Dalton Transactions



View Article Online

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Cite this: Dalton Trans., 2025, **54**, 1838

Received 30th October 2024, Accepted 10th December 2024 DOI: 10.1039/d4dt03020f

rsc.li/dalton

Introduction

Carboxylate-bridged paddlewheel diruthenium(II,II) complexes $([Ru_2^{II,II}])^1$ are intriguing entities that act as secondary building units² for the construction of metal-organic frameworks.³⁻⁶ These complexes exhibit reversible redox activity, derived from oxidized $[Ru_2^{II,III}]^+$, without significant structural change.^{7,8} $[Ru_2^{II,III}]$ and $[Ru_2^{II,III}]^+$ species are both paramagnetic with multiple spin states (S = 1 and 3/2, respectively) and are useful magnetic building units⁹⁻¹² and they have the potential ability

Introduction of substituents for tuning the redox properties of benzoate-bridged paddlewheel diruthenium(II,II) complexes: what does the OH group bring?[†]

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Benzoate-bridged paddlewheel diruthenium(II,II) complexes ($[Ru_2^{I,II}(R_nArCO_2)_4(L_{ax}]_2]$ (L_{ax} = axial ligand); $[Ru_2^{I,II}]$) exhibit reversible redox activity involving the oxidized species $[Ru_2^{I,III}]^+$. The redox activity can be finely tuned over a broad potential range by altering the substituent R on the benzoate-bridging ligand $R_nArCO_2^-$. The electronic contributions of the substituents R depend on their type and position, as was empirically demonstrated by Hammett for substituents at the *meta-* and *para*-positions. However, the substituent effect at the *ortho*-position is not solely determined by the electronic contribution of R but also by steric hindrance between the *o*-substituents and adjacent carboxylate groups. Nevertheless, an OH group at the *o*-position did not provide any steric hindrance, leading to a strong electron-withdrawing effect owing to intramolecular hydrogen bonding between the *o*-OH group and the adjacent carboxylate group, despite the electron-donating ability of the *m*- and *p*-OH groups. The OH group at the *o*-position induced a significant shift in the redox potential and HOMO energy levels of the $[Ru_2^{I,II}]$ complexes, thereby stabilizing the $[Ru_2^{I,II}]$ state. The redox potential and HOMO can be adjusted by introducing additional substituents, such as F, CI, Me, OMe, and CF₃ groups, to cover a wide range, in accordance with an extended Hammett law that considers the contribution of the *o*-position.

for catalytic activity.¹³⁻¹⁸ The redox properties and HOMO energy levels of [Ru^{II,II}] can be precisely controlled by chemical modification of the carboxylate ligands.¹⁹⁻²² For example, for the series of [Ru^{II,II}] complexes with substituted benzoate ligands, $[Ru_2^{II,II}(R_nArCO_2)_4(L_{ax})_2] (R_nArCO_2^- = substituted ben$ zoate; Lax = axial ligand), the redox properties and HOMO energy levels can be predicted within the scale of Hammett's law for the congeners substituted at the meta- and parapositions.²³⁻²⁵ However, evaluation of the ortho-substituted congeners is less straightforward because of steric hindrance between the o-substituents and adjacent carboxylate groups, which constrains or weakens electronic conjugation between the aryl ring and carboxylate groups, in addition to the electronic effect of the o-substituents. Thus far, our group has synthesized various benzoate-bridged [Ru^{II,II}] complexes with substituents such as F, Cl, Me, OMe, CF₃, and OH, and demonstrated that the redox properties of these complexes follow an extended Hammett's law that includes the pseudo-Hammett constant, σ_o , obtained empirically by taking into account both the electronic and steric hindrance effects (Table 1),19,20,22 in addition to the common Hammett constants σ_m and σ_p for mand *p*-substituents, respectively.²⁶⁻³⁰ Interestingly, the strongly electron-withdrawing nature of the o-OH group was revealed,²⁰

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[†]Electronic supplementary information (ESI) available: Tables of crystallographic data, magnetic parameters, additional lists of electrochemical data, and HOMO levels of relevant compounds. Figures for magnetic data, ORTEP drawings of several compounds, molecular diagrams highlighting intermolecular hydrogen bonds, plots of $E_{1/2}$ vs. pK_{a} , HOMO levels vs. pK_{a} , and HOMO levels vs. $E_{1/2}$, and the structural models, which were subjected to DFT calculations to clarify the effect of the intramolecular hydrogen bonds. CCDC 2394123–2394139. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4dt03020f

 Table 1
 Hammett constants of the relevant substituents

Substituent	F	Cl	Br	Ме	ОМе	CF_3	Ph	ОН
para ^a meta ^a ortho	$0.062 \\ 0.337 \\ 0.217^{b}$	$0.227 \\ 0.373 \\ 0.272^{b}$	0.232 0.391	-0.170 -0.069 -0.070	-0.268 0.115 -0.397	0.54 0.43 0.50	0.144 0.06	-0.370 0.121 0.667 ^b

^{*a*} Hammett constants σ_m and σ_p were obtained from ref. 24. ^{*b*} Hammett constants σ_p were taken from ref. 20 and 22.

where o-OH exerted a large electron-withdrawing effect, with $\sigma_o(OH) = 0.667$ compared with $\sigma_o(F) = 0.217$ and $\sigma_o(Cl) = 0.272$, although the *m*- and *p*-OH groups exhibit electron-donating ability.25 This was first observed for the series of trans-heteroleptic $[Ru_2^{II,II}]$ complexes, $[Ru_2\{2,6-(CF_3)_2ArCO_2\}_2\{(OH)_rArCO_2\}_2$ $(THF)_2$], where $(OH)_x ArCO_2^-$ and $2,6-(CF_3)_2 ArCO_2^-$ indicate hydroxy-substituted benzoates and 2,6-(bistrifluoromethyl)benzoate, respectively (Chart 1).22 The o-OH group formed an intramolecular hydrogen bond with the oxygen atom of the bridging carboxylate and o-OH substituent, which not only retained the planarity of the benzoate ligand (associated with the electronic conjugation), but also strongly suppressed the electron-donating ability, consequently lowering the HOMO energy level of the [Ru₂^{II,II}] unit.²² This effect suggests that introducing additional substitutions such as F, Cl, Me, OMe, and CF₃ groups into the *m*- and/or *p*-positions in addition to the presence of the o-OH group should adjust the redox potentials and HOMO energy levels over a wide range.

This study presents 17 new $[Ru_2^{II,II}]$ complexes with the general formulas (i) $[Ru_2^{II,II} \{n-X-4-(OH)ArCO_2\}_4(THF)_2]$ (*nX4OH*), (ii) $[Ru_2^{II,II} \{n-X-2-(OH)ArCO_2\}_4(THF)_2]$ (*nX2OH*), and (iii) $[Ru_2\{2,6-(CF_3)_2ArCO_2\}_2\{n-X-2-(OH)ArCO_2\}_2(THF)_2]$ (*ht-nX2OH*), where X indicates a substituent and *n* is the position of the substituent on the aryl ring; (i) *n*-X-4-(OH)ArCO_2⁻ = 2-chloro-4-hydroxybenzoate, **3Cl4OH**; 3-fluoro-4-hydroxybenzoate, **3F4OH**; 3-chloro-4-hydroxybenzoate, **3Cl4OH**; 3-bromo-4-hydroxybenzoate, ate, **3Br4OH**; (ii) *n*-X-2-(OH)ArCO_2⁻ = 3-fluoro-2-hydroxybenzoate

ate, 3F2OH; 4-fluoro-2-hydroxybenzoate, 4F2OH; 4-chloro-2hydroxybenzoate, 4Cl2OH; 4-methyl-2-hydroxybenzoate, 4Me2OH; 5-chloro-2-hydroxybenzoate, 5Cl2OH; 5-bromo-2hydroxybenzoate, 5-methyl-2-hydroxybenzoate, 5Br2OH; **5Me2OH**; (iii) n-X-2-(OH)ArCO₂⁻ = 4-fluoro-2-hydroxybenzoate, ht-4F2OH; 4-chloro-2-hydroxybenzoate, ht-4Cl2OH; 4-methyl-2hydroxybenzoate, ht-4Me2OH; 4-methoxy-2-hydroxybenzoate, ht-40Me20H: 4-trifluoromethyl-2-hydroxybenzoate, ht-4CF₃2OH; 5-methyl-2-hydroxybenzoate, ht-5Me2OH (Chart 1). Families nX4OH and nX2OH have homoleptic paddlewheel motifs, whereas ht-nX2OH has a trans-heteroleptic paddlewheel motif. The redox activities of these compounds are evaluated via electrochemical measurements in the same medium. Density functional theory (DFT) calculations based on the atomic coordinates of the solid-state structures are used to estimate the HOMO energies of the compounds. Considering the $\sigma_o(OH)$ value, all of the complexes adhered to the extended Hammett's law on a unified scale.

Results and discussion

Syntheses and characterization

The present compounds were synthesized using previously reported methods.^{31,32} The homoleptic $[Ru_2^{II,II}{n-X-4-(OH)} ArCO_2]_4(THF)_2]$ (*nX4OH*) and $[Ru_2^{II,II}{n-X-2-(OH)ArCO_2}_4(THF)_2]$ (*nX2OH*) series were synthesized *via* ligand substitution of



Chart 1 Homoleptic $[Ru_2{R_nArCO_2}_4(THF)_2]$ and heteroleptic $[Ru_2{2,6-(CF_3)_2ArCO_2}_2{R_nArCO_2}_2(THF)_2]$ paddlewheel diruthenium(II,II) complexes described in this study.

 $[\operatorname{Ru}_{2}^{\mathrm{II,III}}(\operatorname{OAc})_{4}\operatorname{Cl}]$ (OAc⁻ = acetate), forming $[\operatorname{Ru}_{2}^{\mathrm{II,III}}\{n-X-4-(\operatorname{OH})\}$ $\operatorname{ArCO}_{2}_{4}(\operatorname{Cl})$ and $[\operatorname{Ru}_{2}^{\operatorname{II},\operatorname{III}}\{n-X-2-(\operatorname{OH})\operatorname{ArCO}_{2}_{4}(\operatorname{Cl})]$, respectively, followed by reduction to the $[Ru_2^{II,II}]$ species of *n*X4OH and nX2OH using Zn power in THF. The trans-heteroleptic complexes of [Ru₂{2,6-(CF₃)₂ArCO₂}₂{*n*-X-2-(OH)ArCO₂}₂(THF)₂] (htnX2OH) were synthesized via the ligand substitution reaction of [Ru₂^{II,III}{*n*-X-2-(OH)ArCO₂}₄(Cl)] with 2,6-bis(trifluoromethyl) benzoic acid 2,6-(CF₃)₂ArCO₂H in a 1:2 stoichiometric ratio to produce $[Ru_2^{II,III}{2,6-(CF_3)_2ArCO_2}_2{n-X-2-(OH)ArCO_2}_2(Cl)]$, followed by reduction to the $[Ru_2^{I,II}]$ species of **ht**-*n*X2OH using Zn powder in THF. All compounds with para-OH substituents contained additional THF molecules as crystallization solvents and proton acceptors of the p-OH group (see Structural Characterization and Elemental Analysis). In the previous study, recrystallization from THF was not successful for [Ru₂] with p-OHArCO₂⁻ (*p***-OH**; recrystallized from MeOH),³⁰ whereas the use of *n*-X-4-(OH)ArCO₂⁻ (n = 3-5, X = F, Cl, and Br) increased the solubility of the compounds in THF, resulting in successful isolation of single crystals as THF di-adducts. All compounds of *n***X4OH** were isolated as $[Ru_2^{II,II}]$, although *p*-**OH** was obtained as $[Ru_2^{II,III}]^{.30}$ This is because the halogen group compensates for the electron-donating ability of the *p*-OH group, stabilizing the low-valence state of $[Ru_2^{II,II}]$, as discussed hereinafter.

The oxidation state of the [Ru₂] unit and the electronic configuration of the frontier orbitals formed by Ru-Ru bonding can be easily determined by measuring the magnetic properties of the compounds. The temperature-dependence of the magnetization (M) of the compounds was determined using polycrystalline samples, in the temperature range of 1.8-300 K, by applying a dc field of 0.1 T (= H_{dc}); dc susceptibility ($\chi = M/$ H_{dc}). The $\chi T vs. T$ plots are shown in Fig. S1.[†] The χ -T plots for all compounds were almost identical, gradually increasing upon cooling from 300 K to approximately 100 K and reaching a plateau, followed by an increase at temperatures below approximately 10 K. The χT values of the compounds at 300 K all merged to a narrow range of 0.91–1.16 cm³ K mol⁻¹, and upon cooling, decreased smoothly to fall within the range of 1.1×10^{-2} to 2.4×10^{-1} cm³ K mol⁻¹ at 1.8 K. These χT -T features agree with those for isolated $[Ru_2^{II,II}]$ complexes with an S = 1 ground state featuring an anisotropic effect due to strong zero-field splitting (ZFS; $D \approx 330-460$ K for general [Ru₂^{II,II}] complexes).^{33–36} The increase in χ at low temperatures can be ascribed to paramagnetic impurities, such as [Ru₂^{II,III}]⁺ species with S = 3/2. Thus, the magnetic data were simulated using a Curie paramagnetic model with S = 1 considering the ZFS, temperature-independent paramagnetism (TIP), and impurities with $S = 3/2 (\rho)$.³⁷ Intermolecular interactions (zJ) have been considered for many magnetically isolated or weakly interacting [Ru₂^{II,II}] complexes within the framework of the mean-field approximation.³⁸ However, the state zJ = 0 was fixed for all the present compounds because it was not required to obtain an adequate fit. The best fits of the parameters (g = 2.0, fixed) for the compounds are listed in Table S2.† The estimated D values in the range of 337-462 K were consistent with the previously reported values for [Ru₂^{II,II}] species.^{33,34} Hence, it was concluded that all complexes had an electron configuration of $\sigma^2 \pi_2^4 \delta^2 {\delta^*}^2 {\pi^*}_2^2 {\sigma^*}^0$ for the Ru–Ru bond frontier orbital sets with degenerate levels of δ^* and two π^* orbitals.

Structures

All of the compounds were structurally characterized using single-crystal X-ray crystallography (Fig. 1 and Fig. S2[†]), confirming their paddlewheel features with Ru-Ru bonds in the homoleptic mode for nX4OH and nX2OH and in the trans-heteroleptic mode for ht-nX2OH, with THF as the axial ligand. The crystallographic data are presented in Table S1.[†] All units had an inversion center at the midpoint of the Ru-Ru bond. Only 4Cl2OH and 4OMe2OH had a mirror plane on the Ru-Ru bond that divided the paddlewheel equally, and a two-fold axis perpendicular to the mirror plane passed through the inversion center, providing high symmetry (C_{2h}) , which imposed disorder on the THF molecules, and only one of the four bridged benzoates was crystallographically unique (Fig. 1d and S2d[†]). The bond lengths around the Ru centers of the compounds are summarized in Table 2. For the series of carboxylate-bridged [Ru2] complexes, the Ru-Oeq (Oeq = equatorial oxygen atoms) bond distance is a good indicator for evaluating the oxidation state (Table 2); these distances are generally in the range of 2.06–2.08 Å and 2.02–2.04 Å for $[Ru_2^{II,II}]$ and $[Ru_2^{II,III}]^+$, respectively.^{1,19,20} The Ru–O_{eq} bond length varied in the range of 2.057-2.071 Å, indicating that all present compounds feature [Ru₂^{II,II}]. This is consistent with the magnetic properties described above. The Ru-Ru and Ru-O_{ax} (O_{ax} = axial THF oxygen atom) bond lengths of the complexes were 2.262-2.275 Å and 2.275-2.365 Å, respectively; these lengths were also in the range of [Ru^{II,II}₂] compounds.^{1,19,20}

The dihedral angle (θ) between the least-squares planes composed of two atomic sets (i) the aryl ring of the substituted benzoate ligand and (ii) the bridging carboxyl group and two Ru atoms (*i.e.*, the atom set of CO_2Ru_2 , Chart in Table 2) in the *n***X2OH** series is very small $(6.6 \pm 2.5^{\circ})$ (Table 2) owing to the formation of intramolecular hydrogen bonds between the o-OH group and carboxylate oxygen, with $O_{OH} \cdots O_{eq}$ (O_{eq} = carboxylate oxygen atom) distances of 2.56–2.62 Å (Table 2). Notably, positional disorder of the o-OH group was observed in 4Cl2OH and 4Me2OH, with an occupancy of 6:4 and 7:3, respectively, and both o-OH groups formed intramolecular hydrogen bonds. In the **ht**-*n*X2OH series, the average θ value for the X-2-(OH)ArCO₂⁻ moiety is small (7.2 \pm 8.4°), in contrast with the large θ value of 76.7 ± 9.7° for the 2,6-(CF₃)₂ArCO₂⁻ moiety.³⁹ A positional disorder of the o-OH group was also observed in ht-4Cl2OH and ht-4CF₃2OH, with the occupancy of 9:1 and 6:4, respectively. Interestingly, a minor part of the o-OH group in ht-4Cl2OH did not form an intramolecular hydrogen bond, but rather formed an intermolecular interaction with the CF₃ group of an adjacent molecule. Surprisingly, except for 2Cl4OH possessing an o-Cl group (θ = 22.8 \pm 0.8°), the value of θ in *n***X4OH** in the absence of *o*-substituents was relatively small $(7.7 \pm 4.5^{\circ}; \text{ Table 2})$,²⁰ which suggests preferential electronic conjugation between the carboxyl group and the aryl ring. The p-OH groups of nX4OH



Fig. 1 ORTEP drawings of **2Cl4OH**, (a) **3Br4OH** (b), **3F2OH** (c), **4Cl2OH** (d), **5Cl2OH** (e), **5Me2OH** (f), **ht-4F2OH** (g), and **ht-4OMe2OH** (h); red, gray, green, light-green, purple, and pink represent O, C, F, Cl, Br, and Ru, respectively. The grey bonds represent disordered atomic positions. Displacement ellipsoids are drawn at 50% probability level. The hydrogen atoms and crystallization solvents are omitted for clarity.

Table 2Relevant bond lengths (Å) and angles θ (°) around the Ru centers, where θ represents the dihedral angle between the least-squares planesdefined by the phenyl ring of the benzoate ligand and a bridging carboxylate system (atom set Ru₂O₂C)

					θ / \circ		
Compound	Ru-Ru/Å	Averaged Ru–O _{eq} /Å	Ru–O _{ax} /Å	Averaged O(<i>o</i> -OH)–O _{eq} /Å	Set-1 ^a	Set-2 ^b	Ref.
<i>о-</i> ОН	2.2681(3)	2.0650(6)	2.3098(12)	2.6035(14)	8.49	7.55	30
2Cl4OH	2.2664(16)	2.057(4)	2.344(7)	_ ()	23.07	22.57	This work
3F4OH	2.2677(3)	2.0608(8)	2.3646(16)	_	8.14	3.91	This work
3Cl4OH	2.2647(3)	2.0633(7)	2.3164(16)	_	8.61	7.13	This work
3Br4OH	2.2642(5)	2.0600(13)	2.325(2)	_	2.99	15.57	This work
3F2OH	2.2718(8)	2.066(2)	2.300(4)	2.595(5)	5.28	2.61	This work
4F2OH	2.2724(3)	2.0690(7)	2.3203(13)	2.6060(14)	6.59	8.31	This work
4Cl2OH	2.2698(12)	2.066(3)	2.312(6)	2.583(7)	3.49	_	This work
4Me2OH	2.2669(8)	2.060(2)	2.301(4)	2.570(7)	4.63	_	This work
5Cl2OH	2.2670(3)	2.0674(7)	2.3142(14)	2.6080(14)	7.92	10.05	This work
5Br2OH	2.2680(4)	2.0705(10)	2.318(2)	2.6175(18)	6.00	8.49	This work
5Me2OH	2.2620(5)	2.0608(10)	2.307(2)	2.601(3)	10.50	5.60	This work
ht-o-OH	2.2674(3)	2.0648(8)	2.3177(15)	2.569(3)	76.70	3.38	22
ht-4F2OH	2.2702(3)	2.0680(8)	2.3245(15)	2.560(3)	79.10	4.14	This work
ht-4Cl2OH	2.2658(3)	2.0659(8)	2.3178(15)	2.580(5)	85.99	4.95	This work
ht-4Me2OH	2.2667(4)	2.0641(8)	2.3207(16)	2.573(3)	84.81	4.91	This work
ht-40Me20H	2.2735(6)	2.0688(15)	2.341(2)	2.565(6)	79.94	2.28	This work
ht-4CF ₃ 2OH	2.2664(9)	2.057(4)	2.275(4)	2.603(9)	69.49	24.16	This work
ht-5Me2OH	2.2752(5)	2.0708(10)	2.309(2)	2.595(̀5)́	60.74	2.83	This work

^a Phenyl group of C2–C7(8). ^b Phenyl group of C9(10)–C14(16).

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form hydrogen bonds with the crystallization solvent (THF) or adjacent [Ru₂] molecules attached to the carboxyl group (Fig. S3[†]). The effects of the hydrogen bonds can also be observed in the OH stretching vibrations in the IR spectra (Fig. S4[†]). The OH stretching vibration in *n*X2OH and ht*n*X2OH showed little compound dependency. The OH group peak positions were concentrated in a narrow region (3220 ± 10 cm⁻¹ for *n*X2OH and 3205 ± 36 cm⁻¹ for ht-*n*X2OH), and the half-width of the peak also tended to be small. On the other hand, the OH stretching vibration in *n*X4OH shows compound dependency, with the peak positions distributed over a wide region (3185 ± 137 cm⁻¹), and the half-width of the peak also becomes wide. This may be because the compounds

*n***X**2**OH** and **h***tn***X**2**OH** form intramolecular hydrogen bonds, making the hydrogen bond properties similar, while the compounds *n***X**4**OH** form hydrogen bonds with the crystal solvent, making the hydrogen bond properties dependent on the crystal structure.

Electrochemistry in solution

The CVs of the compounds were acquired in N₂-saturated THF solutions using *n*-Bu₄N(PF₆) as the supporting electrolyte and Ag/Ag⁺ as the reference electrode (Fig. 2). The electrochemical data are summarized in Table 3, along with some relevant pK_a data for the corresponding benzoic acids and the summation of the Hammett constants.²⁴ For all compounds, a reversible,



Fig. 2 Cyclic voltammograms of nX4OH (a), nX2OH (b), and ht-nX2OH (c) in THF containing 0.1 M $n-Bu_4N(PF_6)$ under N₂ (mV vs. Ag/Ag⁺). The ferrocene/ferrocenium couple, Fc/Fc = 213 mV, was observed under the same conditions.

Table 3	Electrochemical data for [Ru ₂ (R _n ArCO ₂) ₄ (THF) ₂] and [Ru ₂ {2,6-(CF ₃) ₂ ArCO ₂) ₂ (R _n ArCO ₂) ₂ (THF) ₂] measured in THF containing	0.1 M /	n-Bu ₄ N
(PF ₆) und	der N ₂ (mV vs. Ag/Ag ⁺) ^a and HOMO levels calculated using density functional theory		

Compound	$E_{\rm a}/{\rm mV}$	$E_{\rm c}/{\rm mV}$	$E_{1/2}/\mathrm{mV}$	$\Delta E_p/\mathrm{mV}$	HOMO energy/eV	pK_a of benzoate ^b	$\sum (x\sigma_m + y\sigma_p)^c$	$\sum (x\sigma_m + y\sigma_p + z\sigma_o)^d$	Ref.
р-ОН	-134	-248	-191	114	(-4.02886)	4.57	-0.370	-0.370	30
2Cl4OH	-23	-249	-136	226	-4.15219	3.44	-0.370	-0.098	This work
3F4OH	220	-417	-99	636	-4.34675	4.23	-0.033	-0.033	This work
3Cl4OH	114	-237	-62	350	-4.30675	4.20	-0.003	-0.003	This work
3Br4OH	91	-237	-75	331	-4.38702	4.18	0.021	0.021	This work
<i>o</i> -OH	479	103	291	376	-4.64689	3.01	0	0.667	30
3F2OH	359	-52	154	412	-4.97615	2.45	0.337	1.004	This work
4F2OH	397	52	225	345	-4.99220	2.85	0.062	0.729	This work
4Cl2OH	458	94	276	364	-5.00771	2.71	0.227	0.894	This work
4Me2OH	330	55	193	276	-4.43981	3.17	-0.170	0.497	This work
5Cl2OH	519	135	327	384	-5.07629	2.64	0.373	1.040	This work
5Br2OH	459	136	298	323	-5.10894	2.61	0.391	1.058	This work
5Me2OH	406	54	230	352	-4.59982	3.30	-0.069	0.598	This work
ht-o-OH	491	91	291	232	-4.59002	2.27/3.01	0	0.667	22
ht-4F2OH	444	73	258	371	-4.75982	2.27/2.85	0.062	0.729	This work
ht-4Cl2OH	484	162	324	322	-4.71329	2.27/2.71	0.227	0.894	This work
ht-4Me2OH	346	71	208	274	-4.52852	2.27/3.17	-0.170	0.490	This work
ht-40Me20H	315	135	225	180	-4.47900	2.27/3.22	-0.268	0.399	This work
ht-4CF ₃ 2OH	470	312	391	158	-4.76036	2.27/2.45	0.540	1.207	This work
ht-5Me2OH	327	161	244	166	-4.55002	2.27/3.30	-0.069	0.598	This work

^{*a*} The ferrocene/ferrocenium couple, Fc/Fc⁺ = 213 mV, was observed under the same conditions described in the Experimental section. ^{*b*} Predicted values were calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02, obtained from the SciFinder-*n* database. ^{*c*} Hammett constants σ_n and σ_p were obtained from ref. 24. ^{*d*} Hammett constants σ_q were taken from ref. 20 and 22.

one-electron redox wave with $I_c/I_a \approx 1$ was observed, which was assigned to $[\text{Ru}_2^{\Pi,\Pi}]/[\text{Ru}_2^{\Pi,\Pi}]^+$. Notably, the redox potentials $(E_{1/2})$ of *n***X2OH** (154–327 mV in THF vs. Ag/Ag⁺) and *ht-n***X2OH** (208–391 mV in THF vs. Ag/Ag⁺) had relatively high, positive values compared to those of the $[\text{Ru}_2^{\Pi,\Pi}]$ compounds reported previously (Tables S4 and S5⁺).^{22,30} The positive shift in the potential was facilitated by substituting halogen groups at the



Fig. 3 Total plot of half-wave redox potential $(E_{1/2})$ vs. pK_a for the corresponding benzoic acids in the homoleptic series [Ru₂(R_nArCO₂)₄(THF)₂] [Ru₂{2,6-(a) and heteroleptic series $(CF_3)_2ArCO_2\}_2(R_nArCO_2)_2(THF)_2]$. The $E_{1/2}$ values were measured in THF using Ag/Ag⁺ reference electrode. Data for the compounds without an ortho substituent were chosen for the non-OH series in ref. 20, 21, 26, 27 and 29. Some of the $OH-[Ru_2]$ data were obtained from ref. 22 and 30. The solid, red line represents linear least-squares fitting line for nono-OH substituted series with equations of y = -360.23x + 1454.3 ($R^2 =$ 0.8677) for (a) and y = -255.72x + 1174.7 ($R^2 = 0.8704$) for (b). The dashed, blue line represents linear least-squares fitting line for mono-o-OH substituted series as the slope was fixed to that of red, solid line with equations of y = -360.23x + 1273.2 for (a) and y = -255.72x + 1032.5 for (b). Definitions: [Ru₂(R_nArCO₂)₄(THF)₂], R for 1, 3,4,5-F₃; 2, 3,5-F₂; 3, 3,4-F2; 4, m-F; 5, p-F; 6, 3,4,5-Cl3; 7, 3,5-Cl2; 8, 3,4-Cl2; 9, m-Cl; 10, p-Cl; 11, m-Me; 12, p-Me; 13, p-CF₃; 14, H; 15, p-Ph; 16, p-MeO; 17, p-CHO; [Ru₂{2,6-(CF₃)₂ArCO₂}₂(R_nArCO₂)₂(THF)₂], R for **46**, o-OH; **47**, m-OH; 48, p-OH; 49, 2,3-(OH)2; 50, 2,4-(OH)2; 51, 2,5-(OH)2; 52, 2,6-(OH)2; 53, 3,4-(OH)₂; 54, p-CF₃; 55, p-Cl; 56, p-F; 57, H; 58, p-Ph; 59, p-Me; 60, p-OMe; 61, p-CHO.

m- and *p*-positions, in addition to the *o*-position of the OH group. The *p*-OH group induced a negative shift of the potential (*e.g.*, -191 mV in THF *vs.* Ag/Ag⁺ for *p*-OH), but the additional substitution of halogen groups at the *m*-position pushed the potential back to the positive region, providing moderate negative $E_{1/2}$ values for *n*X4OH (-136 to -62 mV in THF *vs.* Ag/Ag⁺) (Table S4⁺).³⁰

The p K_a value of the corresponding benzoic acid (R_nArCO_2H) is a useful parameter for measuring the electronic effect of the benzoate ligands ($R_nArCO_2^-$) on the [Ru_2] dinuclear center.⁴⁰ Fig. 3 shows the plots of $E_{1/2}$ as a function of p K_a



Fig. 4 Total plot of half-wave redox potential $(E_{1/2})$ vs. $\sum (x\sigma_m + y\sigma_p + z\sigma_o)$ for homoleptic series of $[Ru_2(R_nArCO_2)_4(THF)_2]$ (a) and heteroleptic series of $[Ru_2(2,6-(CF_3)_2ArCO_2)_2(R_nArCO_2)_2(THF)_2]$ (b). The $E_{1/2}$ values were measured in THF using Ag/Ag⁺ reference electrode. The data for non-OH compounds were obtained from ref. 20, 21, 26, 27 and 29. Some of the OH– $[Ru_2]$ data were obtained from ref. 20, 21, 26, 27 and 29. Some of the OH– $[Ru_2]$ data were obtained from ref. 22 and 30. The solid line represents the linear least-squares fitting line with equations of y = 361.76x - 60.86 ($R^2 = 0.9177$) for (a) and y = 228.21x + 100.77 ($R^2 = 0.9379$) for (b). Definitions: $[Ru_2(R_nArCO_2)_4(THF)_2]$, R for **18**, F₅; **19**, 2,3,5.6-F₄; **20**, 2,3,4,5-F₄; **21**, 2,3,6-F₃; **22**, 2,4,5-F₃; **23**, 2,3,4-F₃; **24**, 2,3,5-F₃; **25**, 2,4,6-F₃; **26**, 2,5-F₂; **27**, 2,3-F₂; **28**, 2,6-F₂; **29**, 2,4-F₂; **30**, o-F; **31**, 2,3,4,5-Cl₄; **32**, 2,3,5-Cl₃; **33**, 2,3,4-Cl₃; **34**, 2,4,5-Cl₃; **35**, 2,5-Cl₂; **36**, 2,3-Cl₂; **37**, 2,6-Cl₂; **38**, 2,4-Cl₂; **39**, o-Cl; **40**, o-Me; **41**, 2,4,5-Me₃; **42**, o-OMe; **43**, 4-Cl-2-OMe; **44**, 4-F-2-OMe; **45**, o-CF₃; [Ru₂(2,6-(CF₃)₂ArCO₂)₂(THF)₂], R for **62**, 2,3,5,6-F₄.

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for the $[Ru_2(R_nArCO_2)_4(THF)_2]$ series and $[Ru_2\{2,6 (CF_3)_2ArCO_2_2(R_nArCO_2)_2(THF)_2$ reported previously.²² Only the data for the non-o-substituted compounds, except for the o-OH series in this study, were plotted in order to avoid the influence of steric hindrance from the o-substituent in the [Ru₂] compounds (2Cl4OH was also excluded from Fig. 3a because it contains an o-Cl group, which demonstrates a good linear relationship for the mono-o-Cl-substituted [Ru₂] series (Fig. S5[†]).²⁰). Although the *o*-OH group did not produce significant steric hindrance, the nX2OH and ht-nX2OH groups were outside the linear scale created by the $[Ru_2(R_nArCO_2)_4(THF)_2]$ and $[Ru_2\{2,6-(CF_3)_2ArCO_2\}_2(R_nArCO_2)_2(THF)_2]$ series, respectively, providing a new group with smaller pK_a and positive $E_{1/2}$ values (Fig. 3). Therefore, the nX2OH and ht-nX2OH groups should be evaluated independently. The relationship is linear depending on the electronic effects of the *m*- and *p*-substituents, with slopes similar to those of $[Ru_2(R_nArCO_2)_4(THF)_2]$ and [Ru₂{2,6-(CF₃)₂ArCO₂}₂(R_nArCO₂)₂(THF)₂], respectively. The dashed lines in Fig. 3 were drawn by fixing the slope to the red lines for $[Ru_2(R_nArCO_2)_4(THF)_2]$ and $[Ru_2\{2,6-(CF_3)_2ArCO_2\}_2]$ $(R_n ArCO_2)_2 (THF)_2$]. Conversely, *n***X4OH** (with a *p*-OH group) has a larger pK_a and more negative $E_{1/2}$, indicating the electron-donating nature of the p-OH group; however, the data for *n***X4OH** followed the linear plot for $[Ru_2(R_nArCO_2)_4(THF)_2]$ (Fig. 3a).

As observed previously, the relationship between $E_{1/2}$ and pK_a depends on the number of substituents at the *o*-position (NSO), which may be due to the alteration of the electronic conjugation between the aryl ring and carboxylate group, due directly to the steric effect of the *ortho*-substituents with NSO = 1 and 2.^{19,20} Because no significant steric hindrance was observed in the case of *o*-OH-substituted benzoate ligands, the discrepancy between the *n***X2OH** and **h***t*-*n***X2OH** groups compared to the non-*o*-OH-substituted series may be due to another contribution of the electronic effect intrinsically caused by intra-



Fig. 5 Frontier orbitals associated with π^* and δ^* orbitals of 2Cl4OH and corresponding energy levels (eV), where δ^* for the β electron corresponds to the HOMO level.

molecular *o*-OH···O_{eq} hydrogen bonding. This electronic effect was evaluated as $\sigma_o(OH) = 0.667$ based on analysis of [Ru₂{2,6-(CF₃)₂ArCO₂}₂{*o*-(OH)ArCO₂}₂(THF)₂] (Table 1).²²

If all the Hammett constants, including the *pseudo*-Hammett constants, σ_o , are considered, the $E_{1/2}$ values of all [Ru₂] compounds should be related in a unified linear plot, that is, through an extended Hammett's law. Fig. 4 shows the plot of $E_{1/2}$ vs. $\sum (x\sigma_m + y\sigma_p + z\sigma_o)$, where *x*, *y*, and *z* represent the number of substituents at the *meta-*, *para-*, and *ortho*-positions, respectively; Fig. 4(a and b) shows the data for the homoleptic and *trans*-heteroleptic [Ru₂] series, respectively. The data for all series are summarized in Table S3,[†] where the Hammett constants summarized in Table 1 were used.^{20,22,24} Note that the slopes of the plot for the homoleptic and hetero-



Fig. 6 Plot of HOMO level *vs.* pK_a for homoleptic series of $[Ru_2(R_nArCO_2)_4(THF)_2]$ (a) and heteroleptic series of $[Ru_2(2,6-(CF_3)_2ArCO_2)_2(R_nArCO_2)_2(THF)_2]$ (b). Data for the compounds without an *ortho* substituent were chosen for the non-OH series from ref. 20, 21, 26, 27 and 29. Some of the OH– $[Ru_2]$ data were obtained from ref. 22, and 30. The solid, red line represents the linear least-squares fitting line for non-*o*-OH substituted series with equations of y = 0.9334x - 8.1874 ($R^2 = 0.8914$) for (a) and y = 0.4963x - 6.5179 ($R^2 = 0.7966$) for (b). The solid, blue line represents the linear least-squares fitting line for mono-*o*-OH substituted series with equations of y = 0.7495x - 6.9863 ($R^2 = 0.7613$) for (a) and y = 0.3122x - 5.5657 ($R^2 = 0.7376$) for (b).

leptic series are different because the compounds are composed of four and two $R_nArCO_2^-$ ligand blades, respectively (Fig. 4a and b). Linear relationships for the homoleptic and heteroleptic series were observed, with $E_{1/2}$ (mV) = $362 \times \sum(x\sigma_m + y\sigma_p + z\sigma_o) - 60.9$ ($R^2 = 0.918$) and $E_{1/2}$ (mV) = $228 \times \sum(x\sigma_m + y\sigma_p + z\sigma_o) + 101$ ($R^2 = 0.938$), respectively. These plots indicate that the redox properties of the [Ru₂] series can be predicted well in the framework of Hammett analyses; that is, the redox properties can be well-tuned by modifying the substituents of the benzoate ligands. Notably, the electron-withdrawing effect of the *o*-OH group was significant even in cases where other substituents were present at the *m*- or *p*-positions.

HOMO energy levels

To determine the energy levels of the molecular orbitals (MOs) of the compounds, DFT calculations were performed based on



Fig. 7 HOMO level vs. half-wave redox potential $(E_{1/2})$ for homoleptic series of $[Ru_2(R_nArCO_2)_4(THF)_2]$ (a) and heteroleptic series of $[Ru_2(2,6-(CF_3)_2ArCO_2)_2(R_nArCO_2)_2(THF)_2]$ (b). The $E_{1/2}$ values were measured in THF using Ag/Ag⁺ reference electrode. Data for the compounds without an *ortho* substituent were chosen for the non-OH series from ref. 20, 21, 26, 27 and 29. Some of the OH– $[Ru_2]$ data were obtained from ref. 22 and 30. The solid line represents the linear least-squares fitting line with equations of $y = (-2.033 \times 10^{-3})x - 4.412$ ($R^2 = 0.7623$) for (a) and $y = (-1.324 \times 10^{-3})x - 4.291$ ($R^2 = 0.8109$) for (b).

Table 4Calculated energy values of the HOMO level of compoundspossessing o-OH substituents with or without intramolecular hydrogenbonds, where the values for o-OH and ht-o-OH were referred from ref.30 and 22, respectively

Compound	Actual model with hydrogen bond (eV)	Hypothetical OH-free model without hydrogen bond (eV)
<i>о</i> -ОН	-4.64689	-3.65231
3F2OH	-4.97615	-3.99926
4F2OH	-4.99220	-4.00334
4Cl2OH	-5.00771	-4.03654
4Me2OH	-4.43981	-3.52061
5Cl2OH	-5.07629	-4.08688
5Br2OH	-5.10894	-4.12579
5Me2OH	-4.59982	-3.53857
ht-o-OH	-4.58993	-4.07649
ht-4F2OH	-4.75982	-4.24416
ht-4Cl2OH	-4.71329	-4.21042
ht-4Me2OH	-4.52852	-4.02429
ht-40Me20H	-4.47900	-3.98402
ht-4CF ₃ 2OH	-4.76036	-4.31301
ht-5Me2OH	-4.55002	-4.07736

the crystal structures (Fig. 5 and S6 and Table S5[†]). For all the compounds, the HOMO, which is most likely involved in the $[Ru_2^{II,II}]/[Ru_2^{II,III}]^+$ redox couple, was assigned to the $\delta^*(\beta)$ frontier orbital.^{19,20,22,30} The HOMO energy levels of the complexes are listed in Table 3. The estimated HOMO levels of the compounds linearly correlated with pK_a (Fig. 6), as observed in the $E_{1/2}$ vs. pK_a plots in Fig. 3. The correlations for the *n***X2OH** and ht-nX2OH groups are different from those of the non-o-OH series of $[Ru_2(R_nArCO_2)_4(THF)_2]$ and $[Ru_2\{2,6-(CF_3)_2ArCO_2\}_2]$ $(R_n ArCO_2)_2 (THF)_2$]. Consequently, the HOMO energy levels and $E_{1/2}$ values are strongly correlated in a unified relationship, even for the o-OH series (Fig. 7).^{19-22,30} The nX4OH compounds have relatively high HOMO energies (-4.387 to -4.152 eV) owing to the strong electron-donating effect of the p-OH group, whereas nX2OH (-5.109 to -4.440 eV) and ht-nX2OH (-4.763 to -4.479 eV) have lower HOMO energies, ascribed to the electron-withdrawing effect of the o-OH group. To evaluate the impact of intramolecular hydrogen bonding, DFT calculations were performed for a model in which the hydrogen atom of the o-OH group was directed outward to interrupt the hydrogen bonding (i.e., the hypothetical model); the atomic coordinates were the same, except for that of H on the o-OH group (Fig. S7[†] and Tables 4 and S6[†]).^{22,30} In these hypothetical non-hydrogen bonding models, the HOMO levels were higher than those of the actual *n***X2OH** ($\Delta E_{HOMO} \sim 1 \text{ eV}$) and **ht**-*n*X2OH ($\Delta E_{HOMO} \sim 0.5 \text{ eV}$), indicating that the intramolecular hydrogen bonding of the o-OH group strongly affects the HOMO levels in the nX2OH and htnX2OH series (Table 4).

Conclusions

Eleven homoleptic complexes (*n*X2OH and *n*X4OH) and six heteroleptic $[Ru_2^{II,II}]$ complexes (*ht-n*X2OH) were synthesized by introducing substituents such as F, Cl, Me, OMe, and CF₃

groups, as well as OH groups, to the bridging benzoate. The o-OH groupacts as a powerful electron-withdrawing group owing to the intramolecular hydrogen bonding between the o-OH group and the oxygen of the bridging carboxyl group, resulting in a *pseudo*-Hammett constant of $\sigma(OH) = 0.667$. The $pK_a, E_{1/2}$, and HOMO levels of $[Ru_2^{II,II}]$ complexes are critical parameters for evaluating their electronic nature. In a previous report, the $E_{1/2}$ values and HOMO levels of *o*-OH-substituted complexes $[Ru_2\{2,6-(CF_3)_2ArCO_2\}_2\{o-OHArCO\}_2(THF)_2]$ were treated on the same scale as those of non-o-OH complexes; however, this was incorrect. The electronic effect of the o-OH group, associated with intramolecular hydrogen bonding, is significant and intrinsic. Therefore, homoleptic and heteroleptic $[Ru_2^{II,II}]$ complexes with an *o*-OH group should be treated differently from the congeners without an o-OH group. We have been gradually expanding the scope of applying this empirical approach to ortho substituents to predict the redox ability of [Ru₂] in several previous papers.^{19,20,22} In the future, as we continue to increase the types of substituents and compounds, we may find out the potential limitations of the applicability of this method, but fortunately, so far, everything has worked well. That is, by adding OH substituents, as well as F, Cl, Me, OMe, and CF₃ groups, to the benzoate ligands, the redox properties of the [Ru₂] complexes can be widely tuned.

Experimental section

General procedures and materials

Specific synthetic procedures were performed under inert atmosphere (N_2) using standard Schlenk-line techniques in a commercial glovebox. All chemicals were of reagent grade and were purchased from commercial sources. The solvents were dried using common drying agents and were distilled under nitrogen atmosphere before use. $[Ru_2^{II,III}(CH_3CO_2)_4Cl]$ was prepared as reported previously.³¹

 $\begin{array}{l} Synthesis of \left[Ru_{2}(3\text{-}F\text{-}4\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (3F4OH), \left[Ru_{2}(2\text{-}Cl\text{-}4\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (2Cl4OH), \left[Ru_{2}(3\text{-}Cl\text{-}4\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (3Cl4OH), \left[Ru_{2}(3\text{-}Br\text{-}4\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (3Br4OH), \left[Ru_{2}(3\text{-}F\text{-}2\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (3F2OH), \left[Ru_{2}(4\text{-}F\text{-}2\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (4F2OH), \left[Ru_{2}(4\text{-}Cl\text{-}2\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (4Cl2OH), \left[Ru_{2}(4\text{-}Me\text{-}2\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (4Me\text{2}OH), \left[Ru_{2}(5\text{-}Cl\text{-}2\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (5Cl2OH), \left[Ru_{2}(5\text{-}Br\text{-}2\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (5Br2OH), and \left[Ru_{2}(5\text{-}Me\text{-}2\text{-}(OH)ArCO_{2})_{4}(THF)_{2}\right] (5Me\text{2}OH) \\ ArCO_{2})_{4}(THF)_{2}\right] (5Me\text{2}OH) \end{array}$

The compounds were synthesized in a step-by-step manner *via* a ligand substitution process involving $[Ru_2^{II,III}]^+$, followed by reduction to the corresponding $[Ru_2^{II,II}]$ products;³² the method is similar to that used for previously reported compounds.³⁰ Only the procedure for **3F4OH** is described here. $[Ru_2^{II,III}]$ (CH₃CO₂)₄Cl] (711 mg, 1.50 mmol) and 3-fluoro-4-hydroxyben-zoic acid (1000 mg, 5.07 mmol) were refluxed in a 1 : 3 solution of MeOH and H₂O (40 mL) for 12 h under aerobic conditions to synthesize $[Ru_2^{II,III}(3-F-4-(OH)ArCO_2)_4Cl]$. The reddish-brown precipitate was collected by filtration, washed with water, and

dried in vacuo. Without further purification, a tetrahydrofuran (THF) solution (50 mL) of the crude, red precipitate was stirred with Zn powder (120 mg, 1.84 mmol) for 24 h under nitrogen atmosphere. The brown solution was filtered, and the filtrate was layered with *n*-hexane and allowed to stand for at least one week, affording 3F4OH as brown crystals in 30% yield. Elemental analysis (%) calculated for C₅₂H₆₄F₄O₁₈Ru₂ (3F4OH·4THF): C 49.75, H 5.14. Found: C 49.36, H 5.03. IR (KBr): $\nu(CO_2) = 1545$, 1391 cm⁻¹. For 2Cl4OH·2THF, yield: 44%. Elemental analysis (%) of C₄₄H₄₈Cl₄O₁₆Ru₂: C 44.90, H 4.11. Found: C 44.79, H 4.28. IR (KBr): $\nu(CO_2) = 1557$, 1392 cm⁻¹. For **3Cl4OH**·4THF, yield: 39%. Elemental analysis (%) calculated for C₅₂H₆₄Cl₄O₁₈Ru₂: C 47.29, H 4.88. Found: C 47.18, H 4.81. IR (KBr): ν (CO₂) = 1543, 1384 cm⁻¹. For 3Br4OH·4THF, yield: 51%. Elemental analysis (%) calculated for C₅₂H₆₄Br₄O₁₈Ru₂: C 41.67, H 4.30. Found: C 41.77, H 4.26. IR (KBr): ν (CO₂) = 1548, 1384 cm⁻¹. For **3F2OH**, yield: 40%. Elemental analysis (%) calculated for C₃₆H₃₂F₄O₁₄Ru₂: C 44.72, H 3.34. Found: C 44.70, H 3.46. IR (KBr): ν (CO₂) = 1559, 1393 cm⁻¹. For **4F2OH**, yield: 27%. Elemental analysis (%) calculated for C₃₆H₃₂F₄O₁₄Ru₂: C 44.72, H 3.34. Found: C 44.72, H 3.36. IR (KBr): ν (CO₂) = 1556, 1450, 1371 cm⁻¹. For 4Cl2OH, yield: 14%. Elemental analysis (%) calculated for C36H32Cl4O14Ru2: C 41.87, H 3.12. Found: C 41.94, H 3.12. IR (KBr): $\nu(CO_2) = 1555$, 1438, 1362 cm⁻¹. For **4Me2OH**, yield: 63%. Elemental analysis (%) calculated for C40H47O15.5Ru2 (4Me2OH·1.5H₂O): C 49.13, H 4.84. Found: C 49.12, H 4.84. IR (KBr): ν (CO₂) = 1547, 1434, 1387 cm⁻¹. For 5Cl2OH, yield: 48%. Elemental analysis (%) calculated for C36H32Cl4O14Ru2: C 41.87, H 3.12. Found: C 41.94, H 3.12. IR (KBr): ν (CO₂) = 1551, 1440, 1367 cm⁻¹. For **5Br2OH**, yield: 37%. Elemental analysis (%) calculated for C₃₆H₃₂Br₄O₁₄Ru₂: C 35.72, H 2.66. Found: C 35.73, H 2.67. IR (KBr): ν (CO₂) = 1551, 1439, 1386 cm⁻¹. For 5Me2OH, vield: 54%. Elemental analysis (%) calculated for C40H46O15Ru2 (5Me2OH·H2O): C 49.58, H 4.79. Found: C 49.64, H 4.65. IR (KBr): ν (CO₂) = 1549, 1431, 1367 cm⁻¹.

 $\begin{array}{l} Synthesis of \left[Ru_{2}\{2,6-(CF_{3})_{2}ArCO_{2}\}_{2}\{4\text{-}F\text{-}2-(OH)ArCO_{2}\}_{2}(THF)_{2}\right] \\ (ht-4F2OH), \left[Ru_{2}\{2,6-(CF_{3})_{2}ArCO_{2}\}_{2}\{4\text{-}C\text{-}2-(OH)ArCO_{2}\}_{2}(THF)_{2}\right] \\ (4Cl2OH), \left[Ru_{2}\{2,6-(CF_{3})_{2}ArCO_{2}\}_{2}\{4\text{-}(OMe\text{-}2-(OH)ArCO_{2}\}_{2}(THF)_{2}\right] \\ (4Me2OH), \left[Ru_{2}\{2,6-(CF_{3})_{2}ArCO_{2}\}_{2}\{4\text{-}(OMe\text{-}2\text{-}(OH) \\ ArCO_{2}\}_{2}(THF)_{2}\right] \\ (4OMe2OH), \left[Ru_{2}\{2,6-(CF_{3})_{2}ArCO_{2}\}_{2}\{4\text{-}(CF_{3})_{2}ArCO_{2}\}_{2}\{4\text{-}(CF_{3})_{2}ArCO_{2}\}_{2}\{4\text{-}(CF_{3})_{2}ArCO_{2}\}_{2}\{4\text{-}(CF_{3})_{2}ArCO_{2}\}_{2}\{4\text{-}(CF_{3})_{2}ArCO_{2}\}_{2}\{4\text{-}(OH)ArCO_{2}\}_{2}(THF)_{2}\right] \\ (4CF_{3}2OH), and \left[Ru_{2}\{2,6\text{-}(CF_{3})_{2}ArCO_{2}\}_{2}\{5\text{-}Me\text{-}2\text{-}(OH)ArCO_{2}\}_{2}(THF)_{2}\right] \\ (5Me2OH) \\ \end{array}$

The compounds were synthesized in a stepwise manner *via* a ligand substitution process involving $[Ru_2^{II,III}]^+$, followed by reduction to the corresponding $[Ru_2^{II,II}]$ products.³² The method is similar to that used for previously reported compounds.²² Only the procedure for **ht-4Me2OH** is described here. $[Ru_2^{II,III}(CH_3CO_2)_4CI]$ (600 mg, 1.27 mmol) and 4-methyl-2-hydroxybenzoic acid (1552 mg, 10.2 mmol) were refluxed in a 1:2 solution of MeOH and H₂O (20 mL) for 12 h under aerobic conditions to synthesize $[Ru_2^{II,III}(4-Me-2-(OH) ArCO_2)_4CI]$ (1 mmol, 834 mg) and 2,6-bis(trifluoromethyl) benzoic acid (2 mmol, 516 mg) were refluxed in a 1:3 solution

of MeOH and H₂O (40 mL) for 12 h under aerobic conditions obtain $[Ru_2^{II,III}(4-Me-2-(OH)ArCO_2)_2(2,6-(CF_3)_2ArCO_2)_2Cl].$ to The obtained reddish-brown precipitate was collected via filtration, washed with water, and dried in vacuo. Without further purification, a THF solution (80 mL) of the crude red precipitate was stirred with Zn powder (117 mg, 1.8 mmol) for 48 h at room temperature under nitrogen atmosphere. The brown solution was filtered, and the filtrate was layered with *n*-hexane and allowed to stand for at least one week, affording ht-4Me2OH as brown crystals in 60% yield. Elemental analysis (%) calculated for $C_{50}H_{52}F_{12}O_{14}Ru_2$ (ht-4Me2OH·2THF): C 45.95, H 4.01. Found: C 46.34, H 3.92. IR (KBr): ν (CO₂) = 1579, 1503 cm⁻¹. For ht-4F2OH, yield: 61%. Elemental analysis (%) calculated for C40H30F14O12Ru2: C 41.03, H 2.58. Found: C 41.11, H 2.68. IR (KBr): ν (CO₂) = 1572, 1439 cm⁻¹. For ht-4Cl2OH, yield: 59%. Elemental analysis (%) calculated for C₄₀H₃₀Cl₂F₁₂O₁₂Ru₂: C 39.91, H 2.51. Found: C 39.77, H 2.57. IR (KBr): ν (CO₂) = 1581, 1436 cm⁻¹. For **ht-4OMe2OH**, yield: 60%. Elemental analysis (%) calculated for C₄₄H₄₀F₁₂O_{14.5}Ru₂ (ht-4OMe2OH-0.5THF): C 42.93, H 3.28. Found: C 42.68, H 3.29. IR (KBr): ν (CO₂) = 1577, 1450 cm⁻¹. For ht-4CF₃2OH, yield: 61%. Elemental analysis (%) calculated for C44H40F12O14.5Ru2 (ht-4CF32OH-0.5THF): C 42.93, H 3.28. Found: C 42.68, H 3.29. IR (KBr): ν (CO₂) = 1577, 1450 cm⁻¹. For ht-5Me2OH, yield: 61%. Elemental analysis (%) calculated for C₅₂H₅₆F₁₂O_{14.5}Ru₂ (ht-5Me2OH·2.5THF): C 46.50, H 4.20. Found: C 46.45, H 4.05. IR (KBr): ν (CO₂) = 1548, 1484 cm⁻¹.

General physical measurements

Infrared spectra were recorded with KBr disks using a Jasco FT-IR 4200 spectrometer. Magnetic susceptibility measurements were conducted with a Quantum Design SQUID magnetometer (MPMS-XL) by applying a magnetic field of 0.1 T in the temperature range of 1.8-300 K, for which polycrystalline samples embedded in liquid paraffin were used. The experimental data were corrected for the diamagnetic contributions of the sample holder and liquid paraffin using Pascal's constants.⁴¹ Cyclic voltammograms (CVs) were recorded in THF with tetra-n-butylammonium hexafluorophosphate (n-Bu₄N (PF_6) , 0.1 M) as the supporting electrolyte, under nitrogen atmosphere, using an electrochemical analyzer (ALS/[H] CH Instruments Model 600A) with a glassy carbon electrode as the working electrode, a Pt counter electrode, and a Ag/AgNO₃ reference electrode. First, the CV data were acquired for the solvent containing only the supporting electrolyte. The desired compounds were then added to this solution ([compound] = 1 \times 10⁻³ M), and the CVs were acquired at a scan rate of 0.05 V s^{-1} . Finally, the CV potentials in THF were adjusted using the ferrocene/ferrocenium couple (Fc/Fc⁺ = 213 mV (ΔE = 91 mV) in THF vs. Ag/Ag^+) as an internal standard.

Crystallography

Crystal data were collected on a Rigaku Saturn 724 CCD area detector and a Rigaku Hypix 6000 hybrid photon-counting X-ray detector with multilayer, mirror-monochromated Mo-K α radiation ($\lambda = 0.71075$ Å). The structures were solved using an

intrinsic phasing method (SHELXT version 2018/2)^{42,43} and expanded using Fourier techniques (SHELXL version 2018/3).44 All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were introduced as fixed contributors. Fullmatrix least-squares refinements on F^2 were based on observed reflections and variable parameters, and converged with unweighted and weighted agreement factors of $R_1 = \sum ||F_0| - |$ $F_{\rm c}||/\sum |F_{\rm o}| \ (I > 2.00\sigma(I)) \ \text{and} \ wR_2 = [\sum w(F_{\rm o}^2 - F_{\rm c}^2)^2 / \sum w(F_{\rm o}^2)^2]^{1/2}$ (all data). All calculations were performed using the OLEX2 crystallographic software package.⁴⁴ 3F4OH, 3Cl4OH, 3Br4OH, and 4F2OH contain a disordered THF, which could be modeled as two distinct parts and optimized for occupancy. 4Cl2OH and 4Me2OH also contained disordered THF imposed by molecular symmetry, whose occupancy was fixed at 0.5. 3F4OH, 4Cl2OH, 4Me2OH, ht-4Cl2OH, and ht-4CF₃2OH contain positional disorder of the substituent (m-F or o-OH) in the benzoate moiety. ht-4Cl2OH and ht-4Me2OH contain rotational disorder in the o-CF₃ group. These disorders were modeled as two distinct parts and were optimized for occupancy. Solvent mask function of OLEX2 software⁴⁴ was used for 4Cl2OH, 4Me2OH, and ht-5Me2OH, which were reasonably modeled in the presence of a 1.4THF, 2.4THF, and 1THF, respectively, per [Ru₂]. The details of the crystal structure analysis are summarized in Table S1.[†] These data have been deposited as CIFs at the Cambridge Data Centre as supplementary publication notes. CCDC 2394123, 2394124, 2394125, 2394126, 2394127, 2394128, 2394129, 2394130, 2394131, 2394132, 2394133, 2394134, 2394135, 2394136, 2394137, 2394138, and 2394139 for 2Cl4OH, 3F4OH, 3Cl4OH, 3Br4OH, 3F2OH, 4F2OH, 4Cl2OH, 4Me2OH, 5Cl2OH, 5Br2OH, 5Me2OH, ht-4F2OH, ht-4Cl2OH, ht-4Me2OH, ht-4OMe2OH, ht-4CF₃2OH, and ht-5Me2OH, respectively.[†] Molecular diagrams were constructed using the VESTA software.45

Computational details

Theoretical ab initio calculations were performed using the DFT formalism, as implemented in Gaussian 16 software,⁴⁶ employing Beck's three-parameter hybrid functional with the correlation functional of Lee, Yang, and Parr (B3LYP).47 Unrestricted open-shell calculations were performed for molecules containing [Ru₂] units. The effective core potential basis function LanL2TZ with polarization (LanL2TZ(f))⁴⁸⁻⁵⁰ was used for Ru atoms, and the 6-31G basis sets with polarization and diffusion functions (6-31+G(d))⁵¹⁻⁵⁵ were used for C, H, F, Cl, Br, and O atoms, respectively. Spin polarization with $S_z = 1$ (triplet spin multiplicity) was used for the [Ru₂] units in the calculations. The atomic coordinates determined by X-ray crystallography were used in the calculations. In the case of the disordered atoms in the benzoate groups, atoms with major occupancy were used. In the calculations for 4Cl2OH and **4Me2OH**, the molecular symmetry must be reduced from C_{2h} to eliminate the structural disorder. C_2 and C_i are the candidates for the lower molecular symmetry, and the structures with the latter symmetry were adopted because they have a lower energy, as indicated by DFT calculations.

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Author contributions

H. M. conceived the study. Y. W., T. K., and C. I. prepared and characterized the materials. W. K. analyzed the data. W. K. and H. M. supervised the experiments. W. K. prepared the original draft. All authors discussed the results and commented on the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.†

Tables of crystallographic data, magnetic parameters, additional lists of electrochemical data, and HOMO levels of relevant compounds. Figures for magnetic data, ORTEP drawings of several compounds, molecular diagrams highlighting intermolecular hydrogen bonds, plots of $E_{1/2}$ vs. pK_a , HOMO levels vs. pK_a , and HOMO levels vs. $E_{1/2}$, and the structural models, which were subjected to DFT calculations to clarify the effect of the intramolecular hydrogen bonds. Computational details are described in the experimental part of the article.

Crystallographic data for 2Cl4OH, 3F4OH, 3Cl4OH, 3Br4OH, 3F2OH, 4F2OH, 4Cl2OH, 4Me2OH, 5Cl2OH, 5Br2OH, 5Me2OH, ht-4F2OH, ht-4Cl2OH, ht-4Me2OH, ht-4OMe2OH, ht-4CF32OH, and ht-5Me2OH have been deposited at the Cambridge Data Centre as supplementary publication as CCDC 2394123, 2394124, 2394125, 2394126, 2394127, 2394128, 2394129, 2394130, 2394131, 2394132, 2394133, 2394134, 2394135, 2394136, 2394137, 2394138, and 2394139, respectively.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This study was supported by a Grant-in-Aid for Scientific Research (No. 18H05208, 20H00381, 21H01900, 21K18925, 22H00324, and 23K21104) from MEXT, Japan, the GIMRT program, and the E-IMR project, Tohoku University.

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