Synthesis and Characterization of Diruthenium Complexes in Low Oxidation States. Formation of Mono- and Bis-CO Adducts

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Introduction

Numerous diruthenium complexes with carboxylate type structures have been synthesized over the past decade.[1−23] The thermodynamically preferred oxidation state of the diruthenium core is Ru_2^{5+} for most complexes,[1,3−8] but stable diruthenium derivatives with Ru_2^{4+} and Ru_2^{6+} cores have also been isolated and structurally characterized.[1−3,9−20] All of the compounds are electroactive, with the most commonly studied redox reactions being the Ru_2^{5+}/Ru_2^{4+} and Ru_2^{5+}/Ru_2^{6+} electron transfer processes.[1−3,5−7,9−14,16,19] The electrogeneration of diruthenium complexes in lower oxidation states, i.e., Ru_2^{3+} and Ru_2^{2+}, is also possible, but, to our knowledge, there are only three papers on this subject in the literature,[2,5,6] two of which describe

compounds with terminal NO or CO axial ligands. One of the easily reducible derivatives was $(N_3Ph_2)_4Ru_2(CO)_2$, which was briefly described as to its electrochemistry but not spectroscopically characterized after electrooxidation or electroreduction. It is the only published example of a bis-CO Ru_2^{4+} complex with four anionic bridging ligands, and no evidence for formation of any diruthenium mono-CO adduct with this type of structure has ever been presented.

In this paper, we report the electrochemical and spectroscopic characterization of a stable monocarbonyl diruthenium(II,II) complex which is represented as $(dpf)_4Ru_2(CO)$ where dpf is the *N,N*′-diphenylformamidinate anion. The initial compound could be converted upon oxidation or reduction to $[(dpf)_4Ru_2(CO)]^n$ where $n = 1$, 0, or −1, each of which was characterized by ESR and thin-layer UV−visible spectroelectrochemistry under a N_2 or CO atmosphere. The initial compound, $(dpf)_4Ru_2(CO)$, was also characterized by single-crystal X-ray diffraction.

Experimental Section

Chemicals and Reagents. The synthesis and characterization of $(dpf)_4Ru_2Cl$ has been described in the literature.[10] Absolute dichloromethane (CH_2Cl_2) was obtained from Fluka Chemical Co. and used as received. Tetra-*n*-butylammonium perchlorate (TBAP, Fluka Chemical Co.) was twice recrystallized from absolute ethanol and dried in a vacuum oven at 40 °C for a week prior to use. UHP nitrogen and carbon monoxide were purchased from Matheson-Trigas Co. HPLC grade acetone, benzene, and hexanes (Aldrich Chemical Co.) were used directly.

Physical Measurements. Cyclic voltammetry was carried out with an EG&G model 173 potentiostat. A three-electrode system was used and consisted of a glassy carbon or platinum disk working electrode, a platinum wire counter electrode, and a homemade saturated calomel electrode (SCE) as the reference electrode. The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE, and all measurements were carried out at room temperature.

Controlled-potential electrolysis was carried out with a BAS model SP-2 synthetic potentiostat. An "H" type cell was used for performing bulk electrolysis and consisted of two cylindrically shaped platinum gauze electrodes which served as working and counter electrode and were separated by a fine fitted disk. Elemental analysis was carried out by Galbraith Laboratories, Inc., Knoxville, TN.

UV−visible spectroelectrochemistry experiments were carried out with a Hewlett-Packard model 8453 diode array spectrophotometer. Infrared spectroelectrochemical measurements were made with a FT-IR Nicolet Magna-IR 550 spectrometer using a specially constructed light-transparent three-electrode cell.[24] The IR spectrum of each electrooxidized or electroreduced complex under N_2 or CO was obtained as a difference spectrum measured against $(dpf)_4Ru_2(CO)$ using CH_2Cl_2, 0.2 M TBAP as background after bubbling N_2 or CO through the spectroelectrochemical cell for 10 min prior to applying a potential. A blanket of N_2 or CO was maintained above the solution during the measurement.

^{1}H NMR measurements were recorded at room temperature on a General Electric QE-300 Plus spectrometer and were referenced to the CD_2Cl_2 solvent. ESR spectra were recorded on a Bruker ER 100E spectrometer. The *g* values were measured with respect to diphenylpicrylhydrazyl (DPPH: $g = 2.0036 \pm 0.0003$).

Synthesis of $(dpf)_4Ru_2(CO)$. The title compound was synthesized by passing CO for 30 min through a CH_2Cl_2, 0.1 M TBAP solution of $(dpf)_4Ru_2$ which had been generated by bulk electrolysis of $(dpf)_4Ru_2Cl$[10] at −0.90 V vs SCE under N_2. During this process, the color changed

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Table 1. Crystal Data and Structure Refinement for $(dpf)_4Ru_2(CO)$

formula	$C_{53}H_{44}N_8ORu_2 \cdot 4CH_2Cl_2$
fw	1350.81
temp (K)	223(2)
λ (Å)	0.71073
cryst syst	tetragonal
space group	$P4/ncc$
unit cell dimens	
a (Å)	15.9265(6)
b (Å)	15.9265(6)
c (Å)	22.8689(12)
V (Å^3)	5800.8(4)
Z	4
density (calcd), g/cm^3	1.547
μ (mm^{-1})	0.937
R1 $(I > 4\sigma(I))^a$	0.0296
wR2 (all data)^b	0.1081

^{a} R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 $= [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

from red to purple. A dark purple product precipitated upon addition of hexanes into the solution. After filtration and washing twice with acetone, $(dpf)_4Ru_2(CO)$ was obtained with a yield of ca. 70%. The isolated $Ru_2{}^{4+}$ derivative is air stable, and no dissociation of the axially bound CO was observed to occur either in solution or under a house vacuum. Crystals of $(dpf)_4Ru_2(CO)$ suitable for X-ray diffraction analysis were obtained by slow diffusion of hexanes into a CH_2Cl_2/benzene (97:3) solution of the compound. Anal. Calcd for $C_{53}H_{44}N_8$-$ORu_2 \cdot CH_2Cl_2$: C, 59.17; H, 4.23; N, 10.22. Found: C, 59.27; H, 4.29; N, 10.20. UV–vis spectrum in CH_2Cl_2 [λ_{max}, nm ($\epsilon \times 10^{-3}$, mol^{-1} L cm^{-1})]: 423 (8.7), 526 (7.4), 628 (4.0). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ = 6.39 (m, 8H, o-phenyl), δ = 6.49 (m, 8H, o-phenyl), δ = 7.06–7.17 (m, 24H, m- and p-phenyl), and δ = 8.24 (s, 4H, N–CH–N) ppm.

X-ray Crystallography. All measurements were made with a Siemens SMART platform diffractometer equipped with a 1K CCD area detector. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 30 s/frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction on I was <1%. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A Ψ-scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 5034 reflections having $I > 10\sigma(I)$, and these, along with other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be 4/mmm, and from the systematic absences noted the space group was shown unambiguously to be $P4/ncc$. The asymmetric unit consists of $^1/_4$ molecule situated about a 4-fold axis, and one molecule of methylene chloride in a general position. The solvent is massively disordered, having three distinct orientations. Each of these was modeled as an ideal rigid body.

Results and Discussion

Synthesis and Structure of $(dpf)_4Ru_2(CO)$. The isolated $Ru_2{}^{4+}$ derivative was obtained by passing CO through a CH_2Cl_2 solution of $(dpf)_4Ru_2$ which had been in situ generated from $(dpf)_4Ru_2Cl$ by controlled-potential reduction at -0.90 V vs SCE under a nitrogen atmosphere.[10] Assignment of the final product as $(dpf)_4Ru_2(CO)$ was made on the basis of structural and spectroscopic data as well as elemental analysis. Selected bond lengths and bond angles of the compound are summarized in Table 2, and the X-ray crystal structure is given in Figure 1. Complete intramolecular bond lengths and angles as well as other structural data are submitted as Supporting Information.

The coordination about Ru1 and Ru2 is essentially octahedral and square pyramidal, respectively, with the four dpf nitrogens
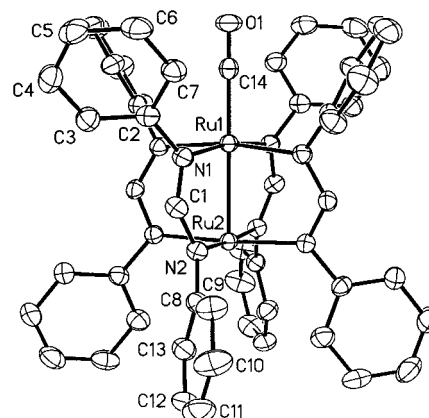
Figure 1. Thermal ellipsoid plot (30% equiprobability envelopes) of $(dpf)_4Ru_2(CO)$. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of $(dpf)_4Ru_2(CO)$

Bond Lengths			
Ru(1)–Ru(2)	2.5544(8)	Ru(1)–N(1)	2.069(3)
Ru(1)–C(14)	1.913(10)	Ru(2)–N(2)	2.028(3)
C(14)–O(1)	1.148(11)		

| Bond Angles			
Ru(1)–Ru(2)–N(2)	88.09(9)	Ru(2)–Ru(1)–N(1)	85.09(9)
Ru(1)–C(14)–O(1)	180	Ru(2)–N(2)–C(8)	123.6(3)
Ru(1)–N(1)–C(1)	121.5(3)	Ru(2)–N(2)–C(1)	119.9(3)
Ru(1)–N(1)–C(2)	124.4(3)	C(14)–Ru(1)–N(1)	94.91(9)
Ru(2)–Ru(1)–C(14)	180		

in each of the equatorial planes having C_{4v} symmetry. The four Ru(1)–N and Ru(2)–N distances are identical about each metal atom and are equal to 2.069(3) and 2.028(3) Å, respectively. These values are comparable to Ru–N bond lengths in other structurally characterized diruthenium complexes.[3,15,16,19] The C–O bond distance of 1.148(11) Å in $(dpf)_4Ru_2(CO)$ is virtually identical to the 1.147(8) Å in $(tcl)_4Rh_2(CO)$ where tcl = ω-thiocaprolactamate.[25]

The Ru–Ru bond length of 2.5544(8) Å is longer than expected for a diruthenium(II,II) complex with a carboxylate type structure.[1] Related diruthenium derivatives with oxygen donor atom equatorial ligands usually have Ru–Ru distances which range from 2.235 to 2.276 Å. A longer Ru–Ru bond in the range 2.399–2.475 Å is observed for compounds having ligands with nitrogen rather than oxygen donor atoms.[1,3,16,18–20] The Ru–Ru distance for $(dpf)_4Ru_2(CO)$ is, however, comparable to the 2.515(4) and 2.532(4) Å values in $(O_2CC_2H_5)_4Ru_2(NO)_2$ and $(O_2CCF_3)_4Ru_2(NO)_2$,[2] respectively. The oxidation state of the diruthenium core in the latter two compounds has been formally assigned as $Ru_2{}^{2+}$. It should be noted that similar Ru–Ru distances of 2.553–2.558 Å are also observed in diruthenium(III,III) complexes.[10,14]

Electrochemistry and IR Spectroelectrochemistry of $(dpf)_4Ru_2(CO)$ under a N_2 Atmosphere. A cyclic voltammogram of $(dpf)_4Ru_2CO$ in CH_2Cl_2 containing 0.1 M TBAP under N_2 is shown in Figure 2a. This compound exhibits a single reversible one-electron reduction at $E_{1/2} = -1.17$ V and a single reversible one-electron oxidation at $E_{1/2} = 0.28$ V vs SCE, leading to the formation of diruthenium complexes containing $Ru_2{}^{3+}$ and $Ru_2{}^{5+}$ cores, respectively.

The infrared spectrum of $(dpf)_4Ru_2(CO)$ in CH_2Cl_2, 0.2 M TBAP under N_2 is characterized by a CO stretching vibration

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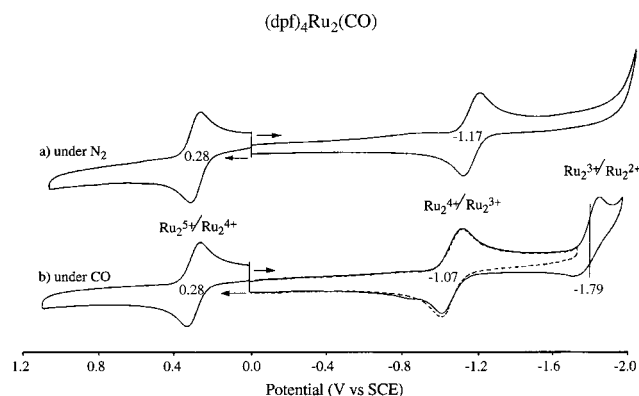
Figure 2. Cyclic voltammograms of $(dpf)_4Ru_2(CO)$ in CH_2Cl_2, 0.1 M TBAP (a) under a N_2 and (b) under a CO atmosphere. Scan rate = 0.1 V/s.

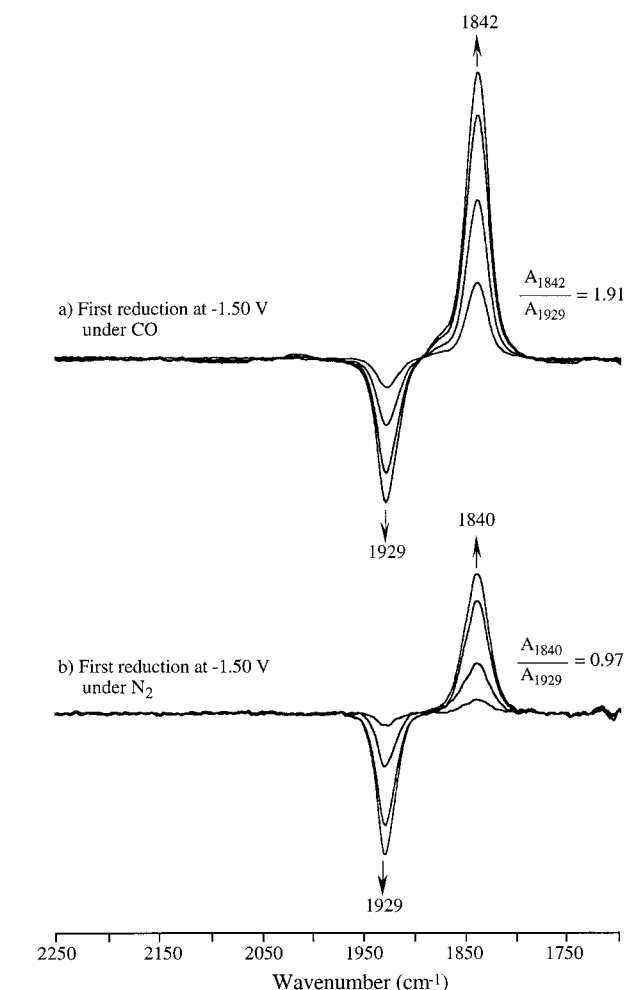**Table 3.** IR, ESR, and UV−Visible Spectral Data for $[(dpf)_4Ru_2(CO)]^n$ in CH_2Cl_2 under N_2 Where n = +1, 0, or −1

compound	ν_{CO} (cm^{-1})	g values		λ_{max}, nm ($\epsilon \times 10^{-3}$)		
$[(dpf)_4Ru_2^{III,II}(CO)]^+$	2019	2.129	1.990	477 (7.6)	537 (6.7)	707 (8.4)
$[(dpf)_4Ru_2^{II,II}(CO)]$	1929	silent	silent	423 (8.7)	526 (7.4)	628 (4.0)
$[(dpf)_4Ru_2^{II,I}(CO)]^-$	1840	2.285	1.742	485 (6.5)		

band at ν_{CO} = 1929 cm^{-1}, and this peak shifts by 89−90 cm^{-1} to higher or lower wavenumbers upon the abstraction or addition of one electron, thus giving ν_{CO} values of 1840, 1929, and 2019 cm^{-1} for $[(dpf)_4Ru_2(CO)]^n$ where n = −1, 0, and +1 (see Table 3). This is illustrated in Figure S1 (Supporting Information), which shows the relevant spectral region for the IR bands of electrogenerated $[(dpf)_4Ru_2^{III,II}(CO)]^+$ and $[(dpf)_4Ru_2^{II,I}(CO)]^-$ after controlled-potential electrolysis of $(dpf)_4Ru_2(CO)$ in the thin-layer cell at +0.50 and −1.50 V, respectively. These spectral changes are reversible, and the original IR spectrum of $(dpf)_4Ru_2(CO)$ could be regenerated upon rereduction or reoxidation, thus indicating that the reduced and oxidized forms of $[(dpf)_4Ru_2(CO)]^n$ (n = +1 or −1) are both stable on the electrochemical and spectroelectrochemical time scales and that the axial CO group remains bound to the complex after the abstraction or addition of one electron.

The 89−90 cm^{-1} shift in the CO stretching vibration upon going from $(dpf)_4Ru_2(CO)$ to $[(dpf)_4Ru_2(CO)]^-$ or $[(dpf)_4Ru_2(CO)]^+$ is consistent with what is expected for metal-centered electron transfers and can be compared to a much smaller $\Delta\nu_{CO}$ observed in the case of ruthenium(II) porphyrins which are oxidized and reduced at the macrocycle, thus retaining the Ru(II) metal oxidation state.[26,27] For example, the CO stretching frequencies shift to higher wavenumbers by 23−39 cm^{-1} upon conversion of $(P)Ru^{II}(CO)(L)$ to the porphyrin π-cation radical, $[(P)Ru^{II}(CO)(L)]^+$, and to lower wavenumbers by 35−50 cm^{-1} upon conversion of $(P)Ru^{II}(CO)(L)$ to the porphyrin π-anion radical, $[(P)Ru^{II}(CO)(L)]^-$, where L = one of several different solvent molecules or axial ligands and P = the dianion of octaethylporphyrin (OEP)[26] or tetraphenylporphyrin (TPP).[27]

Electrochemistry and IR Spectroelectrochemistry of $(dpf)_4Ru_2(CO)$ under a CO Atmosphere. The electrochemistry of $(dpf)_4Ru_2(CO)$ in CH_2Cl_2, 0.1 M TBAP was also carried out under a CO atmosphere in order to examine the possible formation of a bis-CO adduct as was previously reported[2] in the case of $(N_3Ph_2)_4Ru_2(CO)_2$. However, a second axial CO ligand was not added to either $(dpf)_4Ru_2(CO)$ or $[(dpf)_4Ru_2-$

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Figure 3. Thin-layer FTIR spectral changes of $(dpf)_4Ru_2(CO)$ obtained during controlled-potential reduction at −1.50 V in CH_2Cl_2, 0.2 M TBAP (a) under CO and (b) under N_2. The spectra of the reduced complexes are displayed as difference spectra with respect to the initial compound. Thus, the negative peak corresponds to a disappearance of the reactant IR band and the positive peak corresponds to an IR band of the electrogenerated product.

$(CO)]^+$ as evidenced by the electrochemical and spectroscopic data which show the same UV−visible spectra, the same CO stretching frequencies, and same oxidation potential for the Ru_2^{4+}/Ru_2^{5+} process under N_2 or under CO. The data do, however, clearly indicate the in situ formation of $[(dpf)_4Ru_2(CO)_2]^-$ upon a one-electron reduction of $(dpf)_4Ru_2(CO)$ under CO as evidenced by the following points:

(i) The half-wave potential for reduction of $(dpf)_4Ru_2(CO)$ under CO shifts positively by 100 mV, from −1.17 V under N_2 to −1.07 V under CO (Figure 2b), consistent with a stabilization of the singly reduced product by binding of a second CO group. At the same time, a second one-electron reduction of $(dpf)_4Ru_2(CO)$ is clearly seen under CO which does not appear under a N_2 atmosphere. This reaction occurs at $E_{1/2}$ = −1.79 V and results from the coordinating of a second CO group to the singly reduced complex, thus generating $[(dpf)_4Ru_2(CO)_2]^-$, which undergoes a one-electron reduction to its Ru_2^{2+} form. The second CO group on $[(dpf)_4Ru_2(CO)_2]^-$ is only present under a CO atmosphere, and the original voltammogram shown in Figure 2a is again obtained upon going from CO to N_2 above the solution.

(ii) The thin-layer FTIR spectra for singly reduced $(dpf)_4Ru_2-(CO)$ under CO show a single CO band at 1842 cm^{-1} as

Scheme 1
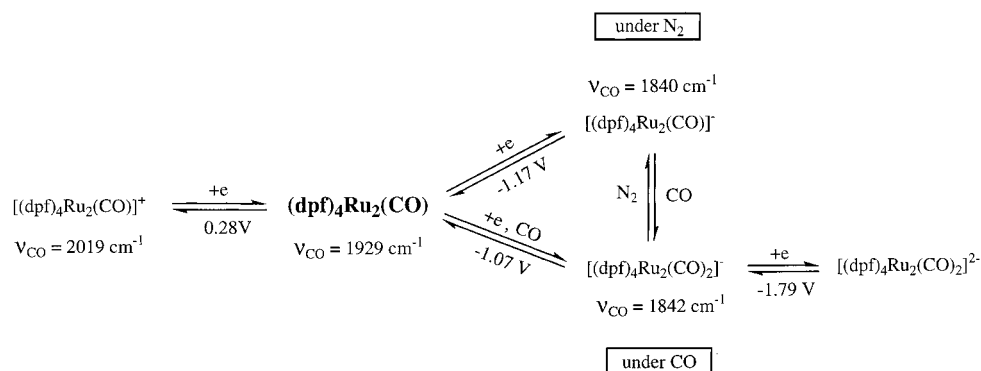
compared to 1840 cm^{-1} for the same compound under N_2. However, the relative intensity of the ν_{CO} bands for the $Ru_2(II,I)$ species at 1840–1842 cm^{-1} over the intensity of the band for the $Ru_2(II,II)$ complex at 1929 cm^{-1} increases from 0.97 under N_2 to 1.91 under CO. This is shown in Figure 3 and suggests formation of a bis-CO adduct, $[(dpf)_4Ru(CO)_2]^-$, after the first reduction under a CO atmosphere. These results are consistent with the electrochemistry data and suggest that the two CO groups in $[(dpf)_4Ru_2(CO)_2]^-$ are equivalent and thus have the same expected IR frequency.[28]

UV–Visible Spectroelectrochemistry. The UV–visible spectra of $[(dpf)_4Ru_2(CO)]^+$ and $[(dpf)_4Ru_2(CO)]^-$ were generated in CH_2Cl_2 by controlled-potential oxidation and reduction of $(dpf)_4Ru_2(CO)$ in a thin-layer cell under a N_2 (see Table 3) or CO atmosphere, and the resulting time-resolved spectral changes are shown in Figures S2 and S3 of the Supporting Information. The spectral changes which occur upon the one-electron oxidation of $(dpf)_4Ru_2(CO)$ under CO are identical to those obtained under N_2 and are thus consistent with the IR and electrochemical results which indicate the absence of a bis-CO adduct for either the Ru_2^{4+} or Ru_2^{5+} species. This contrasts with the case of reduction where different UV–visible spectra are obtained for the electrogenerated Ru_2^{3+} species under N_2 or under CO. As earlier indicated, the one electron reduction product of $(dpf)_4Ru_2(CO)$ is assigned as $[(dpf)_4Ru_2(CO)]^-$ under N_2 and $[(dpf)_4Ru_2(CO)_2]^-$ under CO.

ESR Spectra of $[(dpf)_4Ru_2(CO)]^+$ and $[(dpf)_4Ru_2(CO)]^-$. The ESR spectrum of $[(dpf)_4Ru_2(CO)]^-$ was generated after controlled-potential reduction of $(dpf)_4Ru_2(CO)$ in CH_2Cl_2, 0.2 M TBAP under N_2 while the spectrum of the Ru(II,III) complex was obtained after bubbling CO through a CH_2Cl_2 solution of $(dpf)_4Ru_2Cl$.

The ESR signal of $[(dpf)_4Ru_2(CO)]^+$ is similar to that of the diruthenium porphyrin $[(TPP)Ru]_2PF_6$ which possesses a Ru_2^{5+} core and has been assigned[29] as having an electronic configuration of $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$. The electrogenerated Ru_2^{3+} species, $[(dpf)_4Ru_2(CO)]^-$, also possesses one unpaired electron, and the axial ESR signal is consistent with an electronic configuration

of $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*1}$ or $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*3}$. To our knowledge, it is the first ESR spectrum of any Ru_2^{3+} species. The g values of the two complexes are summarized in Table 3 while the ESR spectra are presented in Figure S4 of the Supporting Information.

The electrochemical and spectroelectrochemical data are thus self-consistent with the formation of mono- and bis-CO adducts for the Ru_2^{3+} and Ru_2^{2+} complexes, and the overall electron transfer reactions of $(dpf)_4Ru_2(CO)$ are summarized by the series of reactions shown in Scheme 1.

All attempts to isolate the electrogenerated bis-CO adducts of Ru_2^{3+} or Ru_2^{2+} for further characterization have so far been unsuccessful, but attempts will be continued using complexes containing other anionic ligands such as F_5ap, F_3ap, or Fap where ap = 2-anilinopyridinate anion which contains five, three, or one substituted fluorine group.[6,9,13] Compounds with all three anionic bridging ligands are more easily reduced than derivatives with the dpf ligands due to the highly electron withdrawing F groups.

Supporting Information Available: Four figures illustrating IR, UV–visible, and ESR spectra of electrooxidized and electro-reduced species plus X-ray crystallographic file in CIF format for the compound $(dpf)_4Ru_2(CO)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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