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Trans-heteroleptic carboxylate-bridged paddlewheel diruthenium(II, II) complexes with 2,6-bis(trifluoromethyl)benzoate ligands

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Carboxylate-ligand substitution reactions of paddlewheel-type diruthenium(II, III) complexes ($[Ru_2^{II,III}(RCO_2)_4]^+$) with 2,6-bis(trifluoromethyl)benzoate ($2,6\text{-}(CF_3)_2PhCO_2^-$) involving a selective reduction to $[Ru_2^{II,II}]$ provide a series of *trans*-substituted paddlewheel-type diruthenium(II, II) complexes, $[Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(RCO_2)_2(THF)_2]$ (R = CH_3, **1**; C_2H_5, **2**; C_3H_7, **3**; C_4H_9, **4**; $C(CH_3)_3$, **5**; 2,3,5,6-F_4Ph, **6**). Crystal structures of **1**–**6** were determined, and their electronic states were investigated by cyclic voltammetry, density functional theory (DFT) and magnetic measurements. This is the first example of *trans*-heteroleptic carboxylate-bridged $[Ru_2^{II,II}]$ complexes.

Introduction

Carboxylate-bridged paddlewheel-type metal complexes with metal–metal bonds, whose general formula is $[M_2(RCO_2)_4(L)_x]^{n+}$ (M = transition metal ion; L = axial ligands, such as solvents or anions; and x = 0, 1 and 2), have been extensively studied over the past four decades.[1] As a result of the diverse combinations of metal ions (M) with carboxylate bridging (RCO_2^-) and axial ligands (L) in an identical core, these complexes have been used for investigation of electronic structures on frontier orbitals influenced by metal–metal bonding and utilized as structure-rigid building blocks for building a variety of supramolecular structures.[2,3,4] Most compounds, independent of the metal ions, have substitution-labile sites in axial positions, allowing them to act as linear-type coordination accepting building blocks with C_4 symmetry. Alternatively, partial substitution of the carboxylate-bridging ligands (e.g. the *cis*- or *trans*-positioned carboxylate blades, hereafter referred to as heteroleptic $[M_2]$ complexes, $[M_2(RCO_2)_2(R'CO_2)_2]^{n+}$, as opposed to homoleptic $[M_2]$ complexes, $[M_2(RCO_2)_4]^{n+}$) is strongly desired for use as terminal equatorial building blocks (Chart 1a), corner-type building blocks (Chart 1b), or anisotropic building blocks with a C_2 symmetry (Chart 1c). Considering the general synthetic procedures for paddlewheel-type metal complexes, the development of a synthetic route for heteroleptic $[M_2]$ complexes remains a challenge. Examples of complexes that show selective equatorial ligand substitutions are seen in the series of $[Mo_2(DAniF)_2(MeCN_{eq})_4]^{2+}$ and $[Mo_2(DAniF)_3(MeCN_{eq})_2]^+$ (DAniF = *N*,*N'*-di-*p*-anisylformamidinate; $MeCN_{eq}$ = equatorial coordinating MeCN) compounds, carried out by Cotton et al.[4,5] In these compounds the $MeCN_{eq}$ can be replaced with various bridging ligands, such as dicarboxylate ligands,[5c] hydroxo,[5b] oxide,[5h] hydride,[5a] diamide,[5f] halide,[5i] oxamidate ions,[5g] $M(OCH_3)_4^{2-}$ (M = Zn, Co),[5f] and EO_4^{2-} (E = S, Mo, W).[5d] Pioneering work on carboxylate-substitutions in $[M_2(RCO_2)_4]^{n+}$ complexes has been done by Chisholm,[6] who mainly focused on paddlewheel $[Mo_2^{II,II}]$ compounds and succeeded in *trans*-substitution for their assembly into multi-dimensional networks.[7]

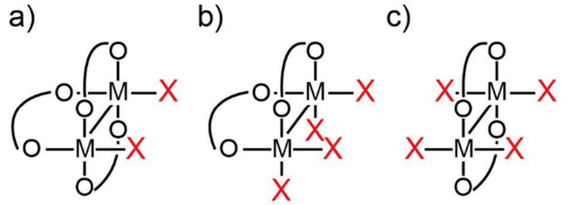

Chart 1 Schematic diagram of the partially substituted carboxylate-bridged paddlewheel-type metal complexes. a) Equatorial terminal building blocks, b) corner-type building blocks and c) *trans*-substituted building blocks.

Diruthenium complexes, $[Ru_2(RCO_2)_4]^{n+}$ (*n* = 0 or 1; abbreviated as $[Ru_2]^{n+}$), are intriguing compounds that show rich electrochemistry between the paramagnetic $[Ru_2^{II,II}]$ and $[Ru_2^{II,III}]^+$ species with multiple spin values of *S* = 1 and *S* = 3/2, respectively. Hence, these compounds are useful as

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electronic/spin building blocks for the design of functional coordination frameworks.[2,3,8] Our groups recently demonstrated the rational construction of magnetic/conductive frameworks using [$Ru_2^{II,II}$] donors (D) and organic acceptors (A), such as 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and *N*,*N′*-dicyanoquinodiimine (DCNQI) derivatives;[9-12] the electron donor/acceptor metal-organic frameworks were abbreviated as D/A-MOFs.[13] The electronic/spin state of D/A-MOFs is tunable by modifying the choice of the D and A units. The degree of charge/electron transfers between the D and A units is based on the energy relationship between the HOMO of D and the LUMO of A.[9d,9e] In these works, we postulated that *trans*-substituted [$Ru_2^{II,II}$] species with C_2 symmetry could be used for controlling inter-framework interactions in low-dimensional frameworks, such as layered and chain systems. Nevertheless, only a few examples of *trans*-substituted [$Ru_2^{II,II}$] species have been reported; however, there have been no reports where the compounds were structurally characterized.[14,15]

We report a series of *trans*-substituted [$Ru_2^{II,II}$] complexes with 2,6-bis(trifluoromethyl)benzoate ($2,6\text{-}(CF_3)_2PhCO_2^-$), *trans*-[$Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(RCO_2)_2(THF)_2$] (R = CH_3, **1**; C_2H_5, **2**; C_3H_7, **3**; C_4H_9, **4**; $C(CH_3)_3$, **5**; 2,3,5,6-F_4Ph ($2,3,5,6\text{-}F_4PhCO_2^-$ = 2,3,5,6-tetrafluorobenzoate), **6**) (Chart 2). These *trans*-substituted [$Ru_2^{II,II}$] complexes were selectively produced using $2,6\text{-}(CF_3)_2PhCO_2^-$ for ligand-substitution reactions of [$Ru_2^{II,III}(RCO_2)_4$]$^+$ involving a reduction reaction to [$Ru_2^{II,II}$]. All compounds were structurally characterized (the first examples for heteroleptic [$Ru_2^{II,II}$] complexes), and their electronic structures were investigated by magnetic measurements, solution electrochemistry and density functional theory (DFT).

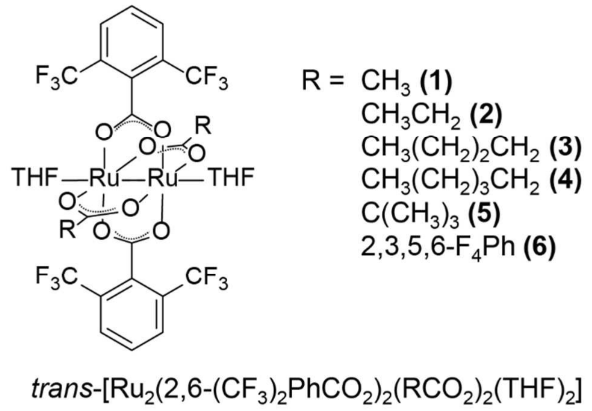


Chart 2. Line drawing of complex **1**–**6**.

Experimental Section

General Procedures and Materials

All synthetic procedures were performed under an inert atmosphere using standard Schlenk-line techniques and a commercial glovebox. All chemicals were purchased from commercial sources and were of reagent grade. Solvents were dried using common drying agents and distilled under nitrogen before use. [$Ru_2^{II,III}(CH_3CO_2)_4(THF)_2$]$BF_4$,[16] [$Ru_2^{II,III}(CH_3CO_2)_4Cl$],[17] [$Ru_2^{II,III}(C_2H_5CO_2)_4(THF)_2$]$BF_4$,[18] [$Ru_2^{II,III}(C_2H_5CO_2)_4Cl$],[19] [$Ru_2^{II,III}(C_3H_7CO_2)_4(THF)_2$]$BF_4$,[20] [$Ru_2^{II,III}(C_3H_7CO_2)_4Cl$],[21] [$Ru_2^{II,III}(C_4H_9CO_2)_4Cl$],[22] [$Ru_2^{II,III}(C(CH_3)_3CO_2)_4(THF)_2$]$BF_4$,[23] and [$Ru_2^{II,III}(C(CH_3)_3CO_2)_4Cl$][23] were prepared following previously reported methods. [$Ru_2^{II,III}(2,3,5,6\text{-}F_4PhCO_2)_4Cl$] was prepared in a similar manner to that reported previously.[24]

[$Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(CH_3CO_2)_2(THF)_2$] (1)

Method A: [$Ru_2^{II,III}(CH_3CO_2)_4(THF)_2$]$BF_4$ (326 mg, 0.49 mmol) and 2,6-bis(trifluoromethyl)benzoic acid (250 mg, 0.97 mmol) were refluxed in 20 mL of *N*,*N*-dimethylaniline (NDMA) for 12 h. After removal of the solvent *in vacuo*, the brown residue was washed with *n*-hexane (10 mL × 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 **1** after one week or more. Yield: 38%. Elemental analysis (%) calcd for $C_{30}H_{28}O_{10}F_{12}Ru_2$: C 36.81, H 2.86. Found: C 36.77, H 2.94. IR (KBr): $\nu(CO_2)$ = 1582, 1403 cm^{-1}.

Method B: [$Ru_2^{II,III}(CH_3CO_2)_4Cl$] (726 mg, 1.5 mmol) and 2,6-bis(trifluoromethyl)benzoic acid (774 mg, 3.0 mmol) were refluxed in a 1:1 solution of MeOH and H_2O (20 mL) for 12 h under aerobic conditions to synthesize [$Ru_2^{II,III}(2,6\text{-}(CF_3)_2PhCO_2)_2(CH_3CO_2)_2Cl$]. A red precipitate was collected by filtration, washed with water and dried *in vacuo*. Without further purification, a THF solution (15 mL) of the crude red precipitate and Zn powder (104 mg, 1.6 mmol) was stirred for 24 h under a nitrogen atmosphere. During this time, most of the solid dissolved. The reddish solution was filtered and the filtrate was layered with *n*-hexane and allowed to stand for at least one week, affording **1** as brown crystals. Yield: 71%.

[$Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(C_2H_5CO_2)_2(THF)_2$](THF) (2)

Method A: Compound **2** was synthesized by a similar method used for **1**; here [$Ru_2^{II,III}(C_2H_5CO_2)_4(THF)_2$]$BF_4$ (255 mg, 0.35 mmol) was used instead of [$Ru_2^{II,III}(CH_3CO_2)_4(THF)_2$]$BF_4$. Yield: 10%. Elemental analysis (%) calcd for $C_{32}H_{32}O_{10}F_{12}Ru_2$: C 38.18, H 3.20. Found: C 38.11, H 3.32. IR (KBr): $\nu(CO_2)$ = 1574, 1404 cm^{-1}.

Method B: Compound **2** was synthesized by a similar method used for **1**; here [$Ru_2^{II,III}(C_2H_5CO_2)_4Cl$] (300 mg, 0.56 mmol) was used instead of [$Ru_2^{II,III}(CH_3CO_2)_4Cl$]. Yield: 60%.

[$Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(C_3H_7CO_2)_2(THF)_2$] (3)

Method A: Compound **3** was synthesized by a similar method used for **1**; here [$Ru_2^{II,III}(C_3H_7CO_2)_4(THF)_2$]$BF_4$ (399 mg, 0.51 mmol) was used instead of [$Ru_2^{II,III}(CH_3CO_2)_4(THF)_2$]$BF_4$. Yield: 47%. Elemental analysis (%) calcd for $C_{34}H_{36}O_{10}F_{12}Ru_2$: C 39.47, H 3.51. Found: C 39.31, H 3.58. IR (KBr): $\nu(CO_2)$ = 1580, 1403 cm^{-1}.

Method B: Compound **3** was synthesized by a similar method used for **1**; here [$Ru_2^{II,III}(C_3H_7CO_2)_4Cl$] (439 mg, 0.75 mmol) was used instead of [$Ru_2^{II,III}(CH_3CO_2)_4Cl$]. Yield: 48%.

$[Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(C_4H_9CO_2)_2(THF)_2]$ (4)

Method A: The synthetic route for **4** is similar to that for **1**, but the starting material $[Ru_2^{II,III}(C_4H_9CO_2)_4]BF_4$ was newly prepared for this procedure. $[Ru_2^{II,III}(C_4H_9CO_2)_4]Cl$ (449 mg, 0.70 mmol) and $AgBF_4$ (136 mg, 0.70 mmol) were stirred for 24 h under aerobic conditions at room temperature and white precipitate formed. The reddish solution was filtered and the solvent was removed *in vacuo*. The brown residue and 2,6-bis(trifluoromethyl)benzoic acid (361 mg, 1.4 mmol) were refluxed in 20 mL of NDMA for 12 h. After removal of the solvent *in vacuo*, the brown residue was washed with *n*-hexane (10 mL × 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 **4** after one week. Yield: 27%. Elemental analysis (%) calcd for $C_{36}H_{40}O_{10}F_{12}Ru_2$: C 40.68, H 3.79. Found: C 40.45, H 3.66. IR (KBr):$\nu(CO_2)$ = 1576, 1404 cm^{-1}.

Method B: Compound **4** was synthesized by a similar method used for **1**; here $[Ru_2^{II,III}(C_4H_9CO_2)_4Cl]$ (640 mg, 1.0 mmol) was used instead of $[Ru_2^{II,III}(CH_3CO_2)_4Cl]$. Yield: 47%.

$[Ru_2^{II,II}(2,6\text{-}CF_3PhCO_2)_2(C(CH_3)_3CO_2)_2(THF)_2]$ (5)

Method A: Compound **5** was synthesized by a similar method used for **1**; here $[Ru_2^{II,III}(C(CH_3)_3CO_2)_4(THF)_2]BF_4$ (246 mg, 0.29 mmol) was used instead of $[Ru_2^{II,III}(CH_3CO_2)_4(THF)_2]BF_4$. Yield: 10%. Elemental analysis (%) calcd for $C_{36}H_{40}O_{10}F_{12}Ru_2$: C 40.68, H 3.79. Found: C 40.77, H 3.74. IR (KBr):$\nu(CO_2)$ = 1578, 1400 cm^{-1}.

Method B: Compound **5** was synthesized by a similar method used for **1**; here $[Ru_2^{II,III}(C(CH_3)_3CO_2)_4Cl]$ (400 mg, 0.62 mmol) was used instead of $[Ru_2^{II,III}(CH_3CO_2)_4Cl]$. Yield: 19%.

$[Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(2,3,5,6\text{-}F_4PhCO_2)_2(THF)_2]$ (6)

Method B: Compound **6** was synthesized by a similar method used for **1**; here $[Ru_2^{II,III}(2,3,5,6\text{-}F_4PhCO_2)_4Cl]$ (629 mg, 0.62 mmol) was used instead of $[Ru_2^{II,III}(CH_3CO_2)_4Cl]$. Yield: 46%. Elemental analysis (%) calcd for $C_{40}H_{24}O_{10}F_{20}Ru_2$: C 38.54, H 1.94. Found: C 38.66, H 2.08. IR (KBr):$\nu(CO_2)$ = 1588, 1403 cm^{-1}.

General Physical Measurements

Infrared spectra were measured on KBr disks with a JASCO FT-IR 620 spectrophotometer. Magnetic susceptibility measurements were conducted with a Quantum Design SQUID magnetometer (MPMS-XL) in the temperature range of 5–300 K with an applied magnetic field of 0.1 T. Polycrystalline samples embedded in liquid paraffin were measured. Experimental data were corrected for the sample holder and liquid paraffin and for the diamagnetic contribution calculated from Pascal constants.[25] Cyclic voltammograms (CVs) were recorded in THF with tetra-*n*-butylammonium hexafluorophosphate $n\text{-}Bu_4N(PF_6)$ (0.1 M) as the supporting electrolyte, under a nitrogen atmosphere using an ALS/[H] CH Instruments Electrochemical Analyzer Model 600A. At the beginning of the measurements, CVs of the solvent with only the supporting electrolyte were measured. To this solution the compounds ([Compound] = 1×10^{-3} M) were added, and the CVs were acquired using a glassy carbon electrode as the working electrode, a Pt counter electrode and a $Ag/AgNO_3$ reference electrode. Finally, CV potentials were adjusted to the ferrocene/ferrocenium couple that was used as an internal standard (Fc/Fc^+ = 213 mV (ΔE = 91 mV) in THF vs. Ag/Ag^+).

Crystallography

Crystal data for **1** and **6** were collected on a Rigaku Saturn 724 CCD area detector with a multi-layer mirror monochromated Mo-Kα radiation (λ = 0.71075 Å). Crystal data for **2**–**5** were collected on a Rigaku Mercury 70 CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71070 Å). Single crystals with dimensions of 0.290 mm × 0.240 mm × 0.070 mm for **1**, 0.538 mm × 0.316 mm × 0.100 mm for **2**, 0.520 mm × 0.180 mm × 0.050 mm for **3**, 0.030 mm × 0.030 mm × 0.015 mm for **4**, 0.370 mm × 0.300 mm × 0.176 mm for **5** and 0.160 mm × 0.150 mm × 0.030 for **6** were mounted on cryo-loops using Nujol and cooled by a stream of cooled N_2 gas. The structures were solved by direct methods (SIR2008[26] for **1**–**5** and SIR2002[27] for **6**) and expanded using Fourier techniques (DIRDIF99)[28] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced as fixed contributors. Full-matrix least-squares refinements on F^2 were based on observed reflections and variable parameters, and converged with unweighted and weighted agreement factors of $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ ($I > 2.00\sigma(I)$), and $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (all data). All calculations were performed using the CrystalStructure crystallographic software package.[29]

Crystallographic Data for 1. Formula: $C_{30}H_{28}F_{12}O_{10}Ru_2$, Mr = 978.67, triclinic, $P{-}1$ (#2), a = 10.172(8) Å, b = 10.241(8) Å, c = 18.093(13) Å, α = 98.064(9)°, β = 92.357(12)°, γ = 112.881(10)°, V = 1710(2) Å^3, T = 98(1) K, Z = 2, D_{calc} = 1.901 g cm^{-3}, F_{000} = 968.00, λ = 0.71075 Å, μ(Mo Kα) = 10.044 cm^{-1}, 12483 measured reflections, 6815 unique (R_{int} = 0.0819). R_1 = 0.0626 ($I > 2\sigma(I)$), R_1 = 0.0836 (all data) and wR_2 = 0.1326 with GOF = 0.917. CCDC-1450743.

Crystallographic Data for 2. Formula: $C_{36}H_{40}F_{12}O_{11}Ru_2$, Mr = 1078.83, monoclinic, $C2/c$ (#15), a = 22.369(7) Å, b = 8.967(2) Å, c = 24.188(9) Å, β = 124.523(8)°, V = 3997(2) Å^3, T = 98(1) K, Z = 4, D_{calc} = 1.793 g cm^{-3}, F_{000} = 2160.00, λ = 0.71070 Å, μ(Mo Kα) = 8.702 cm^{-1}, 19166 measured reflections, 4527 unique (R_{int} = 0.0439). R_1 = 0.0445 ($I > 2\sigma(I)$), R_1 = 0.0553 (all data) and wR_2 = 0.1194 with GOF = 1.214. CCDC-1450744.

Crystallographic Data for 3. Formula: $C_{34}H_{36}F_{12}O_{10}Ru_2$, Mr = 1034.77, orthorhombic, $Pbca$ (#61), a = 19.302(2) Å, b = 10.5836(11) Å, c = 19.7267(19) Å, V = 4029.9(7) Å^3, T = 88(1) K, Z = 4, D_{calc} = 1.705 g cm^{-3}, F_{000} = 2064.00, λ = 0.71070 Å, μ(Mo Kα) = 8.573 cm^{-1}, 42087 measured reflections, 4598 unique (R_{int} = 0.0355). R_1 = 0.0333 ($I > 2\sigma(I)$), R_1 = 0.0359 (all data) and wR_2 = 0.0827 with GOF = 1.127. CCDC-1450745.

Crystallographic Data for 4. Formula: $C_{36}H_{40}F_{12}O_{10}Ru$, Mr = 1062.83, monoclinic, $P2_1/c$ (#14), a = 10.2128(18) Å, b = 19.643(3) Å, c = 10.2777(17) Å, β = 106.857(4)°, V = 1973.2(6) Å^3, T = 123(1) K, Z = 2, D_{calc} = 1.789 g cm^{-3}, F_{000} = 1064.00, λ = 0.71070 Å, μ(Mo Kα) = 8.780 cm^{-1}, 21623 measured reflections, 4468 unique (R_{int} = 0.0394). R_1 = 0.0400 ($I > 2\sigma(I)$), R_1 = 0.0452 (all data) and wR_2 = 0.0850 with GOF = 1.097. CCDC-1450746.

Crystallographic Data for 5. Formula: $C_{36}H_{40}F_{12}O_{10}Ru_2$, Mr = 1062.83, monoclinic, $P2_1/n$ (#14), a = 11.642(2) Å, b = 9.6284(16) Å, c = 18.579(4) Å, β = 98.218(5)°, V = 2061.1(7) Å^3, T = 123(1) K, Z = 2, D_{calc} = 1.712 g cm^{-3}, F_{000} = 1064.00, λ = 0.71070 Å, μ(Mo Kα) = 8.406 cm^{-1}, 21272 measured reflections, 4680 unique (R_{int} = 0.0486). R_1 = 0.0506 ($I > 2\sigma(I)$), R_1 = 0.0536 (all data) and wR_2 = 0.1375 with GOF = 1.072. CCDC-1450747.

Crystallographic Data for 6. Formula: $C_{40}H_{24}F_{20}O_{10}Ru_2$, Mr = 1246.73, triclinic, P−1 (#2), a = 10.425(2) Å, b = 10.840(2) Å, c = 11.572(2) Å, α = 104.622(5)°, β = 109.022(3)°, γ = 108.258(4)°, V = 1078.6(4) Å^3, T = 97(1) K, Z = 1, D_{calc} = 1.919 g cm^{-3}, F_{000} = 612.00, λ = 0.71075 Å, μ(Mo Kα) = 8.446 cm^{-1}, 7316 measured reflections, 3720 unique (R_{int} = 0.0318). R_1 = 0.0274 ($I > 2\sigma(I)$), R_1 = 0.0306 (all data) and wR_2 = 0.0729 with GOF = 1.102. CCDC-1450748.

Computational Details

Theoretical *ab initio* calculations were performed using DFT formalism, as implemented in the Gaussian 09 software,[30] with Beck's three-parameter hybrid functional and the correlation functional of Lee, Yang and Parr (B3LYP).[31] Unrestricted open-shell calculations were performed in the calculations of the molecules containing [Ru_2] units. An effective core potential basis set LanL2TZ with polarization (LanL2TZ(f))[32] for Ru atoms and 6-31G basis sets with polarization and diffuse functions (6-31+G(d))[33] for C, H, F and O atoms were adopted. In the calcul-

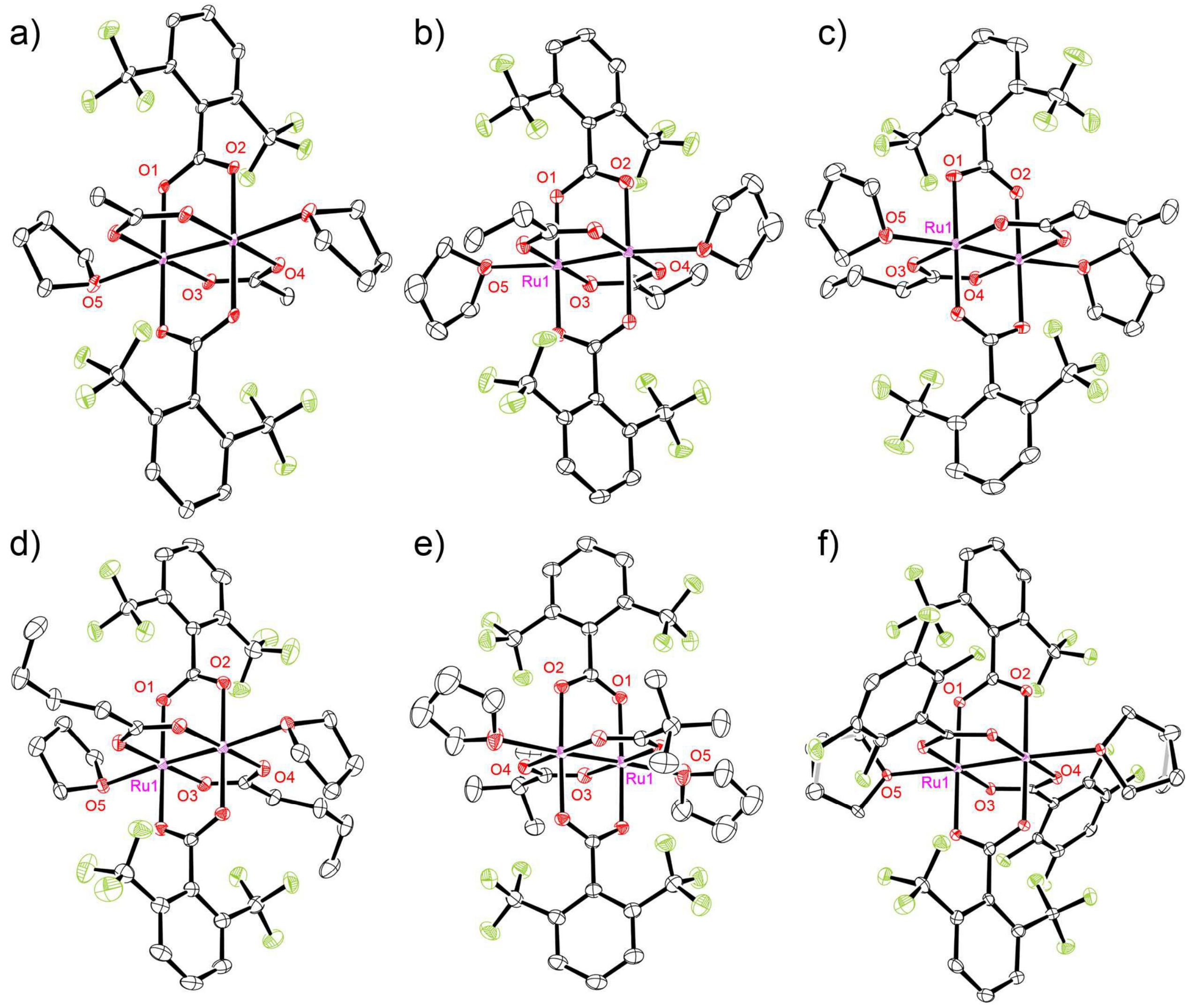
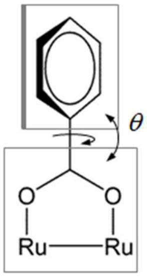


Figure 1. (a–f) ORTEP drawings of **1**–**6**, respectively. Red, grey, green and purple represent O, C, F and Ru, respectively. The grey bonds represent disordered atomic positions. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and crystallization solvent are omitted for clarity.

Table 1. Selected bond length (Å) and angles (°) in **1**–**6**, where θ represents dihedral angle between the least squares planes defined by the phenyl ring of benzoate ligand and a carboxylate-bridging mode (atom set of Ru_2O_2C).



	1	**2**	**3**	**4**	**5**	**6**
Ru1–O1	2.072(5)	2.070(2)	2.0778(17)	2.074(2)	2.069(2)	2.077(2)
Ru1–O2*	2.055(5)^{a}	2.090(2)^{c}	2.0634(15)^{b}	2.073(2)^{b}	2.071(3)^{d}	2.072(2)^{e}
Ru1–O3	2.073(4)	2.071(4)	2.0667(16)	2.067(2)	2.059(3)	2.064(2)
Ru1–O4*	2.066(4)^{a}	2.062(4)^{c}	2.0577(16)^{b}	2.056(2)^{b}	2.070(3)^{d}	2.063(2)^{e}
Ru1–O5	2.327(4)	2.324(3)	2.3386(16)	2.3506(18)	2.339(4)	2.351(2)
Ru2–O6	2.074(5)	–	–	–	–	–
Ru2–O7*	2.062(5)^{b}	–	–	–	–	–
Ru2–O8	2.068(5)	–	–	–	–	–
Ru2–O9*	2.063(5)^{b}	–	–	–	–	–
Ru2–O10	2.345(4)	–	–	–	–	–
Ru1–Ru1*	2.2637(13)^{a}	2.2696(6)^{c}	2.2676(4)^{b}	2.2638(4)^{b}	2.2632(6)^{d}	2.2760(5)^{e}
Ru2–Ru2*	2.2638(13)^{b}	–	–	–	–	–
θ						
$2,6-(CF_3)_2PhCO_2^-$ Set-1 for $[Ru(1)_2]$	78.1	67.0	70.5	79.1	53.2	70.9
Set-2 for $[Ru(2)_2]$	76.5	–	–	–	–	–
$2,3,5,6-F_4PhCO_2^-$	–	–	–	–	–	43.5

* Symmetry codes: (a) $-x + 2, -y + 1, -z + 2$, (b) $-x + 1, -y + 1, -z + 1$, (c) $-x + 1, -y + 2, -z + 1$, (d) $-x, -y + 1, -z + 1$, (e) $-x + 1, -y + 1, -z + 2$.

lation, spin polarization with $S_Z = 1$ (triplet spin multiplicity) for the $[Ru_2]$ units was used. The atomic coordinates determined by X-ray crystallography were used in calculations of the $[Ru_2]$ unit.

Results and Discussion

Syntheses

Since the starting materials for **1**–**6** are $[Ru_2^{II,III}(RCO_2)_4]^+$ (R = CH_3, C_2H_5, C_3H_7, C_4H_9, $C(CH_3)_3$ and 2,3,5,6-F_4Ph, respectively), two processes for the ligand-substitution reaction and reduction from $[Ru_2^{II,III}]^+$ to $[Ru_2^{II,II}]$ were necessary. Except for **6**, all compounds were synthesized by a one-pot reaction using NDMA. The ligand-substitution and reduction of the complex occur concurrently because NDMA acts as both the solvent and the reducing agent (Method A).[34] These compounds could also be obtained through the stepwise method used for **6**, starting with the ligand-substitution reaction of $[Ru_2^{II,III}(RCO_2)_4Cl]$, and then followed by the reduction to $[Ru_2^{II,II}]$ using Zn powder as a reducing agent (Method B). Both synthetic methods provided identical crystalline samples, which were confirmed by single-crystal X-ray crystallography and elemental analyses. Note that the requisite amount of 2,6-$(CF_3)_2PhCO_2H$ for the substitution reaction was found to be 2 eq., as described in Experimental Section. *Trans*-substitution was also achieved only if an excess amount of ligand was used.

Structures

All compounds were structurally characterized by single-crystal X-ray crystallography. ORTEP drawings of the structures of **1**–**6** are depicted in Figure 1, and the bond lengths around the Ru centres are summarized in Table 1. To the best of our knowledge, this is the first example that reveals crystal structures of *trans*-substituted $[Ru_2^{II,II}]$ complexes. All compounds show an inversion centre at the midpoint of the Ru–Ru bond. Only **1** contains two structurally independent molecules in the unit cell, but both are very similar to each other (Figure 1a shows one). The 2,6-$(CF_3)_2PhCO_2^-$ and RCO_2^- ligands are respectively located in *trans*-positions around the Ru centres, forming *trans*-heteroleptic $[Ru_2]$ core structures.

The Ru–Ru bond lengths of the complexes range between 2.263–2.276 Å, which is similar to those of previously reported for $[Ru_2^{II,II}]$ compounds.[1,24,35] The Ru–O_{eq} (O_{eq} = equatorial oxygen atoms) bond lengths vary in the range 2.06–2.09 Å. In the family of carboxylate-bridged paddlewheel $[Ru_2]$ complexes, the Ru–O_{eq} bond length is a good indicator for evaluating the oxidation state, generally found in the range of 2.06–2.08 Å for $[Ru_2^{II,II}]$ and 2.02–2.04 Å for $[Ru_2^{II,III}]^+$;[1,8,24] hence, all compounds are concluded to be $[Ru_2^{II,II}]$. The Ru–O_{ax} (O_{ax} = oxygen atom of THF) bond lengths for **1**–**6** are in the range 2.26–2.27 Å, which are also characteristic of the $[Ru_2^{II,II}]$ valence state.[8,24,35]

The selective formation of *trans*-heteroleptic $[Ru_2^{II,II}]$ complexes using $2,6\text{-}(CF_3)_2PhCO_2^-$ as a substitution ligand can be ascribed to the steric hindrance provided by the CF_3 groups in *ortho*-positions (i.e. 2,6-positions) of the benzoate. One of the indicators of the steric hindrance caused by *ortho*-substitutions of benzoate ligands is the dihedral angle (θ) defined by the phenyl ring of the benzoate ligand and the carboxylate-bridging mode (Ru_2O_2C), as shown in the inset figure of Table 1. The θ values for **1**–**6** are listed in Table 1. The observed θ values of 53.2–79.1° are relatively larger than those observed in homoleptic benzoate-substituted $[Ru_2^{II,II}]$ complexes (Table S1).[24,35] Indeed, the θ angle for the $2,3,5,6\text{-}F_4PhCO_2^-$ ligand in **6** is 43.5°. That is, the $2,6\text{-}(CF_3)_2PhCO_2^-$ ligand leads to a large θ angle to minimize the steric hindrance between the bulky CF_3 groups in the *ortho*-positions and the carboxylate moiety. This situation may prevent homoleptic substitutions of $[Ru_2]$ with $2,6\text{-}(CF_3)_2PhCO_2^-$; we propose that the bulky CF_3 groups will create new steric hindrance between the CF_3 groups in neighboring $2,6\text{-}(CF_3)_2PhCO_2^-$ ligands in homoleptic $[Ru_2]$ complexes, if produced. Thus, steric interference is the likely cause of the *trans*-heteroleptic substitution of $[Ru_2]$ complexes in reactions with $2,6\text{-}(CF_3)_2PhCO_2^-$.

Magnetic properties

The temperature dependence of the dc susceptibility (χ) of **1**–**6** was measured on polycrystalline samples in a temperature range of 5.0–300 K at 0.1 T; the χ and χT vs T plots are shown in Figure 2. The χT values at 300 K were determined to be in the range of 0.92–1.00 cm^3 K mol^{-1}, which decrease smoothly upon cooling to a range of 2.81×10^{-2}–10.1×10^{-2} cm^3 K mol^{-1} at 5.0 K. Conversely, the χ values increase with a decrease in temperature to about 100 K, which then reach a plateau followed by an increase at temperatures below 10 K. The features of the χ and χT vs. T plots are consistent with those for isolated $[Ru_2^{II,II}]$ complexes with an S = 1 ground state affected by strong zero-field splitting (ZFS; $D \approx$ 230–320 cm^{-1} for general $[Ru_2^{II,II}]$ complexes).[1,8,24,35] The increase in χ at low temperatures is likely caused by a paramagnetic impurity, such as a $[Ru_2^{II,III}]^+$ species with S = 3/2. The magnetic data were simulated using a Curie paramagnetic model with S = 1, taking into account ZFS, temperature-independent paramagnetism (TIP), an impurity with S = 3/2 (ρ) and intermolecular interactions (zJ) commonly used for magnetically isolated or weakly interacting $[Ru_2^{II,II}]$ complexes (see ESI). zJ was introduced in the framework of the mean-field approximation but not required for obtaining adequate fitting ($zJ \approx 0$ for all complexes). The best fit of parameters for the compounds are listed in Table 2. The g value was fixed at 2.00. The estimated D value is typical for general $[Ru_2^{II,II}]$ species. The magnetic data indicate that all complexes have an electronic configuration of $\sigma^2\pi_2^4\delta^2\delta^{*2}\pi^*_2{}^2\sigma^{*0}$ on Ru–Ru bond frontier orbital sets with degenerated levels of δ^* and two π^* orbitals.[1]

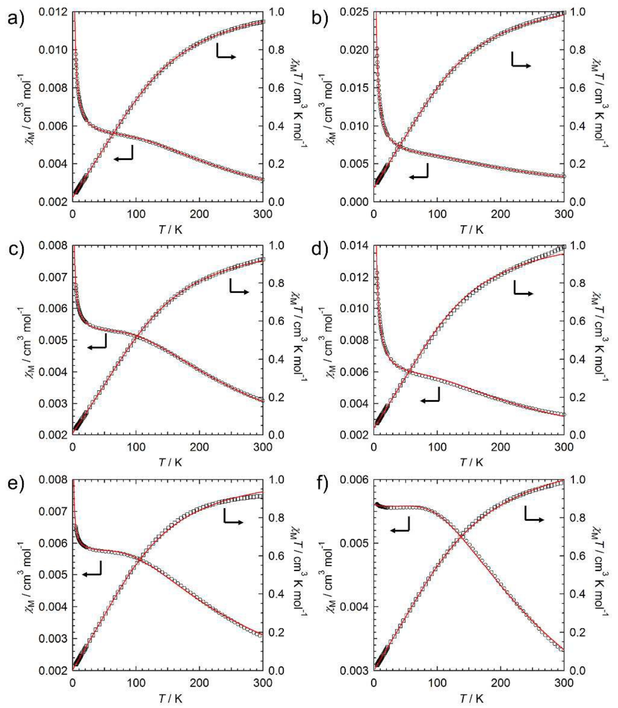


Figure 2. (a–f) Temperature dependence of χ (○) and χT (□) for **1**–**6**, respectively, where the red solid lines represent simulated curves based on a Curie paramagnetic model with S = 1 taking into account zero-field splitting (D), temperature-independent paramagnetism (χ_{TIP}) and an impurity with S = 3/2 (ρ).

Table 2. Magnetic parameters of **1–6**, where D, χ_{TIP}, and ρ stand for parameters of zero-field-splitting, temperature-independent paramagnetic contribution, and extrinsic paramagnetic impurity as S = 3/2 possibly from $[Ru_2^{II,III}]$ species, respectively (see ESI).

Compound	D/k_B (K)	χ_{TIP} ($\times 10^{-6}$ cm^3 mol^{-1})	ρ ($\times 10^{-3}$)
1	383.5(3)	108(3)	12.07(2)
2	361.2(5)	108(5)	39.40(3)
3	389.6(5)	48(4)	4.28(2)
4	370(3)	88(25)	19.32(15)
5	354.6(8)	55(8)	2.25(5)
6	380.4(6)	212(6)	0.069(33)

Electrochemistry in solution and DFT calculations

Cyclic voltammograms (CVs) of **1**–**6** were measured in a N_2-purged THF solution with $n\text{-}Bu_4N(PF_6)$ as the supporting electrolyte, as shown in Figure 3. All compounds show a quasi-reversible one-electron redox couple with $i_c/i_a \approx 1$ and $\Delta E_p \approx$ 84–195 mV assigned to $[Ru_2^{II,II}]/[Ru_2^{II,III}]^+$; the electrochemical data are summarized in Table 3. The redox potential of previously reported *trans*-substituted [$Ru_2^{II,II}$] complexes, *trans*-[$Ru_2^{II,II}(CH_3CO_2)_2(TiPB)_2$] (TiPB = 2,4,6-triisopropylbenzoate)[14] and *trans*-[$Ru_2^{II,II}(CH_3CO_2)_2(ArCO_2)_2$] ($ArCO_2$ = 2,6-di(p-tolyl)benzoate),[15] are $E_{1/2}$ = −177 mV and −227 mV (*vs*. Ag/Ag^+ in MeOH), respectively. Except for **6**, **1**–**5** with saturated fatty acid salts (RCO_2^-) showed an $E_{1/2}$ value in the narrow potential range of 14–21 mV (*vs*. Ag/Ag^+ in THF), while **6** with 2,3,5,6-$F_4PhCO_2^-$ for RCO_2^- showed a large positive shift to $E_{1/2}$ = 314 mV (*vs*. Ag/Ag^+ in THF). The electrochemical data indicate that the equatorial RCO_2^- ligands strongly influence the redox properties of the complexes, which can especially be seen from the difference between **1**–**5** and **6**: saturated fatty acid salts (RCO_2^-) in **1**–**5** vs. electron-withdrawing fluorine-substituted benzoate in **6**, so the redox potential of **6** was largely shifted to the positive potential direction compared to those of **1**–**5**. Thus, even in the *trans*-heteroleptic series of [$Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(RCO_2)_2(THF)_2$], the redox potential and electronic properties of compounds can be tuned by modifying the RCO_2^- ligands.[24,35]

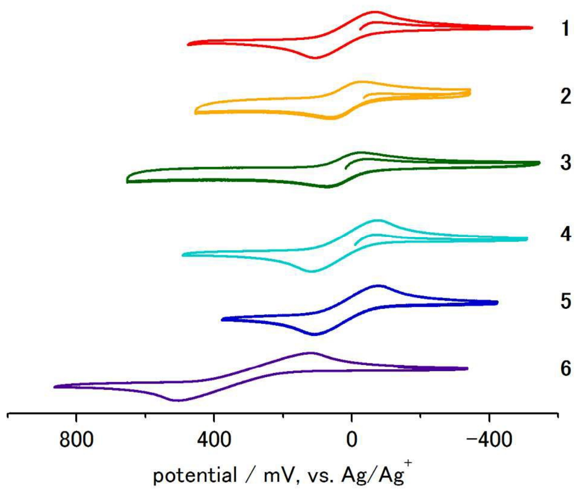


Figure 3. Cyclic voltammograms of **1**–**6** in THF containing 0.1 M *n*-$Bu_4N(PF_6)$ under N_2.

Table 3. Electrochemical data of **1**–**6** in THF containing 0.1 M n-$Bu_4N{\cdot}PF_6$ under N_2 (mV vs. Ag/Ag^+)[a] and the HOMO level calculated by density functional theory.

Compounds	E_a/mV	E_c/mV	$E_{1/2}$/mV	ΔE_p/mV	HOMO energy/eV
1	108	−69	19	177	−4.3511[b]
2	56	−28	14	84	−4.3391
3	71	−35	18	106	−4.3097
4	119	−76	21	195	−4.3446
5	107	−77	15	184	−4.3165
6	507	121	314	386	−4.7960

[a] The ferrocene/ferrocenium couple, Fc/Fc^+ = 213 mV, was observed in the same conditions described in the Experimental Section. [b] Average value.

To determine the energy levels of molecular orbitals in **1**–**6**, calculations based on DFT at the UB3LYP level[31] with basis functions LANL2TZ(f)[32] for Ru and 6-31+G(d)[33] for other atoms were carried out using Gaussian 09,[30] where the atomic coordinates determined by X-ray crystallography were used, and an S_z = 1 (spin multiplicity of 3) spin state was assumed (Figure S1a–S1f). For all compounds, the HOMO level most likely involved in the [$Ru_2^{II,II}$]/[$Ru_2^{II,III}$] couple was assigned to be the $\delta^*(\beta)$ frontier orbital; the energy of $\delta^*(\beta)$ is listed in Table **3**. The HOMO level was found to closely correlate with the redox potential. Indeed, **6** has a lower HOMO level (−4.7960 eV) than those of **1**–**5** (ca.–4.3 eV).

Conclusions

Trans-heteroleptic [$Ru_2^{II,II}$] complexes were synthesized through ligand substitution of [$Ru_2^{II,II}(RCO_2)_4$] (R = CH_3, C_2H_5, C_3H_7, C_4H_9, $C(CH_3)_3$ and 2,3,5,6-F_4Ph) using 2,6-$(CF_3)_2PhCO_2^-$. The series of [$Ru_2^{II,II}(2,6\text{-}(CF_3)_2PhCO_2)_2(RCO_2)_2(THF)_2$] represent the first structurally characterized compounds of this type. The structural analyses revealed that the 2,6-$(CF_3)_2PhCO_2^-$ bridging moiety creates a large distortion, with a large dihedral angle between the phenyl ring of the benzoate group and the plane composed of the bridging carboxylate and diruthenium sites. This distortion likely arises from the steric hindrance between the bulky CF_3 groups in the *ortho*-positions of 2,6-$(CF_3)_2PhCO_2^-$ and the carboxylate bridging moiety; the same steric interface likely prevents full substitution to form a homoleptic [$Ru_2^{II,II}$] species with neighboring 2,6-$(CF_3)_2PhCO_2^-$ ligands. The synthesis of these *trans*-substituted [$Ru_2^{II,II}$] complexes can be expanded to include other series. In addition, these types of *trans*-substituted [$Ru_2^{II,II}$] complexes can be useful as structurally anisotropic building blocks with C_2 symmetry for the design of low-dimensional assembled frameworks.

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