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Neutral Paddlewheel Diruthenium Complexes with Tetracarboxylates of Large π-Conjugated Substituents: Facile One-Pot Synthesis, Crystal Structures, and Electrochemical Studies

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A one-pot reaction of a cationic diruthenium complex, $[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2](BF_4)$, with arylcarboxylic acids, $ArCO_2H$, ($PhCO_2H$ = benzoic acid, $NapCO_2H$ = 1-naphthoic acid, $AntCO_2H$ = 9-anthracenecarboxylic acid) in NDMA (NDMA = *N*,*N*-dimethylaniline) has led to isolation of neutral paddlewheel-type diruthenium complexes, $[Ru^{II}_2(O_2CAr)_4(THF)_2]$ (Ar = Ph (**1**), Nap (**2**), Ant (**3**)). Paramagnetic variable temperature (VT) ^{1}H NMR studies and GC-MS studies show that the reaction consists of two steps: a one-electron reduction of the Ru_2 core by NDMA and a simple carboxylate-exchange reaction. All compounds **1**–**3** were structurally characterized by X-ray crystallography. While the structural features of the Ru_2 core are very similar in all the compounds, the dihedral angles between the carboxylate plane and the aromatic ring are larger with the expanding of aryl groups from phenyl to anthracene. The effect of π–π stacking leads to the formation of a 1-D chain structure in compound **3**, whereas compounds **1** and **2** are fully isolated from each other. The electrochemical measurements show that the quasireversible one-electron oxidation step is observed at +0.06, +0.09, and +0.17 V (vs Ag/Ag$^+$) for **1**–**3**, respectively, assigned to the $Ru^{II}_2/Ru^{II,III}_2$ redox couple. These potentials are found to demonstrate a linear relationship with the substituent constants for aryl compounds, $\sigma^-_{\pi,B}$.

Introduction

The design and synthesis of extended frameworks with metal−metal bonded dinuclear complexes[1] provide a new area of supramolecular chemistry due to their structurally and physically unique properties.[2] The recent development is based on the neutrality of dimetal moieties (M_2L_4) consisting of common M^{II}_2 (M = Mo, Rh) cationic centers with four monoanionic functional groups (L^-_4) and the choice of suitable linkers into the equatorial and axial positions of dimetal environments through coordination bonds. Hence, the recent studies have achieved a first step by the utilization of stable and synthetically established Mo_2[3] and Rh_2[4] building units, which have the common property of a closed-shell electron configuration. The next challenge is to focus on other metals (M = V, Cr, Re, Ru, Os, Ir, Pd, Pt, and Cu), potentially available to form homologous structures with M_2L_4 paddlewheel motifs. In the synthesis of supramolecular assemblies, one of the priorities is to find readily accessible

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or, at least, easily prepared building blocks. Therefore, we have explored a versatile synthetic method for dimetal precursors, which could possess the capabilities of coordination and/or noncovalent interactions such as hydrogen bonding and $\pi-\pi$ stack interactions for molecular assemblies.

From this viewpoint, diruthenium complexes with tetracarboxylate derivatives,[5] $[Ru_2(O_2CR)_4]^{n+}$ ($n \geq 0$), are intriguing molecular units because of their rich redox chemistry and magnetic properties characteristic of the oxidation states of the Ru_2 core ($S = 1$ for the neutral complex and $S = {}^3/_2$ for the cationic complex) with unusually large zero-field splittings.[6] However, the diruthenium chemistry has principally focused on the cationic core[7] ($n = 1$) rather than the neutral core ($n = 0$). This is because the synthesis of cationic compounds is easier than that of the corresponding neutral compounds. In practice, the well-accepted synthesis of the neutral compound is the direct way via "blue solution"[8] prepared by reduction of $RuCl_3{\cdot}3H_2O$ by H_2 in the presence of excess alkali metal carboxylate.[9-11] The reaction should go through a very air-sensitive neutral intermediate, $[Ru^{II}_2(O_2CH)_4]$ or $[Ru^{II}_2(O_2CCH_3)_4]$, followed by a substitution reaction with the desired carboxylates, and therefore, several steps are needed to isolate the intended compounds. This synthetic difficulty of preparing the neutral compounds has, to date, limited the process to producing only a few examples of supramolecular arrays.[12]

Our strategy for the construction of molecular assemblies of the Ru^{II}_2 core is the introduction of large π-conjugated aromatic rings such as anthracene, which could display an effective intermolecular $\pi-\pi$ stack interaction. In order to investigate geometrical and electronic structures of the unit molecule itself and its assemblies, three neutral diruthenium complexes with arylcarboxylates, $[Ru^{II}_2(O_2CAr)_4(THF)_2]$ (Ar = Ph (**1**), Nap (**2**), Ant (**3**), $PhCO_2H$ = benzoic acid, $NapCO_2H$ = 1-naphthoic acid, $AntCO_2H$ = 9-anthracenecarboxylic acid), were prepared and structurally characterized.[13] For this investigation, a simple synthetic route for diruthenium complexes was also developed, what we call a one-pot reaction of $[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2](BF_4)$[14] with carboxylate derivatives in *N*,*N*-dimethylaniline (NDMA). Moreover, electrochemical studies show an excellent linear correlation between the half-wave potentials of **1**−**3** and the substituent constants for aryl compounds, $\sigma^{-}_{\pi,\mathrm{B}}$ ($R^2 > 0.99$).

Experimental Section

Materials and Reagents. All the syntheses were performed under dry nitrogen atmosphere using standard Schlenk techniques. THF and hexane were dried and then distilled under nitrogen following conventional methods. *N*,*N*-Dimethylaniline was purchased from Wako Pure Chemical Industries and deoxygenated before use. Benzoic acid and 1-naphthoic acid were purchased from Wako Pure Chemical Industries, and 9-anthracenecarboxylic acid was purchased from Aldrich, and used without further purification. The starting cationic diruthenium complex, $[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2](BF_4)$,[14] was prepared by literature method.

Synthesis of $[Ru_2(O_2CPh)_4(THF)_2]$ (1). $[Ru_2(O_2CCH_3)_4(THF)_2](BF_4)$, 69.1 mg (0.132 mmol), and benzoic acid, 67.7 mg (0.554 mmol), were refluxed in 20 mL of *N*,*N*-dimethylaniline for 12 h. After removal of solvent in vacuo, the addition of anhydrous THF afforded a red solution of the neutral complex, $[Ru^{II}_2(O_2CPh)_4(THF)_2]$, and gray precipitates (**4**). Pure compound was isolated as a red crystalline material by the recrystallization with THF/hexane (88.0 mg, 0.106 mmol, 80% yield). Elemental analysis calcd for $C_{18}H_{18}O_5Ru$: C 52.04, H 4.37. Found: C 52.13, H 4.87. HRMS (FAB) calcd for $C_{28}H_{20}O_8Ru_2$ $[Ru_2(O_2CPh)_4]$ (M+) 678.9245, found 678.9244.

Synthesis of $[Ru_2(O_2CNap)_4(THF)_2]$ (2). The compound was prepared in a similar way to **1**, except that 1-naphthoic acid was used as the starting material (67% yield). Elemental analysis calcd for $C_{26}H_{22}O_5Ru$: C 60.58, H 4.30. Found: C 60.93, H 4.47. HRMS (FAB) calcd for $C_{44}H_{28}O_8Ru_2$ $[Ru_2(O_2CNap)_4]$ (M+) 887.9871, found 887.9870.

Synthesis of $[Ru_2(O_2CAnt)_4(THF)_2]$ (3). The compound was prepared in a similar way to **1**, except that 9-anthracenecarboxylic acid was used as the starting material (68% yield). Elemental analysis calcd for $C_{34}H_{26}O_5Ru$: C 66.33, H 4.26. Found: C 66.25, H 4.35. HRMS (FAB) calcd for $C_{60}H_{36}O_8Ru_2$ $[Ru_2(O_2CAnt)_4]$ (M+) 1088.0497, found 1088.0482.

Identification of Gray Powder (4). The gray precipitate, **4**, was obtained as a residue after the filtration of the red solution of compounds **1**−**3**. This powder was analyzed by FAB-MS spectroscopy, GC-MS spectroscopy, and ^1H NMR spectroscopy. The results indicate that the oxidative products of NDMA are *N*,*N*-dimethyl-*p*-toluidine and 4,4′-methylenebis(*N*,*N*-dimethylaniline). The latter compound is not detected by NMR spectroscopy. This should be caused by the low yield of the compound. For *N*,*N*-dimethyl-*p*-toluidine: MS (FAB), 136 ($M + H^+$); GC-MS (EI), the first fraction, 135 (M^+); ^1H NMR in THF-d_8, 2.00 (s, 3H), 2.81 (s, 6H), 6.57 (d, 2H), 6.91 (d, 2H). For 4,4′-methylenebis(*N*,*N*-dimethylaniline: MS (FAB), 255 ($M + H^+$); GC-MS (EI), the second fraction, 254 (M^+).

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Table 1. Crystallographic Data for **1**−**3**

	1	**2**	**3**
formula	$C_{18}H_{18}O_5Ru_5$	$C_{26}H_{22}O_5Ru$	$C_{68}H_{52}O_{10}Ru_2$
fw/g·mol^{-1}	830.81	1031.04	1231.27
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/a$
T/K	223	223	223
λ/Å	0.7107	0.7107	0.7107
a/Å	10.318(3)	9.462(2)	10.336(3)
b/Å	10.406(3)	10.747(2)	22.802(7)
c/Å	16.003(4)	12.156(3)	22.722(7)
α/deg		75.787(10)	
β/deg	91.144(6)	85.32(1)	94.586(5)
γ/deg		65.474(6)	
V/Å^3	1717.8(7)	1089.9(5)	5337.6(2)
Z	4	2	4
D_{calcd}/g·cm^{-3}	1.606	1.571	1.532
μ(Mo Kα)/cm^{-1}	0.936	0.755	0.631
unique reflns	2422 ($I > 3.00\sigma(I)$)	4316 ($I > 4.00\sigma(I)$)	7517 ($I > 2.00\sigma(I)$)
no. variables	217	289	721
GOF	1.156	1.561	0.694
$R1^a$	0.0469	0.0276	0.0293
$wR2^{b,c}$	0.1090	0.0940	0.0626

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $w = 1/[\sigma^2 F_o^2 + (p(\max(F_o^2, 0) + 2F_c^2)/3)^2]$, where $p = 0.05$ for **1**−**3**.

Table 2. Selected Carboxylate Stretching Frequencies for Ru_2 Complexes

compd	$\nu_{sym}(CO_2)$/cm^{-1}	$\nu_{asym}(CO_2)$/cm^{-1}	$\Delta\nu = \nu_{asym}(CO_2) - \nu_{sym}(CO_2)$/cm^{-1}
1	1407	1548	141
2	1414	1552	138
3	1393	1542	149
$Ru^{II}_2(O_2CCH_3)_4(THF)_2$[9,10]	1440	1560	120
$Ru^{II}_2(O_2CCF_3)_4(THF)_2$[11]	1462	1643	167
$[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2](BF_4)$[14]	1400	1460	60
$[Ru_2^{II,III}(O_2CPh)_4]Cl$[16,17]	1410	1470	60

Physical Measurements. Infrared spectra were measured on KBr disks with a Perkin-Elmer System 2000 FT-IR spectrometer. Mass spectra and high-resolution mass spectra (HRMS) were obtained with a JEOL JMS-HX110A mass spectrometer using *m*-nitrobenzylalchol as a matrix. GC-MS was measured with a JEOL JMS-BU20 GC-Mate mass spectrometer combined with an HP 6890 series GC system gas chromatograph.

VT ^1H NMR spectra were recorded on a JEOL A-500 spectrometer, and chemical shifts are referenced to residual protons of deuterated solvents. The isotropic shift was calculated using analogous dirhodium tetraacetates $Rh_2(O_2CCH_3)_4$ in DMF-d_7 chemical shift as a diamagnetic shift standard (1.7 ppm). Sample solutions were prepared for two solutions: $[Ru_2(O_2CCH_3)_4(THF)_2](BF_4)$ in DMF-d_7 (A) and in DMF-d_7 containing 15 wt % NDMA (B).

Cyclic voltammograms (CVs) were recorded on a BAS CV-50W voltammetric analyzer with carbon working electrode, Pt counter electrode, and Ag/Ag$^+$ reference electrode. The measurements were carried out in a glovebox. Sample solutions were ca. 1.0 mM in THF (*n*-tetrabutylammonium tetrafluoroborate [TBA(BF_4)] = 0.1 M as a supporting electrolyte). The ferrocene/ferrocenium couple occurs at $E_{1/2} = +0.21$ V under the same conditions of the cyclic voltammograms for the diruthenium compounds in THF.

X-ray Crystallographic Analyses. Measurements were conducted on Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The data were collected up to 55°. The structures were solved by Patterson methods (DIRDIF92/PATTY) and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were introduced as fixed contributors. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[15] Crystal data and details of the structure determination of **1**−**3** are summarized in Table 1.

Results and Discussion

One-Pot Synthesis and Characterization. The current synthesis of neutral diruthenium tetracarboxylate complexes, $[Ru^{II}_2(O_2CR)_4]$, requires intermediate species of $[Ru^{II}_2(O_2CH)_4]$ or $[Ru^{II}_2(O_2CCH_3)_4]$,[10] which are very air sensitive, and therefore, the preparation of the complexes with various substituents, R, has been limited. Herein, we describe a facile synthesis of this family, which resulted in obtaining the three diruthenium complexes, **1**−**3**; they were synthesized by a simple and relevant one-pot reaction of $Ru_2^{II,III}$ complexes with carboxylate derivatives in NDMA, as a consequence of one-electron reduction followed by a substitution reaction. An NDMA solution of $[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2](BF_4)$ and $ArCO_2H$ (1:4 mol/mol) was refluxed under a nitrogen atmosphere. After solvent was removed in vacuo, the addition of anhydrous THF produced a red solution of the neutral complex, $[Ru^{II}_2(O_2CAr)_4(THF)_2]$ and gray precipitates (**4**). The red crystals of **1**−**3** were obtained by the diffusion method in THF/hexane. The yields of **1**−**3** were about 80%, 67%, and 68% based on $[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2](BF_4)$, respectively.

The symmetric ($\nu_{sym}(CO_2)$) and asymmetric ($\nu_{asym}(CO_2)$) bridging carboxylate stretching modes in the infrared spectra are diagnostic features for oxidation states of diruthenium tetracarboxylate compounds.[5] The values of $\nu_{sym}(CO_2)$ and $\nu_{asym}(CO_2)$ and their separations, $\Delta\nu = \nu_{asym}(CO_2) - \nu_{sym}(CO_2)$, for **1**−**3** are listed in Table 2. The $\Delta\nu$ values of **1**−**3** are 141, 138, and 149 cm^{-1}, respectively, similar to that of $[Ru^{II}_2(O_2CCH_3)_4(THF)_2]$[9,10] (120 cm^{-1}), while dissimilar to that of 60 cm^{-1} for $[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2](BF_4)$,[14] indicating that these complexes have an Ru^{II}_2 oxidation state. X-ray crystal structure determination and electrochemical studies, as mentioned below, also support the assignment of this oxidation state to these complexes.

Reaction Processes. When $[Ru_2^{II,III}(O_2CCH_3)_4Cl]_n$[16,17] was used as a $Ru_2^{II,III}$ starting material, the desired Ru^{II}_2 compounds could not be obtained. This is because the compound has a 1-D structure of dimetal units linked by chloride ions, and the axial ligand exchange reaction with NDMA is not favored due to the strong electrostatic attractive interaction between the diruthenium core and the chloride ion, compared with the fully isolated complex, $[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2](BF_4)$, where two solvent molecules occupy the axial

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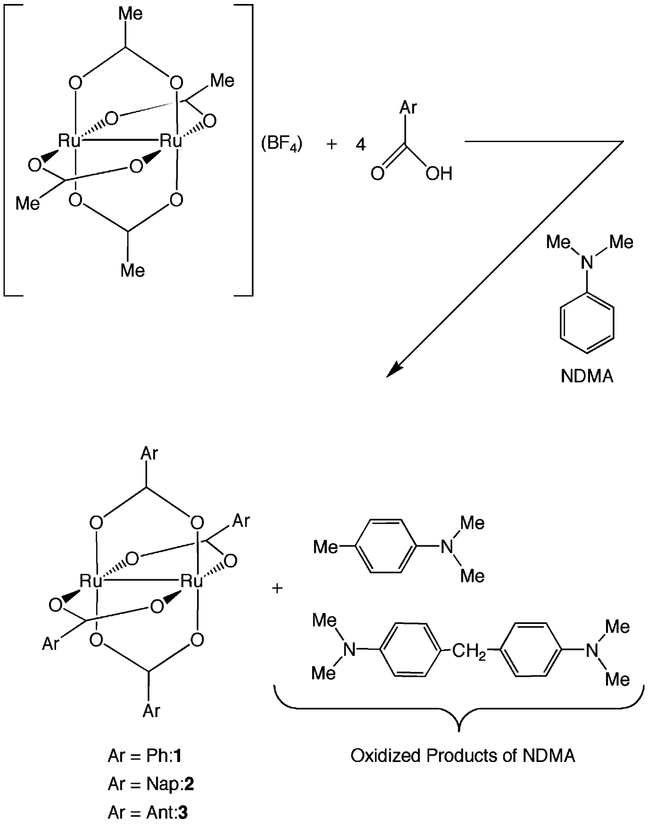
Scheme 1



positions. This indicates the importance of NDMA ligation to the axial position of the dimetal core as a first step for this reaction.

In this reaction, two possible mechanisms could be considered: one is a disproportionation reaction ($2Ru_2^{II,III} \rightarrow Ru^{II}_2 + Ru^{III}_2$),[18] and the other is a simple one-electron reduction reaction. The yield of these complexes, 80% for **1**, 67% for **2**, and 68% for **3**, all higher than 50%, exhibits a reduction process rather than a disproportionation. This is also supported by the identification of the gray powder **4** by FAB-MS, GC-MS, and NMR spectroscopy. Two major peaks in the GC-MS were obtained: in the first fraction the maximum peak is *m*/*z* 135 while in the second one it is *m*/*z* 254, and these are undoubtedly assigned to the NDMA oxidation products, *N*,*N*-dimethyl-*p*-toluidine and 4,4′-methylenebis(*N*,*N*-dimethyl-aniline), respectively. The former compound was also identified by ^1H NMR spectroscopy, whereas the latter one did not show a signal because of the low yield (Scheme 1). A similar oxidation reaction of NDMA was reported with palladium(II) acetate as oxidant.[19]

For a better understanding of the reaction, paramagnetic ^1H NMR spectra were measured because the isotropic shifts of protons are highly influenced by the spin multiplicities and/or the oxidation state of the Ru_2 core ($S = 1$ for Ru^{II}_2 and $S = {}^3/_2$ for $Ru_2^{II,III}$). Owing to the paramagnetic nature of the Ru_2 core for the neutral and cationic species, their NMR resonances show a downfield shift from the values observed for the analogous diamagnetic compound (eq 1). Here, the dirhodium compound is used as a diamagnetic shift standard. The isotropic shift results from the distribution of unpaired spin density via contact and dipolar mechanisms (eq 2).

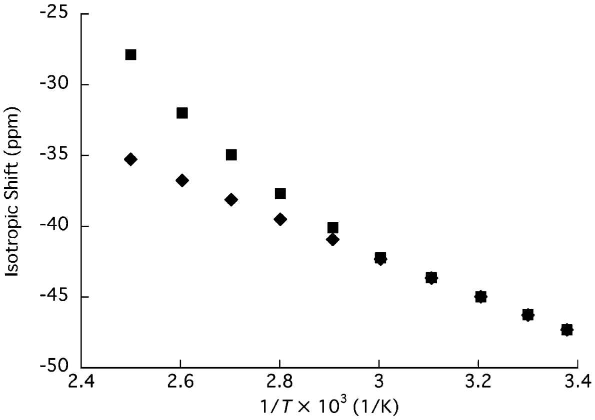


Figure 1. 1/*T* dependence of the isotropic shift for $[Ru_2^{II,III}(O_2CCH_3)_4](BF_4)$ in DMF-d_7 (sample A, ◆) and in DMF-d_7 containing 15 wt % NDMA (sample B, ■).

$$\delta_{\text{observed}} = \delta_{\text{diamagnetic}} + \delta_{\text{isotropic}} \qquad (1)$$

$$\delta_{\text{isotropic}} = \delta_{\text{contact}} + \delta_{\text{dipolar}} \qquad (2)$$

The paramagnetic ^1H NMR spectra for the paddlewheel diruthenium compounds have been thoroughly investigated in the tetraoctanoate compounds.[20] According to that study, both dipolar and contact mechanisms influence the isotropic shifts of equatorial carboxylates, causing downfield and upfield shifts, respectively. However, it is worth noting that the α-CH_2 protons of the cationic compound have the larger contact contribution inducing upfield shifts (−42.4 ppm) while the dipolar shift can be negligible. On the other hand, those signals in the neutral compound were observed at 3.2 ppm, showing that the total isotropic shift is much smaller than that for the cationic species. This is because the dipolar contribution is also expected to be large because of the very large zero-field splitting.

Temperature-dependent ^1H NMR spectroscopy was carried out for two solutions, $[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2](BF_4)$ in DMF-d_7 (A) and in DMF-d_7 containing 15 wt % NDMA (B). Figure 1 plots the isotropic shifts for the methyl group of the acetate bridge versus 1/*T* in the range 23−127 °C. For both solutions, the acetate protons undergo upfield shifts (−46 ppm) at 23 °C. These shifts are dominated by a contact shift rather than a dipolar shift, consistent with those shown in the tetraoctanoate compounds.

$$\delta_{\text{contact}} = \frac{A_{\text{con}}\bar{g}\beta S(S+1)}{3g_n\hbar kT} \qquad (3)$$

Equation 3 predicts that the chemical shift obeys a linear relationship with 1/*T*. This typical behavior of a paramagnetic

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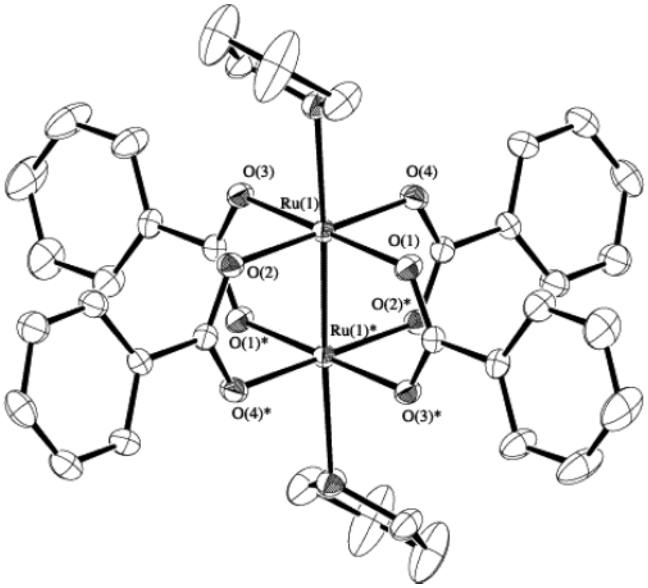

Figure 2. ORTEP view of $[Ru_2(O_2CPh)_4(THF)_2]$ (**1**) at the 40% probability level. Hydrogen atoms have been omitted for the sake of clarity.

compound is shown in sample A. On the other hand, sample B shows a nonlinear correlation, curving away from the linear correlation and producing a concave-shaped curve upon increasing the temperature. In other words, the contribution of the isotropic shift in the high-temperature region is smaller than the expected shift shown in sample A. This behavior could be attributed to the change of the spin multiplicity, S, from $S = {}^3/_2$ to $S = 1$ accompanying the reduction of the $Ru_2^{II,III}$ core to the Ru^{II}_2, giving rise to a decrease in the contact contribution due to the $S(S + 1)$ factor in eq 3. Moreover, the decreased value of the total isotropic shift corresponds to that shown in the neutral tetraoctanoate compounds. The coordination of NDMA does not explain this observation because a simple binding to the axial positions does not change the oxidation state of the Ru_2 core. The NMR spectra show the simple reduction of the Ru_2 core in the absence of additional carboxylic acids;[21] namely, a two-step reaction proceeded: the first step is an electron-transfer reaction between the diruthenium complex and NDMA, while the second step is a simple carboxylate-exchange reaction.

Description of Structures. Compounds **1** and **2** have one crystallographically independent molecule in the unit cell, as shown in Figures 2 and 3, respectively. On the other hand, **3** possesses two distinct but similar Ru_2 molecules, named **3**α and **3**β (Figure 4). The selected bond distances and angles are listed in Tables 3−5. For all the complexes, the inversion center is located on the midpoint of the Ru−Ru bond in each compound. Thus, the molecule is constructed from one Ru atom, two arylcarboxylates (I and II), and one THF molecule in the asymmetric unit. Figures 2−4 illustrate the overall ligand arrangement around the Ru_2 core. The Ru−Ru distances (2.2642(8) Å for **1**, 2.2672(3) Å for **2**, 2.2633(7) Å for **3**α, and 2.2649(8) Å for **3**β) are very similar to those of typical paddlewheel diruthenium complexes.[5] The average bond distances of $Ru-O_{eq}$ in **1**, **2**, **3**α, and **3**β are 2.065, 2.068, 2.062, and 2.068 Å, respectively, consistent with those of $[Ru^{II}_2(O_2CCH_3)_4(THF)_2]$[9,10] (2.060 Å) and $[Ru^{II}_2(O_2CCF_3)_4(THF)_2]$[11] (2.073 Å), and dissimilar to those of $[Ru_2^{II,III}(O_2CCH_3)_4(H_2O)_2](BF_4)$[17,22] (2.008 Å) and $Ru_2^{II,III}(O_2CCH_3)_4Cl$[16,17] (2.017 Å). This also supports the formation of the Ru^{II}_2 oxidation state.

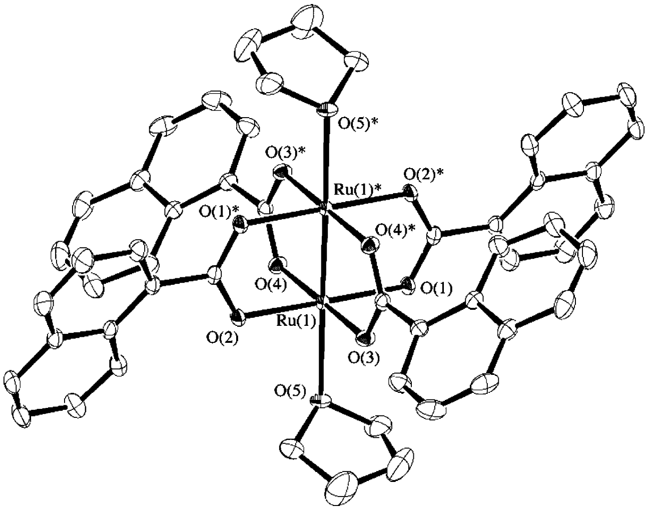

Figure 3. ORTEP view of $[Ru_2(O_2CNap)_4(THF)_2]$ (**2**) at the 40% probability level. Hydrogen atoms have been omitted for the sake of clarity.

The crystal-packing feature (Figure 5) for **3** is attributed to the formation of a 1-D chain through effective $\pi-\pi$ stack interactions, which is different from the cases of **1** and **2**. The molecules of **1** and **2** are clearly isolated from each other, indicating that any effective interaction between the molecules does not operate despite the presence of the aromatic substituents. On the other hand, $[Ru^{II}_2(O_2CAnt)_4(THF)_2]$ (**3**) shows a unique packing mode, dissimilar to the others, displaying two types of intermolecular arrangement regarding the anthracene moieties; one is a face-to-face orientation, and the other is a face-to-edge orientation. In the former, the center-to-center separation for the parallel-arranged anthracenes is 3.395 Å, indicative of a typical $\pi-\pi$ stack interaction, whereas an appreciable interaction is not detected in the latter one. From the symmetry operation, the molecules form the 1-D structure through π-stacking.

The dihedral angles, θ, defined by the carboxylate plane and the aromatic ring (Scheme 2) in **1**−**3** are summarized in Table S1. In the case of the phenyl derivative (**1**), the carboxylate planes are almost coplanar with the aromatic rings, $\theta = 13.6°$ and $22.3°$, which are very close to those of the *p*-toluate complex, $[Ru^{II}_2(O_2C\text{-}p\text{-}tol)_4(THF)_2]$[20] ($\theta = 13.8°$ and $16.6°$). Interestingly, the dihedral angle becomes larger as the π-conjugated moieties expand. This is associated with the steric repulsion between peri-CH and O in the carboxylic

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[20] Chisholm, M. H.; Christou, G.; Folting, K.; Huffman, J. C.; James, C. A.; Samuels, J. A.; Wesemann, J. L.; Woodruff, W. H. *Inorg. Chem.* **1996**, *35*, 3643.

[21] In order to isolate the neutral tetraacetate compound, the simple reaction of $[Ru_2^{II,III}(O_2CCH_3)_4(THF)_2](BF_4)$ in NDMA in the absence of additional carboxylic acids was carried out, but we could not obtain the corresponding $Ru_2^{II,II}$ compound. On the other hand, the reaction with excess acetic acid produced X-ray quality crystals of the previously reported neutral compound, $[Ru^{II}_2(O_2CCH_3)_4(H_2O)_2]$.

[22] Marsh, R. E.; Schomaker, V. *Inorg. Chem.* **1981**, *20*, 299.

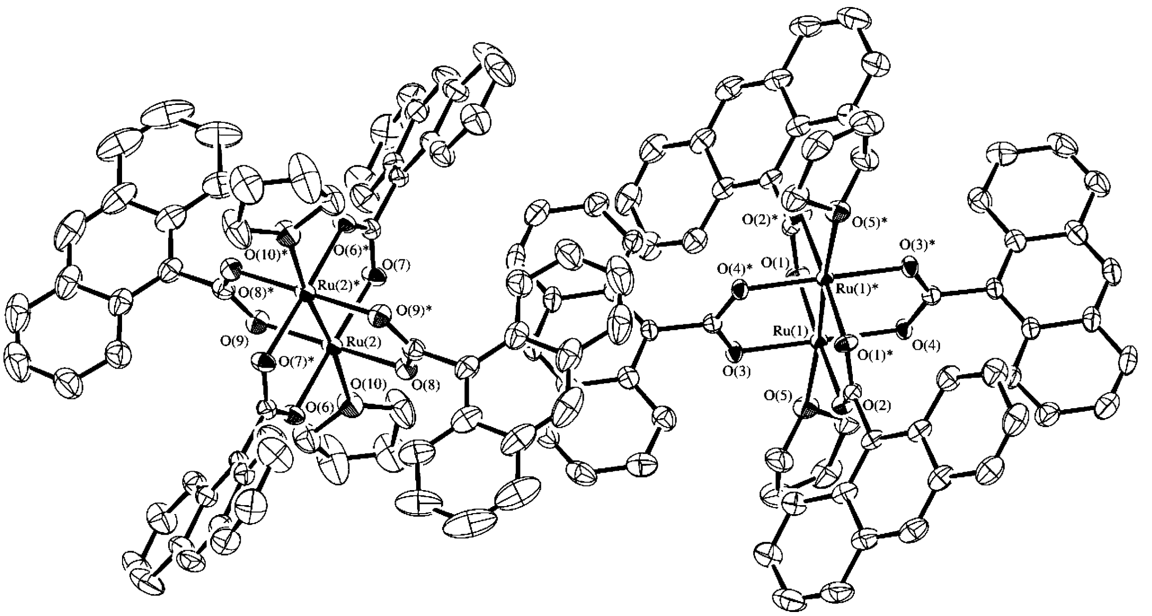

Figure 4. ORTEP view of $[Ru_2(O_2CAnt)_4(THF)_2]$ (**3**) at the 40% probability level. In one unit cell, there are two distinct Ru_2 complexes, named **3**α (right) and **3**β (left). Intermolecular interactions (3.395 Å) are exhibited between **3**α and **3**β on the anthracene moieties. Hydrogen atoms have been omitted for the sake of clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**

Distances (Å)			
Ru(1)−Ru(1)*	2.2642(8)	Ru(1)−O(1)	2.066(3)
Ru(1)−O(2)	2.071(3)	Ru(1)−O(3)	2.064(3)
Ru(1)−O(4)	2.057(3)	Ru(1)−O(5)	2.341(4)
Angles (deg)			
Ru(1)−Ru(1)*−O(1)	89.38(9)	Ru(1)−Ru(1)*−O(2)	89.39(10)
Ru(1)−Ru(1)*−O(3)	89.96(10)	Ru(1)−Ru(1)*−O(4)	89.91(10)
Ru(1)−Ru(1)*−O(5)	177.75(10)	O(1)−Ru(1)−O(2)	93.0(1)
O(1)−Ru(1)−O(3)	178.6(1)	O(1)−Ru(1)−O(4)	87.3(1)
O(1)−Ru(1)−O(5)	90.3(1)	O(2)−Ru(1)−O(3)	88.3(1)
O(2)−Ru(1)−O(4)	179.3(1)	O(2)−Ru(1)−O(5)	88.4(1)
O(3)−Ru(1)−O(4)	91.5(1)	O(3)−Ru(1)−O(5)	90.4(1)
O(4)−Ru(1)−O(5)	92.3(1)		

Table 4. Selected Bond Distances (Å) and Angles (deg) for **2**

Distances (Å)			
Ru(1)−Ru(1)*	2.2672(3)	Ru(1)−O(1)	2.070(2)
Ru(1)−O(2)	2.064(2)	Ru(1)−O(3)	2.065(2)
Ru(1)−O(4)	2.072(2)	Ru(1)−O(5)	2.347(2)
Angles (deg)			
Ru(1)−Ru(1)*−O(1)	89.22(5)	Ru(1)−Ru(1)*−O(2)	89.93(5)
Ru(1)−Ru(1)*−O(3)	89.68(5)	Ru(1)−Ru(1)*−O(4)	89.71(5)
Ru(1)−Ru(1)*−O(5)	175.03(4)	O(1)−Ru(1)−O(2)	178.94(5)
O(1)−Ru(1)−O(3)	88.34(7)	O(1)−Ru(1)−O(4)	92.54(6)
O(1)−Ru(1)−O(5)	90.88(6)	O(2)−Ru(1)−O(3)	91.02(7)
O(2)−Ru(1)−O(4)	88.08(7)	O(2)−Ru(1)−O(5)	89.95(6)
O(3)−Ru(1)−O(4)	178.92(5)	O(3)−Ru(1)−O(5)	88.35(6)
O(4)−Ru(1)−O(5)	92.25(6)		

Table 5. Selected Bond Distances (Å) and Angles (deg) for **3**

Distances (Å)			
Ru(1)−Ru(1)*	2.2633(7)	Ru(1)−O(1)	2.063(2)
Ru(1)−O(2)	2.055(2)	Ru(1)−O(3)	2.065(2)
Ru(1)−O(4)	2.064(2)	Ru(1)−O(5)	2.340(2)
Ru(2)−Ru(2)*	2.2649(8)	Ru(2)−O(6)	2.053(2)
Ru(2)−O(7)	2.075(2)	Ru(2)−O(8)	2.069(2)
Ru(2)−O(9)	2.076(2)	Ru(2)−O(10)	2.342(2)
Angles (deg)			
Ru(1)−Ru(1)*−O(1)	89.79(6)	Ru(1)−Ru(1)*−O(2)	89.24(6)
Ru(1)−Ru(1)*−O(3)	88.41(6)	Ru(1)−Ru(1)*−O(4)	90.97(6)
Ru(1)−Ru(1)*−O(5)	175.83(6)	O(1)−Ru(1)−O(2)	177.83(8)
O(1)−Ru(1)−O(3)	90.08(8)	O(1)−Ru(1)−O(4)	90.05(8)
O(1)−Ru(1)−O(5)	90.78(8)	O(2)−Ru(1)−O(3)	91.84(8)
O(2)−Ru(1)−O(4)	88.02(8)	O(2)−Ru(1)−O(5)	90.33(8)
O(3)−Ru(1)−O(4)	179.37(8)	O(3)−Ru(1)−O(5)	87.45(8)
O(4)−Ru(1)−O(5)	93.16(8)	Ru(2)−Ru(2)*−O(6)	89.41(6)
Ru(2)−Ru(2)*−O(7)	89.76(6)	Ru(2)−Ru(2)*−O(8)	90.20(6)
Ru(2)−Ru(2)*−O(9)	89.16(6)	Ru(2)−Ru(2)*−O(10)	174.07(6)
O(6)−Ru(2)−O(7)	177.76(9)	O(6)−Ru(2)−O(8)	88.33(9)
O(6)−Ru(2)−O(9)	91.70(9)	O(6)−Ru(2)−O(10)	86.60(8)
O(7)−Ru(2)−O(8)	89.59(9)	O(7)−Ru(2)−O(9)	90.37(9)
O(7)−Ru(2)−O(10)	94.38(8)	O(8)−Ru(2)−O(9)	179.36(8)
O(8)−Ru(2)−O(10)	94.07(9)	O(9)−Ru(2)−O(10)	86.57(9)

groups. The angles of **2** ($\theta = 23.2°$ and $50.1°$) correspond to that of the metal complexes containing O_2CNap moieties, $\theta = 28.7°$ for $[ZrCl(CpMe)_2(O_2CNap)]$[23] (CpMe = methylcyclopentadienyl). In complex **3**, the mean plane of the π-stacking anthracene moieties and the plane of the carboxylate at the face-to-face orientation are almost perpendicular to each other with dihedral angles of 82.2° and 87.3°, while those at the face-to-edge orientation have angles, $\theta = 46.4°$ and $43.7°$, which are almost consistent with that of the free AntCOOH[24] ($\theta = 54.87(6)°$). $[Re(O_2CAnt)(bpy)(CO)_3]$[25] ($\theta = 85.7(2)°$) (bpy = 2,2′-bipyridine) also shows a the perpendicular inclination of anthracene-carboxylate for the $\pi-\pi$ stack interaction. These results indicate a significant role for $\pi-\pi$ stack interactions to control the dihedral angles and/or the effective intermolecular interactions.

Electrochemical Properties. The redox behavior of compounds **1**−**3** was investigated by cyclic voltammetry (CV) in THF containing n-$Bu_4N(BF_4)$ as the supporting electrolyte (vs Ag/Ag^+). Half-wave potentials for the redox reactions of compounds **1**−**3** are listed in Table 6. The rest

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[23] Wang, Z.-Q.; Lu, S.-W.; Guo, H.-F.; Hu, N.-H.; Liu, Y.-S. *Polyhedron* **1991**, *10*, 2341.

[24] Fitzgerald, L. J.; Gerkin, R. E. *Acta Crystallogr.* **1997**, *C53*, 71.

[25] Wolcan, E.; Torchia, G.; Tocho, J.; Piro, O. E.; Julianrena, P.; Ruiz, G.; Féliz, M. R. *J. Chem. Soc., Dalton Trans.* **2002**, 2194.

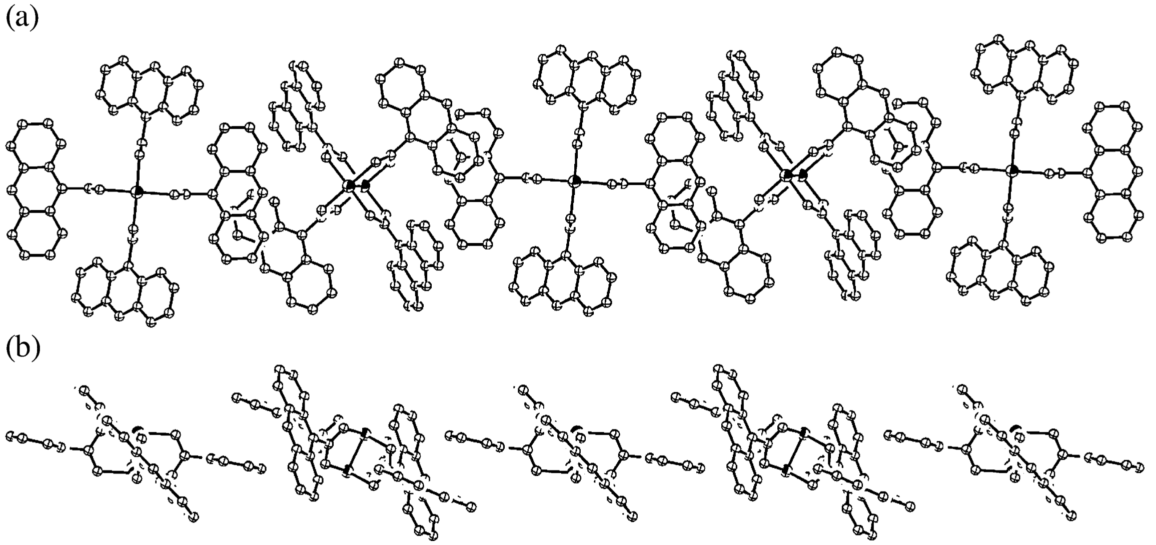


Figure 5. Crystal packing view of $[Ru_2(O_2CAnt)_4(THF)_2]$ (**3**) from the (a) top view and (b) side view. Axially coordinated THF molecules and hydrogen atoms have been omitted for the sake of clarity.

Scheme 2

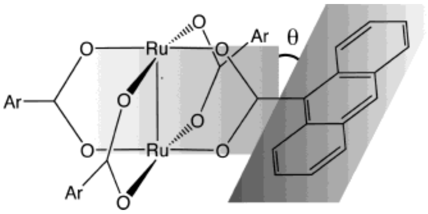
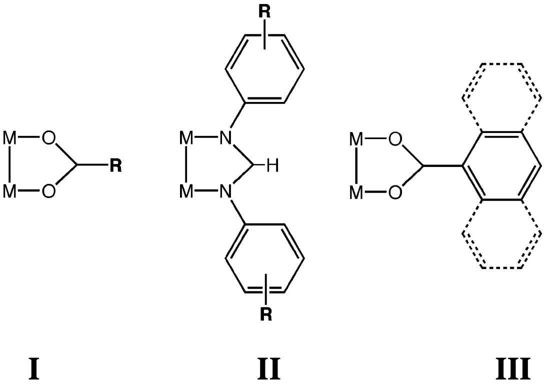


Table 6. Substituent Constants and Oxidation Potentials for Ru^{II}_2 Complexes in THF

compd	substituent	$4\sigma^-_{\pi,B}$ [a]	$E_{1/2}$[b]/V (vs Ag/Ag$^+$)
1	Ph	0.0	+0.06
2	Nap	1.92	+0.09
3	Ant	5.40	+0.17

[a] Reference 36. [b] The ferrocene/ferrocenium couple occurs at $E_{1/2}$ = +0.21 V under the same conditions of the cyclic voltammograms for the diruthenium compounds in THF.

Scheme 3



potentials for **1**−**3** are around 0.00 V. All compounds undergo a quasireversible one-electron oxidation at $E_{1/2}$ = +0.06, +0.09, and +0.17 V for **1**, **2**, and **3**, respectively, assigned to the metal-centered oxidation described as $Ru^{II}_2/Ru_2^{II,III}$. Potential separations between the anodic peaks and the cathodic peaks are in the range 100−130 mV at a scan rate of 10 mV/s, which increases as the scan rate increases. No reductions are observed, and only oxidation occurs. As the size of the Ar group is varied from Ph to Ant, a small shift is observed in the oxidation potential such that the large π-conjugated group makes the oxidation difficult and acts as an electron-withdrawing group. This feature is probably attributed to the influence on the stabilization of the electron delocalization to the whole aromatic core. The magnitude of the interaction can be quantitatively estimated by the linear free energy relationship (LFER).

The electrochemical LFER in dinuclear paddlewheel compounds has been thoroughly investigated for $[Rh_2(O_2CR)_4]^{n+}$,[26] for $[M_2(form)_4]^{n+}$ [27] (M = Mo,[28] Ni,[29] Ru,[30] and Rh,[31] form = di-R-arylformamidinates), for $[Ru_2(ap)_4]^{n+}$ [32] (ap = 2-(R-anilino)pyridinate), and for $[Ru_2(O_2CCH_3)_2(R\text{-}salpy)_2]^{n+}$ [33] (R-salpy = *N*-(2-pyridyl)-2-oxy-5-R-benzylaminate). In these studies, R was varied over a wide range of substituent constants from electron-withdrawing to electron-donating groups. From the viewpoint of their structural features, these complexes are classified into two groups (see Scheme 3). (1) The group I compounds contain the bridging units (carboxylates) connected with R-substituents directly. The dirhodium tetracarboxylates compounds, $[Rh_2(O_2CR)_4]^{n+}$, belong to this group. For a series of these compounds, the Taft polar substituent constants, σ*,[34] are

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(26) Das, K.; Kadish, K. M.; Bear, J. L. *Inorg. Chem.* **1978**, *17*, 930.
(27) Ren, T. *Coord. Chem. Rev.* **1998**, *175*, 43.
(28) (a) Lin, C.; Protasiewicz, J. D.; Smith, E. T.; Ren, T. *J. Chem. Soc., Chem. Commun.* **1995**, 2257. (b) Lin, C.; Protasiewicz, J. D.; Smith, E. T.; Ren, T. *Inorg. Chem.* **1996**, *35*, 6422.
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(30) Lin, C.; Ren, T.; Valente, E. J.; Zubkowski, J. D.; Smith, E. T. *Chem. Lett.* **1997**, 753.
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(32) Kadish, K. M.; Wang, L.-L.; Thuriere, A.; Van Caemelbecke, E.; Bear, J. L. *Inorg. Chem.* **2003**, *42*, 834.
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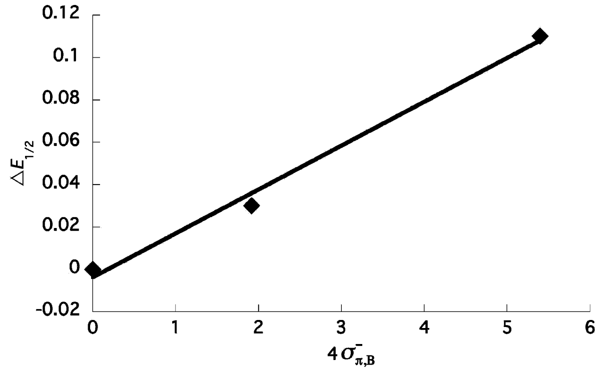

Figure 6. Dependence of $\Delta E_{1/2}$ on the substituent constant, $\sigma^{-}_{\pi,\mathrm{B}}$. The solid line is the least-squares fit.

found to show an LFER with the half-wave redox potentials. (2) The group II compounds are constructed from the bridging ligands containing the phenyl-substituted moieties. The other compounds as listed above belong to this group. The Hammett constants, σ,[35] are used as the substituent constants for these compounds.

In this respect, our complexes **1**−**3** should not be classified into either group, since the whole aromatic system is not treated as a substituent. The extension of the aromatic ring could directly cause an effective change in the π electronic system, regarded as a perturbation similar to those caused by substituents. Therefore, this system is classified as group III. For the treatment of these large π-conjugated aromatic systems, the resonance interaction between the substituent (aromatic rings) and the redox active moiety (dimetal core) plays a significant role as well as the inductive or polar effects. In organic electrochemistry, the substituent constant, $\sigma^{-}_{\pi,\mathrm{B}}$, can be used as the first approximation for the treatment of electrochemical data in these series.[36,37] The respective redox potentials for **1**−**3** exhibit an excellent linear correlation with $\sigma^{-}_{\pi,\mathrm{B}}$. Figure 6 shows a plot of $\Delta E_{1/2}$ versus $4\sigma^{-}_{\pi,\mathrm{B}}$, where 4 is the number of substituents per compound. Herein, a linear least-squares fit gives a correlation in the form of eq 4

$$\Delta E_{1/2} = E_{1/2}(\mathrm{X}) - E_{1/2}(\mathrm{Ph}) = 4\sigma^{-}_{\pi,\mathrm{B}}\rho \qquad (4)$$

where ρ is the reactivity constant. From this correlation, the calculated value of ρ is 20.7 mV, and the correlation coefficient (R^2) is 0.992.

The reactivity constant for $[\mathrm{Ru_2(O_2CAr)_4}]$ is significantly smaller than that estimated for the oxidation for $\mathrm{Rh_2(O_2CR)_4}$ (ρ = 64 mV) and for $[\mathrm{M_2(form)_4}]$ (ρ = 69.3, 88.9, and 87.2 mV for $\mathrm{Ru^{II}_2/Ru_2^{II,III}}$, $\mathrm{Ru_2^{II,III}/Ru^{III}_2}$, and $\mathrm{Mo^{II}_2/Mo_2^{II,III}}$, respectively). In groups I and II, the polar effect is the main contribution to the substitution effects, which arises from the resulting change in the electron density propagated by an inductive mechanism.[38] On the other hand, the extension of the aromatic ring system for group III usually induces a small perturbation but does not directly affect the electron density on the metal core. Therefore, the main pathway is the resonance interaction through the π−π conjugation between the aryl moiety and the carboxylate.[39] The smaller value of the reactivity constants for **1**−**3** is due to this difference in the contribution to the substitution effects.

Regardless of the magnitude of the reactivity constant, the excellent linear correlation between $\Delta E_{1/2}$ and $\sigma^{-}_{\pi,\mathrm{B}}$ unambiguously shows that the paddlewheel diruthenium compounds are sensitive toward the small perturbation of the π-conjugated aromatic system. To the best of our knowledge, these compounds are the first examples of redox tuning by the extension of the aromatic system in metal complexes. This sensitivity originates from the characteristic electronic configuration of these series, $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*2}$ for the $\mathrm{Ru^{II}_2}$ core and $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*}$ for the $\mathrm{Ru_2^{II/III}}$ core.[5] Hence, the oxidation involves removal of an electron from the δ^* orbital where the π orbital on the aromatic rings directly influences the system via π conjugation on the carboxylate group.

Conclusion

We have described a straightforward, one-pot, facile procedure for the synthesis of the neutral paddlewheel diruthenium compound with tetraarylcarboxylates, $[\mathrm{Ru_2(O_2CAr)_4(THF)_2}]$ (Ar = Ph, **1**; Nap, **2**; Ant, **3**), starting from the cationic diruthenium tetraacetates. In this procedure, a simple reflux of the reaction solution containing $[\mathrm{Ru_2^{II,III}(O_2CCH_3)_4(THF)_2}](\mathrm{BF_4})$, a desired carboxylic acid, and NDMA (used as solvent) produces the desired neutral diruthenium compound in good yield as a consequence of one-electron reduction followed by a carboxylate-exchange reaction. The detailed investigation of the reaction mechanism shows that the $\mathrm{Ru_2^{II,III}}$ core is coordinated to an NDMA molecule at the axial position, followed by reduction to the $\mathrm{Ru^{II}_2}$ core. This versatile synthesis without isolation of the very air-sensitive

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(35) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970.

(36) Zuman, P. *Substituent Effects in Organic Polarography*; Plenum Press: New York, 1967.

(37) The value of $\sigma^{-}_{\pi,\mathrm{B}}$ is calculated from electrochemical measurements of these aromatic polycyclic systems bound to various electroactive groups. The value of the reactivity constant, ρ, estimated from eq 4 can be used in the informative discussion of reactions for those calculated from the Taft constant and the Hammett constant.

(38) In order to investigate the significant conjugation between the phenyl substituent and the dinuclear core for $[\mathrm{Mo_2(form)_4}]$, fittings with both σ^+ and σ^- were carried out with less satisfactory results, which clearly indicates the absence of a dominant resonance contribution from the substituents.[28] This is because the phenyl group has rotational freedom with respect to the first coordination sphere of the dimetal core, which eliminates any significant contribution through conjugation.

(39) The possibility of the steric effects is also considered. Shown in the solid-state structure of complexes **1**−**3**, the peri effect obviously enlarges the dihedral angles between planes as the π-conjugated moiety expands. This steric restriction of the motion probably confines the free rotation about the carboxylate carbon $\mathrm{O_2C{-}C_{Ar}}$ bond even in solution. Recently, Chisholm and co-workers reported that the rotational constraint of the anthracene moiety for a dimer of dimer compound $[\{\mathrm{M_2(O_2CtBu)_3}\}_2(\mu\text{-9,10-Ant(CO_2)_2})]$ (M = Mo, W) limits the extent of $\mathrm{M_2}$ δ to bridge π to $\mathrm{M_2}$ δ communication by the peri repulsions.[40] In this complex, the coupling of the two $\mathrm{M_2}$ centers through the conjugation is muted but not lost. In the case of our compounds, the definite information on the structure in solution has not been investigated; however, it seems reasonable to suppose that this obstruction of the rotation would allow the significant contribution through π-conjugation even though the planes are not flat in a manner similar to that of the dimer of dimer compound.

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intermediate makes this process an attractive alternative method for the preparation of the series of the neutral diruthenium compounds.

The stepwise extension of the aromatic ring system of arylcarboxylates of **1**−**3** influences the redox property of the unit molecule itself and the intermolecular interaction of its assemblies. In electrochemical studies, electron delocalization to whole aromatic rings acts as an electron-withdrawing group; thus, the larger π-conjugated substituent stabilizes the Ru^{II}_2 oxidation state. The excellent fit of the linear free energy relationship between $\Delta E_{1/2}$ and $\sigma^{-}_{\pi,B}$ shows that the diruthenium compound is sensitive toward the small perturbation of the π-conjugated aromatic system. This feature is probably attributed to the direct interaction between the δ^* orbital (HOMO) on the Ru^{II}_2 core and the π orbital on the aromatic rings. In the solid state, the size of the aryl moieties plays a significant role in controlling the effective intermolecular interaction such that only **3** shows the formation of a 1-D chain through the $\pi-\pi$ stack interactions. Investigations of supramolecular assemblies based on **1**−**3** are underway with various axial linkers.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **1**−**3**, Figures S1 and S2 (crystal packing view of **1** and **2**, respectively), Figure S3 (cyclic voltammograms for **1**−**3**), and Table S1 (the table of dihedral angles of **1**−**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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