 3/2) since the  $\delta^*$  and  $\pi^*$ orbitals are degenerate. In other words, if an electron is added or removed from the  $\delta^*$  orbital of the Ru–Ru bond during reduction or oxidation, respectively, the Ru-O<sub>eq</sub> bond is affected, and the

**Table 2** Relevant bond lengths around Ru centers in  $[Ru_2^{II,II}(F_xPhCO_2)_4(X)_2]$  and related compounds (where  $O_{eq}$  means oxygen atoms of equatorial positions and  $X_{ax}$  is axially-coordinating atoms) and dihedral angles defined by LS planes composed of atom sets of phenyl group (Plane 1) and carboxyl groups and diruthenium (Plane 2)

		Averaged Ru–O <sub>eq</sub> /Å		Dihedral angles between Plane 1 and Plane 2/°					
Compound	Ru–Ru/Å		Ru–X <sub>ax</sub> /Å	Set-1	Set-2	Set-3	Set-4	Average	Ref
[Ru <sub>2</sub> <sup>II,II</sup> ] compounds									
$\frac{[Ru_2^{II,II}(CH_3CO_2)_4(THF)_2]}{[Ru_2^{II,II}(CH_3CO_2)_4(H_2O)_2]}$	2.261(3) 2.262(3)	2.060 2.068	2.391(5) 2.335(4)						15b 15b
$[\operatorname{Ru}_{2}^{\mathrm{II},\mathrm{II}}(\operatorname{EtCO}_{2})_{4}(\operatorname{Me}_{2}\operatorname{CO})_{2}]$	2.260(3)	2.068	2.363(5)						15b
$[Ru_2^{II,II}(C_{10}H_{15}CO_2)_4(MeOH)_2]$	2.2809(9)	2.017	2.287(5)						19
$[\operatorname{Ru}_{2}^{II,II} \{ L-C_{6}H_{5}(OH)CHCO_{2} \}_{4} - (H_{2}O)_{2} ]$	2.266(1)	2.062	2.348ª						18
	2.265(1)	2.069	2.351ª						
$[Ru_2^{II,II}(CF_3CO_2)_4]_{\infty}$	$2.2679(5)^{b}$	$2.066(2)^{b}$	$2.363(2)^{b}$						23
$[Ru_2^{II,II}(CF_3CO_2)_4(THF)_2]$	2.276(3)	2.073	2.268(6)						16
$[Ru_2^{II,II}(CF_3CO_2)_4(C_{16}H_{16})]_{\infty}$	2.2993(5)	2.064(3)	2.670(3)						23
$[Ru_2^{II,II}(CF_3CO_2)_3(C_2H_5CO_2)]$	2.2613(7)	2.064(3)	2.347(3)						23
$[\operatorname{Ru}_{2}^{II,II}(\operatorname{CF}_{3}\operatorname{CO}_{2})_{4}(\operatorname{Tempo})_{2}]$	$2.300(2)^{c}$	2.068 <sup>c</sup>	$2.136(5)^{c}$						4b
$[Ru_2^{II,II}(PhCO_2)_4(THF)_2]$	2.2642(8)	2.065	2.341(4)						22
$[\operatorname{Ru}_{2}^{II,II}(p-\operatorname{MePhCO}_{2})_{4}(\operatorname{THF})_{2}]$	2.2689(11)	2.064	2.3696(24)						20
$[\operatorname{Ru}_{2}^{II,II}(p-\operatorname{MePhCO}_{2})_{4}(\operatorname{CH}_{3}\operatorname{CN})_{2}]$	2.2727(10)	2.063	2.331(5)						20
$[Ru_2^{II,II}(NapCO_2)_4(THF)_2]$	2.2672(3)	2.068	2.347(2)						22
$[Ru_2^{II,II}(AntCO_2)_4(THF)_2]$ (unit 1)	2.2633(7)	2.062	2.340(2)						22
(unit 2)	2.2649(8)	2.068	2.342(2)						
<i>o</i> -F	2.2669(2)	2.067	2.312(2)	37.489	17.691			27.59	
<i>m</i> -F	2.2691(4)	2.065	2.331(2)	3.168	19.521			11.34	
<i>p</i> -F	2.2677(2)	2.061	2.3537(15)	19.476	15.782			17.63	
2,6-F <sub>2</sub>	2.2706(2)	2.065	2.332ª	41.986	32.675	31.249	43.651	37.39	
3,4-F <sub>2</sub>	2.2744(4)	2.064	2.354(3)	19.798	14.040			16.92	
3,5-F <sub>2</sub>	2.2708(8)	2.0728	2.310(5)	20.112	8.082			14.10	
2,3,4-F <sub>3</sub>	2.2712(2)	2.066	2.3334(11)	22.621	17.685			20.15	
2,3,6-F <sub>3</sub>	2.2719(2)	2.070	2.3022(17)	61.174	41.925			51.55	
2,4,5-F <sub>3</sub>	2.2703(3)	2.068	2.329(2)	11.441	15.118			13.28	
2,4,6-F <sub>3</sub>	2.2723(2)	2.071	2.2829(16)	51.836	76.474			64.16	
3,4,5-F <sub>3</sub>	2.2767(5)	2.067	2.307(2)	18.224	27.779			23.00	
2,3,4,5-F <sub>4</sub>	2.2774(4)	2.068	2.299 <sup>a</sup>	29.769	21.556	35.452	18.028	26.20	
2,3,5,6-F <sub>4</sub>	2.2731(3)	2.065	2.298(2)	36.677	26.341			31.51	
$F_5$ (unit 1)	2.2754(7)	2.070	2.318(2)	25.842	33.434			29.64	
(unit 2)	2.2804(8)	2.068	2.308(3)	42.000	38.666	_	_	40.33	
[Ru <sub>2</sub> <sup>II,III</sup> ] <sup>+</sup> compounds									
[Ru <sub>2</sub> <sup>II,III</sup> (CH <sub>3</sub> CO <sub>2</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]BF <sub>4</sub>	2.248(1)	2.00	2.31 <sup>a</sup>						34
[Ru <sub>2</sub> <sup>II,III</sup> ( <i>p</i> -	2.2618(16)	2.06	2.258(6)						20
MePhCO <sub>2</sub> ) <sub>4</sub> (THF) <sub>2</sub> ]BF <sub>4</sub>	. /								
$[Ru_2^{II,III}(PhCO_2)_4Cl]$	2.290(1)	2.019	2.532(1)						35
$[\mathrm{Ru}_{2}^{\mathrm{II},\mathrm{III}}(\mathrm{CH}_{3}\mathrm{CO}_{2})_{4}\mathrm{Cl}]$	2.287(2)	2.017	2.577(1)						36
<sup><i>a</i></sup> Averaged value. <sup><i>b</i></sup> at 100 K. <sup><i>c</i></sup> at 201	К.								

Ru– $O_{eq}$  bond lengths vary in the range of 2.00–2.02 Å and 2.06–2.07 Å for  $[Ru_2^{II,II}]^+$  and  $[Ru_2^{II,II}]$ , respectively.<sup>1</sup> In the case of the present compounds, the bond lengths are about 2.06–2.07 Å, consistent with  $[Ru_2^{II,II}]$ . The bond lengths involving the axial THF (Ru– $O_{ax}$ ) of *ca.* 2.3–2.4 Å are also characteristic of the  $[Ru_2^{II,II}]$  valence state.

Magnetic data correlated well with the orbital states of the spin ground state of  $[Ru_2^{II,II}]$  compounds. The temperature dependence of the dc susceptibilities of all compounds was measured on polycrystalline samples in the temperature range of 1.8–300 K at 1 T for *o*-F and *m*-F and 0.1 T for the other complexes (the  $\chi$  and  $\chi T vs. T$  plots are shown in Fig. S4†). The  $\chi T$  values at 300 K were determined to be in the range of 0.74–1.07 cm<sup>3</sup> K mol<sup>-1</sup>, which,

upon cooling, decreased smoothly to be in the range of  $9.6 \times 10^{-3}$ –  $2.0 \times 10^{-2}$  cm<sup>3</sup> K mol<sup>-1</sup> at 1.8 K. However, the  $\chi$  values increased with a decrease in the temperature to about 100 K and then reached a plateau, followed by an increase at temperatures below 10 K. These features of the  $\chi$  and  $\chi T$  vs. T plots are consistent with those for isolated [Ru<sub>2</sub><sup>II,II</sup>] complexes with an S = 1 ground state affected by strong zero-field splitting (ZFS;  $D \approx 230-320$  cm<sup>-1</sup>). The increase in  $\chi$  at low temperatures was ascribed to a paramagnetic [Ru<sub>2</sub><sup>II,III</sup>]<sup>+</sup> species with S = 3/2. The magnetic data were simulated by using a Curie paramagnetic model with S = 1 taking into account ZFS, temperature-independent paramagnetism (TIP), an impurity with S = 3/2 ( $\rho$ ), and intermolecular interactions (*zJ*) commonly used for magnetically isolated or weakly interacting

**Table 3** Magnetic parameters of  $[Ru_2(F_xPhCO_2)_4(THF)_2]$  with g = 2.00 (fix) and zJ' = 0 (fix)

Compounds	$D/k_{\rm B}/{ m K}$	$TIP  [\times  10^{-6} \ cm^3 \ mol^{-1}]$	ho [× 10 <sup>-3</sup> ]	R <sup>a</sup> [×10 <sup>-8</sup> ]
<i>o</i> -F	333(1)	251(14)	2.84(3)	40.1
<i>m</i> -F	366(1)	476(15)	3.90(5)	41.4
p-F	449(1)	287(9)	6.91(1)	9.47
2,6-F <sub>2</sub>	341(1)	347(15)	4.03(3)	49.4
$3, 4-F_2$	356(1)	362(12)	2.46(6)	19.8
3,5-F <sub>2</sub>	385.7(5)	215(5)	1.243(9)	4.52
$2,3,4-F_3$	358.1(4)	695(4)	0.511(8)	3.99
$2,3,6-F_3$	367(1)	610(17)	3.18(3)	52.7
$2,4,5-F_3$	370.3(6)	298(6)	1.11(1)	6.41
$2,4,6-F_3$	374.5(6)	341(6)	4.73(3)	4.33
3,4,5-F <sub>3</sub>	375(1)	762(14)	6.24(4)	28.4
2,3,4,5-F <sub>4</sub>	368.2(8)	619(8)	4.77(1)	12.4
2,3,5,6-F <sub>4</sub>	345.5(4)	530(5)	0.516(8)	4.33
$F_5$	396.5(4)	388(4)	0.046(7)	2.67
<sup><i>a</i></sup> $R = \Sigma (\chi_{calc} -$	$(\chi_{\rm obs})^2 / \Sigma \chi_{\rm obs}$	2 ( · ) 2 ( · )		,

 $[\operatorname{Ru}_2^{II,II}]$  complexes.<sup>13,23,37</sup> The intermolecular interaction (zJ) was introduced in the framework of the mean-field approximation but not required to obtain adequate fitting (so,  $zJ \approx 0$  for all complexes). The best fit of parameters for all compounds are listed in Table 3, where the *g* value was fixed to 2.00. The estimated *D* value is typical for general [ $\operatorname{Ru}_2^{II,II}$ ] species.<sup>17,18,21,23</sup>

Understanding the effects of the F-substituents on the redox properties is the main subject of this report. Cyclic voltammograms (vs. Ag/Ag<sup>+</sup>) of each compound acquired in N<sub>2</sub>-saturated THF solutions with *n*-Bu<sub>4</sub>N(PF<sub>6</sub>) as the supporting electrolyte are shown in Fig. 2. For all compounds, a reversible one-electron redox wave, assigned to  $[Ru_2^{II,II}]/[Ru_2^{II,III}]^+$ , was observed with  $I_c/I_a \approx 1$  and  $\Delta E_p \approx 47-183$  mV. It should be emphasized that the redox potential of the present series was observed over a wide range of potentials from -40 to *ca.* 350 mV, showing that the substituent had an effect on the redox properties of the complexes. The electrochemical data are summarized in Table 4 together with  $pK_a$  of the corresponding F-substituted benzoic acids and the summation of the Hammett constants for *m*- and *p*-F groups,  $\Sigma(x\sigma_m + y\sigma_p)$ , where  $\sigma_m = 0.337$ ,  $\sigma_p = 0.062^{38}$  and *x* and *y* the are numbers of *m*- and *p*-F-substituents, respectively.

Because there are F atoms at the *o*-positions in some complexes, it can be difficult to evaluate the compounds using a unified methodology, such as a general Hammett analysis. Therefore, in order to compare all of the redox potentials, the half-wave potential  $(E_{1/2})$  of the  $[\mathbf{Ru}_2^{II,II}]/[\mathbf{Ru}_2^{II,III}]^+$  redox wave of the complexes and  $[Ru_2(PhCO_2)_4(THF)_2]^{22}$  were plotted as a function of  $pK_a$  of the corresponding benzoic acids (Fig. 3). The correlation between  $E_{1/2}$  and p $K_a$  of the ligands is seemingly complicated. However, the ligands could be classified into three groups independent of the other substituent positions: non-, mono-, and di-o-substituted complexes. These classifications show that: (1) The  $pK_a$  value, which represents the electronic state at the terminal oxygen atoms of the carboxylate ligands, is strongly affected by the presence of o-F atoms. The p $K_a$  ranges for each group are 3.5–4.2, 2.5–3.3, and 1.5-2.5 for the non-, mono-, and di-o-substituted carboxylates, respectively. (2) In the respective groups,  $E_{1/2}$  is dependent on the electronic effect of m- and p-F groups, which obeys the general Hammett law (vide infra), leading to a linear relationship within each group and similar slopes. (3) The separation between neighboring lines ( $\Delta p K_a$ ) is almost identical, meaning that the *o*-F



**Fig. 2** Cyclic voltammograms of a series of  $[Ru_2^{II,II}(F_xPhCO_2)_4(THF)_2]$ in THF containing 0.1 M *n*-Bu<sub>4</sub>N(PF<sub>6</sub>) under N<sub>2</sub>.



**Fig. 3** Plot of half-wave redox potential  $(E_{1/2})$  vs.  $pK_a$ , where  $E_{1/2}$  are values measured in THF with a Ag/Ag<sup>+</sup> reference electrode. The red, green, and blue solid lines represent the linear least-squares fitted lines for non-, mono-, and di-*o*-F substituted groups, respectively.

atoms could have an electronic effect rather than a steric effect at least in solution. If a steric effect due to *o*-F atoms is dominant,  $\Delta pK_a$  between the non- and mono-*o*-F subgroups would be much larger than that between lines of the mono- and di-*o*-F groups.

 $E_{1/2}$  was plotted as a function of  $\Sigma(x\sigma_m + y\sigma_p)$ , as shown in Fig. 4a. Linear trends in respective non-, mono-, and di-*o*-F groups as well as the p $K_a$  dependence were observed, although mismatches in the data from the linear least-squares fitted lines

Compounds	$E_{\rm a}/{\rm mV}$	$E_{\rm c}/{\rm mV}$	$E_{1/2}/{ m mV}$	$\Delta E_{\rm p}/{ m mV}$	$I_{\rm a}/I_{\rm c}$	$pK_a$ of $F_x$ PhCO <sub>2</sub> H	$\Sigma (x\sigma_{\rm m}+y\sigma_{\rm p})^b$	$\Sigma (x\sigma_{\rm m} + y\sigma_{\rm p} + z\sigma_{\rm o})^{c}$
$[Ru_2^{II,II}(PhCO_2)_4(THF)_2]^d$	nd	nd	60	nd	nd	4.20	0	0
<i>o</i> -F	84	-14	35	98	1.00	3.27	0	0.200
<i>m</i> -F	99	-15	42	114	0.99	3.86	0.337	0.337
<i>p</i> -F	11	-89	-39	100	0.99	4.14	0.062	0.062
2,6-F <sub>2</sub>	115	-14	51	129	1.02	2.34	0	0.400
3,4-F <sub>2</sub>	235	52	144	183	0.96	3.80	0.399	0.399
3,5-F <sub>2</sub>	230	125	178	105	1.08	3.59	0.674	0.674
2,3,4-F <sub>3</sub>	278	139	209	139	1.06	2.87	0.399	0.599
2,3,6-F <sub>3</sub>	394	277	336	117	1.01	2.00	0.337	0.737
2,4,5-F <sub>3</sub>	263	164	214	99	1.01	2.87	0.399	0.599
2,4,6-F <sub>3</sub>	244	99	172	145	1.10	2.28	0.062	0.462
3,4,5-F <sub>3</sub>	334	213	274	121	1.06	3.46	0.736	0.736
2,3,4,5-F <sub>4</sub>	383	246	315	137	1.09	2.53	0.736	0.936
2,3,5,6-F <sub>4</sub>	412	308	360	104	1.00	1.66	0.674	1.074
<b>F</b> <sub>5</sub>	429	287	358	142	0.99	1.60	0.736	1.136

**Table 4** Electrochemical data of  $[Ru_2(F_xPhCO_2)_4(X)_2]$  measured in THF containing 0.1 M *n*-Bu<sub>4</sub>N(PF<sub>6</sub>) under N<sub>2</sub> (mV vs. Ag/Ag<sup>+</sup>)<sup>*a*</sup> (nd = no referential data)

<sup>*a*</sup> The ferrocene/ferrocenium couple, Fc/Fc<sup>+</sup> = 213 mV ( $I_c/I_a \approx 1$ ,  $\Delta E_p = 91$  mV), was observed at the same condition described in the Experimental Section in the text. <sup>*b*</sup>  $\sigma_m = 0.337$ ,  $\sigma_p = 0.062$  referred from ref. 38 <sup>*c*</sup>  $\sigma_o = 0.2$  was experimentally estimated in this work. <sup>*d*</sup> Ref. 22.



**Fig. 4** Plots of half-wave redox potential  $(E_{1/2}) vs.$  (a)  $\Sigma(x\sigma_m + y\sigma_p)$  and (b)  $\Sigma(x\sigma_m + y\sigma_p + z\sigma_o)$ , where  $\sigma_m = 0.337$ ,  $\sigma_p = 0.062$ , and  $\sigma_o = 0.2$  and x, y, and z are numbers of *m*-, *p*-, and *o*-F-substitutions, respectively. The solid lines in (a) represent the linear least-squares fitted line for respective subgroups, and the solid line in (b) represents that for all data.

occurred. Considering the results of the  $pK_a$  dependence, only the number of *o*-F atoms had an effect. Namely, the separation among the lines of the non-, mono-, and di-*o*-F groups is mainly caused

by the electronic effect of the *o*-F atoms. Thus, we estimated a Hammett constant for *o*-F ( $\sigma_o$ ) to be 0.2 and revised Fig. 4a as a function of  $\Sigma(x\sigma_m + y\sigma_p + z\sigma_o)$  (Fig. 4b), where *z* is 0 to 2 for the non-, mono-, and di-*o*-F groups, respectively. The relationship was found to be linear. It should be pointed out that the electronic effect of the *o*-F atoms affecting the redox properties of [Ru<sub>2</sub><sup>II,II</sup>] complexes is intermediate between those of the *m*- and *p*-F atoms. Thus, by adding fluorine atoms on the benzoate ligand, we were able to tune systematically the redox properties of [Ru<sub>2</sub><sup>II,II</sup>] complexes.

In order to determine the energy levels of molecular orbitals in the present compounds, calculations based on density functional theory (DFT) at the B3LYP (UB3LYP) level with basis functions LANL2TZ(f)<sup>32</sup> for Ru and LANL2DZpd<sup>33</sup> for other atoms, where the atomic coordinates determined from X-ray crystallography were used, an  $S_z = 1$  (spin multiplicity of 3) spin state was assumed because of their paramagnetic character confirmed by using magnetic measurements, and the charge of molecules was zero, were carried out using Gaussian 03. As a representative example, the energy levels of the frontier orbitals involving the  $\pi^*$  and  $\delta^*$  orbitals on the diruthenium unit of **2,6-F**<sub>2</sub> are shown in Fig. 5 (Fig. S5<sup>†</sup> for others). Taking into account the correlations between electrons, on the basis of the calculations using the UB3LYP function with a spin multiplicity of 3 ( $S_z = 1$ ), the configurations of the  $\alpha$  and  $\beta$  electrons are given,<sup>39</sup> and the HOMO level corresponds to  $\delta^*(\beta)$ , which is most likely involved in the [Ru2<sup>II,II</sup>]/[Ru2<sup>II,III</sup>]<sup>+</sup> couple. The list of energy levels calculated for each complex is given in Table S2.<sup>†</sup>

Fig. 6 shows a plot of the HOMO ( $\delta^*$  for  $\beta$  spin) energy levels *vs.*  $pK_a$  of the ligands. We observed a similar trend to that in the plot of  $E_{1/2}$  *vs.*  $pK_a$  in Fig. 3, in which three groups made up of non-, mono-, and di-*o*-F substituted complexes obeying quasi-linear relationships dependent on the presence of *m*- and *p*-F substituents, where the solid lines represent the leastsquares fitted lines for each group. Thus, the effect of the F atoms corresponds to the energy levels estimated by using DFT calculations based on solid-state structures. The real HOMO level is directly associated with  $I_D$  of the complexes. Therefore, understanding the relationship between the calculated HOMO



Fig. 5 Frontier orbitals associated with  $\pi^*$  and  $\delta^*$  orbitals of the diruthenium unit of **2,6-F**<sub>2</sub> and their energy levels (eV), where  $\delta^*$  for  $\beta$  electron corresponds to HOMO level. See Fig. S5<sup>†</sup> and Table S2<sup>†</sup> for the other complexes.



**Fig. 6** Plot of HOMO ( $\delta^*(\beta)$ ) level *vs.* p $K_a$ . The red, green, and blue solid lines represent the least-squares linear fit lines for non-, mono-, and di-*o*-F substituted groups, respectively.

level in the solid state and  $E_{1/2}$  in solution is very convenient for estimating the real HOMO level of the complexes in redox reaction media (*i.e.*, in solution). In the plot of the HOMO ( $\delta^*$  for  $\beta$  spin) energy levels vs.  $pK_a$  (Fig. 6), lines for the mono- and di-o-F groups are not parallel to that for the non-o-F group, whereas they are almost parallel to each other in the plot of  $E_{1/2}$  vs. p $K_a$  (see Fig. 3). This is most likely because there is a structural (steric) effect in the estimated energy levels in addition to the electronic effect due to the use of the solid-state atomic coordinates. A plot of the HOMO energy level vs.  $E_{1/2}$  is shown in Fig. 7, where the solid line is the least-squares fitted (LS) line for the non-o-F group. We define the LS line for the non-o-F group as a standard line to show the electronic effect of the F atoms. Some of complexes are considerably far from the standard line, which could be due to both electronic and steric effects occurring at the same time. Although quantitative analysis of the steric effect is nearly impossible, we could find a rough trend where the complexes that lie far from the standard line tend to have a large dihedral angle defined by the plane of phenyl group (plane 1) and the plane composed of a carboxy group and a diruthenium unit (plane 2) (Table 2). In other



**Fig. 7** Plot of HOMO ( $\delta^*(\beta)$ ) level *vs.*  $E_{1/2}$ , where the solid line represents the least-squares linear fitting line for the non-*o*-F group in relation to a standard line based mainly on the electronic effect of the F atoms.

words, complexes with small dihedral angles (<  $23^{\circ}$ ) are located near the line, although there are a few exceptions (**2,6-F**<sub>2</sub> and **2,4,6-F**<sub>3</sub>). As seen in the plots of  $E_{1/2}$  vs. p $K_a$  and Hammett constants, the main effect of *o*-substitution on the redox potential was found to be an electronic effect in solution. This fact suggests that the phenyl groups of the  $F_x$ PhCO<sub>2</sub> ligands rotate freely in solution without significant barrier even in mono- and di-*o*-F complexes. Consequently, the steric factor due to substitution at the *ortho* position does not have an effect in solution. On the other hand, the DFT calculations directly reflect a static state structure. Therefore, steric effects should be included in the results. Thus, the HOMO energy levels of complexes in solution media are expected to be near the standard line in Fig. 7.

#### Conclusions

A series of  $[Ru_2^{II,II}(F_xPhCO_2)_4(THF)_2]$  was synthesized using comparatively-simple synthetic routes, and the addition of fluorine groups on the benzoate ligands made it possible to tune the redox potential over a wide range from -40 mV to 350 mV (in THF). Thus, although most of the compounds were air-sensitive, **2,3,6-F**<sub>3</sub>, **2,3,4,5-F**<sub>4</sub>, **2,3,5,6-F**<sub>4</sub>, and **F**<sub>5</sub>, which have  $E_{1/2} > 300$  mV, were relatively stable in air.

The redox potential of the  $[\operatorname{Ru}_2^{II,II}]/[\operatorname{Ru}_2^{II,II}]^+$  redox couple in THF, which is a general reaction medium, is strongly dependent on the electronic effect of *o*-F atoms, whereas substituents at the *m*- and *p*-positions shift the redox potentials in the positive direction in relation to the general Hammett law. The F atoms affected both the redox potential and the HOMO energy levels. However, since the HOMO energy levels were calculated using atomic coordinates of the solid-state structures, they contained contributions from steric effects. Thus, the HOMO energy level of the present complexes correlated to the redox potential. Namely, the main factor determining  $I_D$  of complexes in a solution, in which the phenyl rings can freely rotate, is the electronic effect of the F atoms.

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