Effect of Axial Ligands on the Oxidation State, Structure, and Electronic Configuration of Diruthenium Complexes. Synthesis and Characterization of $Ru_2(dpf)_4Cl$, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$, and $Ru_2(dpf)_4(CN)_2$ (dpf = *N*,*N*′-Diphenylformamidinate)

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The effect of axial ligands on the structure, oxidation state, and electronic configuration of two diruthenium(II,III) and two diruthenium(III,III) complexes is reported. The investigated compounds are represented by $Ru_2(dpf)_4Cl$ (**1**), $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ (**2**), $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ (**3**), and $Ru_2(dpf)_4(CN)_2$ (**4**), where dpf is the *N*,*N*′-diphenylformamidinate ion. The chloro and mono(phenylacetylide) complexes, which contain a Ru_2^{5+} core, are paramagnetic and contain three unpaired electrons, while the bis(phenylacetylide) and bis(cyano) species, which contain a Ru_2^{6+} core, are diamagnetic. Compound **1**, $Ru_2(dpf)_4Cl$, was prepared by heating $Ru_2(CH_3COO)_4Cl$ and excess molten *N*,*N*′-diphenylformamidine (Hdpf) for 10 h at 130 °C under an argon atmosphere. Compound **2**, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$, was prepared by reaction of purified $Ru_2(dpf)_4Cl$ with $LiC{\equiv}CC_6H_5$ (in a 1:5 ratio) in THF at room temperature (2 h). Compound **3**, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$, was also obtained from $Ru_2(dpf)_4Cl$ by using excess $LiC{\equiv}CC_6H_5$. A related diruthenium(III,III) complex, $Ru_2(dpf)_4(CN)_2$ (**4**), was also synthesized in order to determine whether the observed octahedral distortion in **3** was due to electronic or steric effects. $Ru_2(dpf)_4(CN)_2$ was prepared by reaction of $Ru_2(dpf)_4Cl$ and a large excess of NaCN in THF at room temperature (10 h). All four compounds were isolated and characterized by single-crystal X-ray diffraction, ^1H NMR, ^{13}C NMR, IR, and UV−visible spectroscopy, and mass spectrometry, as well as by electrochemistry. Compound **1** crystallizes in the tetragonal space group *P*4/*ncc*, with $a = 14.837(2)$ Å, $c = 21.599(5)$ Å, and $Z = 4$, while compound **2** belongs to the monoclinic space group *I*2/*c*, with $a = 18.590(5)$ Å, $b = 30.913(12)$ Å, $c = 17.360(4)$ Å, $\beta = 93.61(2)°$, and $Z = 8$. The magnetic moments of the two diruthenium(II,III) species, **1** and **2**, are 3.89 and 3.87 μ_B, respectively, in the solid state at 297 K, consistent with three unpaired electrons and an electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\delta^*\pi^*)^3$. Compounds **3** and **4** are diamagnetic in their neutral form but paramagnetic upon controlled-potential reduction by one electron. The two reduced $Ru^{II}Ru^{III}$ species, $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ and $[Ru_2(dpf)_4(CN)_2]^-$, were characterized by ESR spectroscopy after electrochemical generation and display a rhombic signal whose shape is consistent with the presence of only a single unpaired electron. Compound **2**, which contains three unpaired electrons, gives a bis adduct $Ru_2(dpf)_4(C{\equiv}CC_6H_5)(CNCH_2C_6H_5)$ upon addition of excess $CNCH_2C_6H_5$ to the solution of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$. The bis adduct species has only one single unpaired electron and shows an ESR spectrum similar to that of electroreduced $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ and $[Ru_2(dpf)_4(CN)_2]^-$. Crystals of **3** and **4** belong to the monoclinic space groups *C*2/*c* and *P*2$_1$, with $a = 35.322(7)$ Å, $b = 15.163(3)$ Å, $c = 31.820(9)$ Å, $\beta = 93.59(2)°$, and $Z = 12$ (compound **3**) and with $a = 16.184(4)$ Å, $b = 15.784(3)$ Å, $c = 12.896(3)$ Å, $\beta = 112.29$ (2)°, and $Z = 2$ (compound **4**). The Ru−Ru bond distances of **1** and **2** are in the expected range for diruthenium(II,III) complexes, i.e., 2.339(1) Å for compound **1** and 2.400(1) Å for compound **2**. Compounds **3** and **4**, however, have Ru−Ru bond distances which are much longer than anticipated for diruthenium(III,III) complexes with the same type of structure. The measured values are 2.556(1) Å for **3** and 2.539(1) Å for **4**. All four compounds can undergo conversions between Ru_2^{6+}, Ru_2^{5+}, and Ru_2^{4+} while compound **3**, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$, also undergoes a Ru_2^{7+}/Ru_2^{6+} redox process. Values of $E_{1/2}$ range between +0.54 and −0.61 V for the Ru_2^{6+}/Ru_2^{5+} process and between −0.64 and −1.54 V for the Ru_2^{5+}/Ru_2^{4+} one.

Introduction

One important feature of multiply bonded diruthenium complexes with carboxylate type structures is how the ordering of these metal-centered molecular orbitals varies with changes in the nature of the axial and equatorial ligands.[1−11] Numerous studies have reported how the σ and π donor properties of the ligands affect the electronic and molecular structure, redox potentials, and chemical reactivity of these diruthenium compounds.[1−11] The thermodynamically preferred oxidation state of the diruthenium unit is Ru_2^{5+} (i.e., $Ru^{II}Ru^{III}$) for most complexes,[1−7] but the Ru_2^{4+}/Ru_2^{5+} and Ru_2^{5+}/Ru_2^{6+} redox

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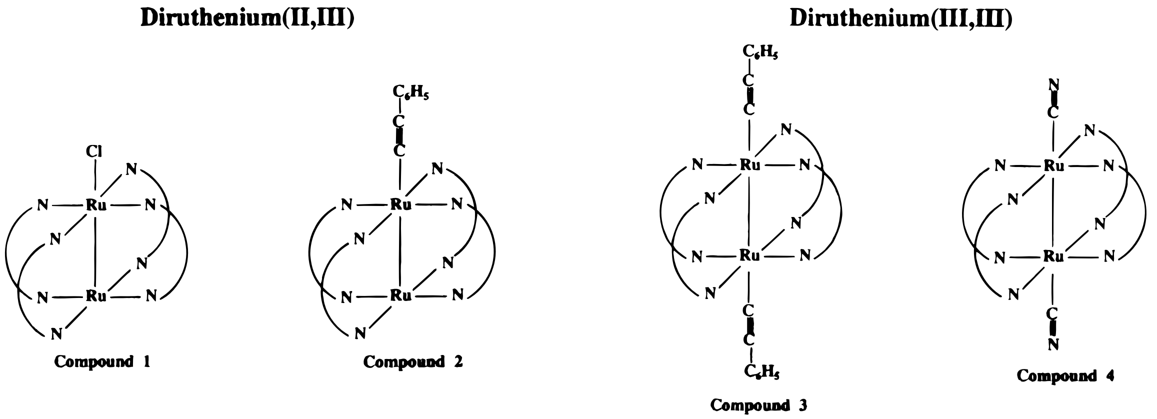
Chart 1



Compound 1

Compound 2

Compound 3

Compound 4

couples can be "tuned" over a wide range through the proper choice of axial and bridging ligands.[1−4,8,9]

The diruthenium(II,III) complexes normally have three unpaired electrons,[1,2,4−7] consistent with a ground-state electronic configuration of $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$. A few Ru_2^{4+} complexes (those with Ru^{II}_2 centers) have also been reported[8−11] and have three possible ground-state electronic configurations which are $(\pi^*)^4$, $(\pi^*)^3(\delta^*)^1$, or $(\pi^*)^2(\delta^*)^2$. The category to which a particular complex belongs is determined by the ordering and energy separation of the δ^* and π^* orbitals.

The synthesis of a stable Ru_2^{6+} complex (containing a Ru^{III}_2 core) has long been of interest.[12−19] Two diruthenium carboxylate complexes were reported to contain a Ru_2^{6+} core,[12,13] but these were later shown[14] to actually be Ru_2^{5+} compounds. In addition, several other structural types of diruthenium(III,III) complexes have been reported.[15−19] The diamagnetic, air-sensitive $Ru_2(L)_2(BF_4)_2$ (L = dibenzotetraaza[14]annulene ligand)[15] and Ru_2L_6 (L = CH_2SiMe_3 or CH_2CMe_3)[16] are examples of Ru_2^{6+} compounds which do not have bridging ligands. Trihalo-bridged $[Ru_2X_9]^{3-}$ (X = Cl or Br)[17] complexes with highly symmetrical cofacial biooctahedral arrangements have also been reported in the literature. Edge-sharing pseudo-octahedral Ru_2^{6+} complexes which contain both three atom and single nitrogen atom bridges represent another structural type.[18,19] $K_2[Ru_2(SO_4)_4(H_2O)_2]$ has been shown to contain Ru_2^{6+} with four dianionic bridging ligands.[20,21]

We recently reported the first two examples of diruthenium(III,III) complexes bridged by four mononegative, three-atom, bidentate bridging ligands.[22,23] The investigated compounds,$Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ (**3**) and the (4,0) isomer of $Ru_2(pfap)_4(C{\equiv}CC_6H_5)_2$, where dpf is the *N,N′*-diphenylformamidinate ion and pfap is the 2,3,4,5,6-pentafluoro-2-anilinopyridinate ion, were shown to have several unexpected and interesting electronic and structural properties. For example, both complexes are diamagnetic, have distinctly nonlinear Ru−Ru−C bond angles (averaging 159.8° for the former and 169.6° for the latter), and a Ru−Ru bond distance more consistent with a Ru−Ru single bond rather than the Ru−Ru triple bond expected from theoretical considerations for this type of structure.[8]

In this paper, we now report the detailed synthesis and characterization of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ as well as spectroscopic, structural, and electrochemical properties of another diruthenium(III,III) species, $Ru_2(dpf)_4(CN)_2$ (**4**), and two related diruthenium(II,III) compounds $Ru_2(dpf)_4Cl$ (**1**) and $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ (**2**). The skeletal structures of these four compounds are shown in Chart 1.

Compound **4** contains two axial CN^- anions which are less basic and less bulky than the two phenylacetylide ligands in compound **3** and was synthesized in order to determine whether the octahedral distortions observed for **3** are due to electronic or steric effects.

Experimental Section

Chemicals and Reagents. $Ru_2(CH_3COO)_4Cl$ was synthesized according to a method reported in the literature.[24] Hdpf (Aldrich Chemical Co.) was purified by recrystallization from CH_2Cl_2. Lithium phenylacetylide ($LiC{\equiv}CC_6H_5$) and deuterated dichloromethane (CD_2Cl_2) and chloroform ($CDCl_3$) were purchased from Aldrich Chemical Co. and used as received. CH_2Cl_2 was obtained as HPLC grade from Fisher Scientific Co. and distilled over phosphorus pentoxide (P_2O_5). Spectroscopic grade THF purchased from Aldrich Chemical Co. was purified by distillation under Ar from sodium/benzophenone just prior to use. Tetra-*n*-butylammonium perchlorate (TBAP, Fluka Chemical Co.) was twice recrystallized from absolute ethanol and dried in the oven at 40 °C prior to use.

Physical Measurements. Mass spectra were obtained from a high-resolution hybrid tandem VG Analytical Model 70-SEQ (EEQQ geometry) mass spectrometer. A standard fast atom bombardment (FAB) source was used, and *m*-nitrobenzyl alcohol (NBA) was the liquid matrix. Elemental analysis was carried out by Galbraith Laboratories, Inc., Knoxville, TN.

^1H and ^{13}C NMR spectra were recorded on a QE-300 FT NMR spectrometer. UV−visible spectra were measured on a Perkin-Elmer 330 spectrophotometer. IR spectra were obtained on an IBM Model IR/32 FTIR spectrometer. Thin-layer spectroelectrochemical measurements were carried out with an IBM Model EC 225 voltammetric analyzer and a Model 6500 Tracor Northern Rapid Scan spectrometer

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Table 1. X-ray Data Collection and Processing Parameters

	compounds			
	$Ru_2(dpf)_4Cl$	$Ru_2(dpf)_4(C{\equiv}CC_6H_5)$	$Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$	$Ru_2(dpf)_4(CN)_2$[a]
space group	*P*4/*ncc*	*I*2/*c*	*C*2/*c*	*P*2$_1$
cell consts				
a, Å	14.837(2)	18.590(5)	35.322(7)	16.184(4)
b, Å		30.913(12)	15.163(3)	15.784(3)
c, Å	21.599(5)	17.360(4)	31.820(9)	12.896(3)
β, deg		93.61(2)	93.59(2)	112.29(2)
V, Å^3	4755	9957	17009	3048
mol formula	$C_{52}H_{44}N_8ClRu_2{\cdot}C_5H_{12}$	$C_{60}H_{49}N_8Ru_2$	$C_{68}H_{54}N_8Ru_2$	$C_{54}H_{44}N_{10}Ru_2$
MW	1090.80	1084.31	1185.44	1290.65
Z	4	8	12	2
ρ, g/cm^3	1.52	1.45	1.39	1.41
μ, cm^{-1}	7.26	6.41	5.69	7.51
T, °C	−50	22	22	−50
λ(Mo Ka), Å	0.710 73	0.710 73	0.710 73	0.710 73
$R(F_o)^b$	0.029	0.026	0.049	0.059
$R_w(F_o)^c$	0.027	0.025	0.045	0.046

[a] The exact molecular formula is $C_{54}H_{44}N_{10}Ru_2{\cdot}2^1/_2CH_2Cl_2{\cdot}{}^1/_2C_6H_{14}$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

coupled to an IBM PC-XT computer. The thin-layer cell utilized an optically transparent platinum gauze as a working electrode and has a similar design as reported in the literature.[25] ESR spectra were taken with a Varian E-4 spectrometer. The *g* values were calculated with respect to diphenylpicrylhydrazide (DPPH) which gives a singlet at $g = 2.0036 \pm 0.0003$.[26]

Cyclic voltammograms were obtained with an IBM Model EC 225 voltammetric analyzer by utilizing a three-electrode electrochemical cell. The working electrode was a platinum button with a surface area of 0.19 mm^2 and the reference electrode was a homemade saturated calomel electrode (SCE). A platinum wire was used as a counter electrode. 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, separated by a fine frit disk, which served as working and counter electrodes.

$Ru_2(dpf)_4Cl$ (1). A mixture containing 0.1 g (ca. 0.21 mmol) of $Ru_2(CH_3COO)_4Cl$ and 6.0 g (ca. 30.6 mmol) of molten Hdpf was heated under an argon atmosphere at 150 °C for 3 h. Excess Hdpf ligand was then sublimed under vacuum at 120 °C, and the residue, which was dark green, was recrystallized three times from a mixture of CH_2Cl_2 and hexane. The yield was nearly 100%. Dark green single crystals suitable for X-ray study were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of **1**. UV−visible data (in CH_2Cl_2): 465, 570, and 665 nm.

$Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ (2). A sample of $Ru_2(dpf)_4Cl$ (0.10 g, 0.098 mmol) was placed in a side-arm flask containing 100 mL of dry THF, after which 0.5 mL of $LiC{\equiv}CC_6H_5$ (0.5 mmol) in THF was added. The mixture was then stirred for 2 h under an argon atmosphere at room temperature. During this period, the color of the solution changed from yellowish green to reddish brown. Upon exposure of the solution to air, the color changed to purple. The solvent was removed using a rotary evaporator and the purple residue washed first with H_2O and then with methanol. The crude product was recrystallized three times from CH_2Cl_2/CH_3CN (1:3). Dark purple-black single crystals suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2 solution of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ to give the final product in a yield of 30%. UV−visible data in CH_2Cl_2 [*λ*, nm]: 380 (sh), 530, 760, and 1150 nm.

$Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ (3). A 0.10 g (ca. 0.098 mmol) sample of $Ru_2(dpf)_4Cl$ was placed in a side-arm flask containing 100 mL of dry deaerated THF, after which 5.0 mL of $LiC{\equiv}CC_6H_5$ (ca. 5.0 mmol) in THF was added under an argon atmosphere. The solution was then stirred for 5 h at room temperature. During this period, the color of the solution changed from yellowish green to red. Upon exposure to air, the color changed to purple. The solution was evaporated to dryness, and the purple residue was chromatographically separated on a silica gel column using CH_2Cl_2 as eluent. The purple band was collected and recrystallized from methanol giving a yield of ca. 30%. Dark reddish-black single crystals of the composition $C_{68}H_{54}N_8Ru_2$ suitable for X-ray analysis were obtained by slow diffusion of hexane into a CH_2Cl_2/benzene (10:1) solution of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$. The compound was found to be soluble in common organic solvents with the exception of pure hexane or methanol. Anal. Calcd: C, 68.80; H, 4.56; N, 9.44. Found: C, 68.27; H, 4.89; N, 9.31. Infrared spectrum (CsI pellet): 2073.7 (s), 1687.9 (w) 1572.2 (s), 1504.7 (s), 1466.1 (s), 1334.9 (s) 1197.9 (s) 1061.0 (w), 1012.8 (w), 920.2 (w), 740.8 (s), 684.8 (s), 557.5 (w), 513.1 (w), 432.11 (w) cm^{-1} (s, strong; w, weak). UV−visible data in CH_2Cl_2 [*λ*, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})]: 410 (6.09) (sh), 510 (18.2), 535 (17.9), 695 (3.15) (sh), 990 (1.89). Mass spectral data [*m*/*e* (fragment)]: 1186.5 ($Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$), 1086.8 ($Ru_2(dpf)_4C{\equiv}CC_6H_5$), 984.2 ($Ru_2(dpf)_4$).

$Ru_2(dpf)_4(CN)_2$ (4). A 0.50 g (ca. 0.49 mmol) sample of $Ru_2(dpf)_4Cl$ was dissolved in THF containing a large excess of NaCN. The mixture was then stirred in air for 72 h at room temperature. During this period, the color of the solution gradually changed from yellowish green to purple. Excess NaCN and other inorganic salts were removed by washing with water several times, and the solvent was removed under vacuum using a rotary evaporator. The purple residue was placed on a silica gel column and eluted with a 1:2 THF/hexane mixture. Two purple bands were collected. Spectroscopic characterization revealed that the first band was the desired diruthenium complex, $Ru_2(dpf)_4(CN)_2$, and the second was the diruthenium(II,III) complex, $Ru_2(dpf)_4(CN)$. The raw product in the first band was twice recrystallized from a mixture of CH_2Cl_2 and hexane. The overall yield of $Ru_2(dpf)_4(CN)_2$ was 54%.

X-ray Crystallography. Single-crystal X-ray diffraction studies of compounds **1**−**4** were performed at the University of Houston X-ray Crystallographic Center using a Nicolet R3m/V automatic diffractomer. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, for compounds **1**−**4** are listed in Table 1. Intensities were measured using the *ω* scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or 100 data collected, and these showed no significant change. During data reduction, Lorentz and polarization corrections were applied; however, no correction for absorption was made due to the small absorption coefficient. The structures of **1**−**4** were solved by use of different methods; however, the usual sequence of isotropic and anisotropic refinement was then followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs. After all shift/esd ratios were less than 0.1 convergence was reached for compounds **1**−**4** at the agreement factors listed in Table 1. No unusually high correlations

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were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density maps showed a maximum peak of about 0.5 e/Å^3 for **1**, 0.30 e/Å^3 for **2**, 0.6 e/Å^3 for **3**, and 0.9 e/Å^3 for **4**.

$Ru_2(dpf)_4Cl$ (1). A dark green square column having approximate dimensions of 0.55 × 0.30 × 0.20 mm was used. The sample was rapidly transferred to the goniometer and placed in a stream of dry nitrogen gas at −50 °C. The Laue symmetry was determined to be 4/*mmm*, and from the systematic absences noted, the space group was shown unambiguously to be *P*4/*ncc*.

The structure was solved by use of the SHELXTL direct methods program. This revealed the positions of all of the non-hydrogen atoms in the asymmetric unit, which consisted of one-quarter molecule situated along a 4-fold axis. A massively disordered area of electron density was found around a 222 symmetry site, which is presumed to be pentane. The four positions having the largest intensity were eventually refined isotropically, with the following populations: C14 = 40%, C15 = 40%, C16 = 25%, and C17 = 25%. The disorder is so severe that no ideal rigid model was possible to refine.

$Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ (2). A purple-black block having approximate dimensions of 0.50 × 0.35 × 0.20 mm was chosen for analysis. The Laue symmetry was determined to be 2/*m*, and from the systematic absences noted, the space group was shown to be either *Ic* or *I*2/*c*. (The conventional *C*-centered lattice has $a = 24.625$ Å and $\beta = 131.11°$.)

Since the unitary structure factors displayed centric statistics, space group *I*2/*c* was assumed from the outset. However, after exhaustive attempts to solve the structure failed using both heavy atom methods and direct methods, space group *Ic* was tried. Eventually direct methods yielded a solution, and it was soon obvious that the two independent molecules found had 2-fold internal symmetry. Therefore, the space group was converted back to *I*2/*c* and the molecules were translated to sites along a 2-fold axis. Thereafter, refinement proceeded normally in the centrosymmetric space group. The asymmetric unit in this case thus consists of two half-molecules situated about a 2-fold axis. In both independent molecules, the axial phenylacetylide ligand is massively disordered having at least four different orientations, none of which are precisely aligned along the 2-fold axis. This was treated by introducing two rigid-body toluene groups at each site which had 25% population factors. The other two major orientations are thus generated by the 2-fold axis.

$Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ (3). A dark reddish-black block having approximate dimensions 0.60 × 0.45 × 0.30 mm was used in the X-ray analysis. The Laue symmetry was determined to be 2/*m*, and from the systematic absences noted, the space group was shown to be *Cc* or *C*2/*c*.

Since the unitary structure factors displayed centric statistics, space group *C*2/*c* was assumed from the outset. The structure was solved by the interpretation of the Patterson map, which revealed the positions of the Ru atoms in the asymmetric unit, consisting of one-half dimer situated about a 2-fold axis and a full dimer located in a general position. Remaining non-hydrogen atoms were found in subsequent difference Fourier syntheses. All of the phenyl carbons were refined isotropically in order to reduce the number of variables to a manageable number.

$Ru_2(dpf)_4(CN)_2$ (4). A black cherry colored wedge having approximate dimensions of 0.65 × 0.40 × 0.15 mm was cut from a large conglomerate and mounted in a random orientation. Since the crystals were known to decompose rapidly outside the mother liquor, the sample was placed in a stream of dry nitrogen gas at −50 °C. The Laue symmetry was determined to be 2/*m*, and from the systematic absences noted, the space group was shown to be either $P2_1$ or $P2_1/m$.

Since the unitary structure factors displayed acentric statistics, space group $P2_1$ was assumed from the outset. The structure was solved by the SHELXTL direct methods program which revealed the position of most of the non-hydrogen atoms in the molecule. Remaining atoms were located in subsequent difference Fourier syntheses. One phenyl ring (C2−C7) was found to be disordered over two slightly different orientations, and this was treated by refining ideal rigid body models which had 50% occupancy at each position. At this point three different sites containing solvent molecules were located. Two of these were determined to be methylene chloride, with the C56 site being disordered over two different orientations. Ideal rigid bodies were employed to model these areas. The third site was found to be massively disordered and appeared to be partially occupied by both methylene chloride and hexane. Due to the complexity of the disorder pattern, rigid bodies could not be used, and thus the bonding geometry is quite poor here. The absolute configuration was determined by refinement of a coefficient multiplying $\Delta F''$, which indicated conclusively that the reported configuration is correct.

Results and Discussion

Synthesis and Reaction Mechanism. The original purpose of our study was to synthesize $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ by a modified procedure reported in the literature[2] and to use this diruthenium(II,III) complex as the starting material in an attempt to synthesize stable diruthenium(III,III) complexes. The reaction between $Ru_2(dpf)_4Cl$ and a large excess of $LiC{\equiv}CC_6H_5$ gives a purple compound following purification on a silica gel column using CH_2Cl_2 as eluent. Initially, it was thought that the product was the desired compound, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$. However, a comparison of cyclic voltammograms for the product and the parent complex, $Ru_2(dpf)_4Cl$, made little sense, based on the number of reversible redox processes and the expected shifts in potentials for a simple substitution of chloride by phenylacetylide.[2,27] Therefore, the crystal structure of the synthesized complex was obtained and this revealed that the isolated product was, in fact, a novel diruthenium(III,III) complex with two σ-bonded axial ligands, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$.

The fact that the expected $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ product was not eluted off the silica gel column led to investigation of the reported reaction in more detail. It was found that the expected diruthenium(II,III) complex, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$, could be obtained only from the addition of 2−5 equiv of $LiC{\equiv}CC_6H_5$ to $Ru_2(dpf)_4Cl$ followed by recrystallization, rather than purification on a silica gel column. It appears either that $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ undergoes decomposition on a silica gel column to generate a compound which cannot be eluted off of the column or that the product itself stays on the silica gel column. For these reasons, only $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ was isolated as a product from chromatographic purification.

The sequence of reactions shown in eqs 1−3 is suggested to occur in the synthesis of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$.

$$Ru_2(dpf)_4Cl + [C{\equiv}CC_6H_5]^- \rightarrow Ru_2(dpf)_4(C{\equiv}CC_6H_5) + Cl^- \quad (1)$$

$$Ru_2(dpf)_4(C{\equiv}CC_6H_5) + [C{\equiv}CC_6H_5]^- \rightarrow [Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^- \quad (2)$$

$$[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^- + O_2 \rightarrow Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2 + O_2^- \quad (3)$$

There is a rapid color change from red to purple when the proposed $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ intermediate in reaction 2 is exposed to air, thus suggesting an oxidation of the anionic species and the formation of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ (see eq 3). The fact that $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ is fairly stable in air with respect to oxidation strongly supports the presence of a high concentration of $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ in the reaction mixture when $LiC{\equiv}CC_6H_5$ is present in large excess. Furthermore, an electrochemically obtained solution of $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ in THF is immediately oxidized upon exposure to air to again generate neutral $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$. This gives additional support for the above reaction mechanism.

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(27) Yao, C.-L.; Park, K. H.; Khokhar, A. R.; Jun, M.-J.; Bear, J. L. *Inorg. Chem.* **1990**, *29*, 4033.

Table 2. Selected Bond Lengths (Å)[a]

$Ru_2(dpf)_4Cl$, **1**

Ru(1)−Ru(2)	2.339(1)	Ru(1)−Cl	2.414(2)
Ru(1)−N(1)	2.090(3)	Ru(2)−N(2)	2.044(4)

$Ru_2(dpf)_4(C{\equiv}CC_6H_5)$, **2**

molecule 1		molecule 2	
Ru(1)−Ru(2)	2.369(1)	Ru(3)−Ru(4)	2.431(1)
Ru(1)−N(3)	2.117(4)	Ru(3)−N(7)	2.086(3)
Ru(1)−N(1)	2.110(3)	Ru(3)−N(5)	2.093(4)
Ru(2)−N(2)	2.045(3)	Ru(4)−N(6)	2.052(4)
Ru(2)−N(4)	2.050(3)	Ru(4)−N(8)	2.051(3)
Ru(1)−C(27)	2.037(7)	Ru(3)−C(59)	2.018(7)
C(27)−C(28)	1.191(13)	C(59)−C(60)	1.237(9)
C(27)−C(28a)	1.216(12)	C(59)−C(60a)	1.260(13)

$Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$, **3**

molecule in the general posn		molecule in the special posn	
Ru(1)−Ru(2)	2.553(1)	Ru(3)−Ru(3′)	2.558(1)
Ru(1)−N(1)	2.087(7)	Ru(3)−N(9)	2.108(7)
Ru(1)−N(3)	2.002(7)	Ru(3)−N(11)	2.005(7)
Ru(1)−N(5)	2.020(7)	Ru(3)−N(10′)	2.019(7)
Ru(1)−N(7)	2.126(7)	Ru(3)−N(12′)	2.085(7)
Ru(2)−N(2)	1.992(7)	Ru(3)−C(95)	1.987(8)
Ru(2)−N(4)	2.101(7)	C(95)−C(96)	1.181(11)
Ru(2)−N(6)	2.095(7)		
Ru(2)−N(8)	2.017(7)		
Ru(1)−C(53)	1.987(8)		
Ru(2)−C(61)	1.986(8)		
C(53)−C(54)	1.185(12)		
C(61)−C(62)	1.170(11)		

$Ru_2(dpf)_4(CN)_2$, **4**

Ru(1)−Ru(2)	2.539(1)	Ru(2)−N(2)	2.001(7)
Ru(1)−N(1)	2.074(6)	Ru(2)−N(4)	2.079(6)
Ru(1)−N(3)	2.006(7)	Ru(2)−N(6)	2.087(7)
Ru(1)−N(5)	2.015(7)	Ru(2)−N(8)	1.994(6)
Ru(1)−N(7)	2.112(6)	Ru(2)−C(54)	1.962(10)
Ru(1)−C(53)	1.980(9)	N(10)−C(54)	1.179(14)
N(9)−C(53)	1.148(13)	N(2)−C(1)	1.347(13)
N(1)−C(1)	1.305(13)		

[a] Individual (not average) values.

Table 3. Selected Bond Angles (deg)[a]

$Ru_2(dpf)_4Cl$, **1**

Ru(2)−Ru(1)−Cl	180.0	N(1)−Ru(1)−N(1′)	174.7(2)
Cl−Ru(1)−N(1)	92.7(1)	N(2)−Ru(2)−N(2′)	179.2(2)
Ru(2)−Ru(1)−N(1)	87.3(1)	Ru(1)−Ru(2)−N(2′)	90.4(1)

Ru2(dpf)4($C{\equiv}CC_6H_5$), **2**

molecule 1		molecule 2	
Ru(2)−Ru(1)−N(1)	86.8(1)	Ru(4)−Ru(3)−N(5)	87.6(1)
Ru(2)−Ru(1)−N(3)	87.4(1)	Ru(4)−Ru(3)−N(7)	87.1(1)
Ru(2)−Ru(1)−C(27)	180.0	Ru(4)−Ru(3)−C(59)	180.0
Ru(1)−Ru(2)−N(4)	89.4(1)	Ru(3)−Ru(4)−N(8)	89.6(1)
N(1)−Ru(1)−N(3)	89.2(1)	N(5)−Ru(3)−N(7)	89.8(1)
N(1)−Ru(1)−C(27)	93.2(1)	N(5)−Ru(3)−C(59)	92.4(1)
N(3)−Ru(1)−C(27)	92.6(1)	N(7)−Ru(3)−C(59)	92.9(1)
N(1)−Ru(1)−N(1′)	173.7(2)	N(5)−Ru(3)−N(5′)	175.2(2)
N(1)−Ru(1)−N(3′)	90.5(1)	N(5)−Ru(3)−N(7′)	90.0(1)
N(2)−Ru(2)−N(4)	88.1(1)	N(6)−Ru(4)−N(8)	89.1(1)
N(2)−Ru(2)−N(2′)	180.0(3)	N(6)−Ru(4)−N(6′)	177.9(2)

$Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$, **3**

molecule in the general posn		molecule in the special posn	
Ru(2)−Ru(1)−N(1)	81.1(2)	Ru(3′)−Ru(3)−N(9)	79.9(2)
Ru(2)−Ru(1)−N(3)	93.0(2)	Ru(3′)−Ru(3)−N(10′)	93.2(2)
Ru(2)−Ru(1)−N(5)	92.6(2)	Ru(3′)−Ru(3)−N(11)	92.0(2)
Ru(2)−Ru(1)−N(7)	79.3(2)	Ru(3′)−Ru(3)−N(12′)	79.6(2)
N(1)−Ru(1)−N(3)	91.3(3)	N(9)−Ru(3)−N(10′)	88.3(3)
N(1)−Ru(1)−N(7)	90.7(3)	N(9)−Ru(3)−N(12′)	90.7(3)
N(3)−Ru(1)−N(5)	86.6(3)	N(10′)−Ru(3)−N(11)	89.4(3)
N(5)−Ru(1)−N(7)	90.5(3)	N(11)−Ru(3)−N(12′)	90.5(3)
N(1)−Ru(1)−N(5)	173.3(3)	N(9)−Ru(3)−N(11)	171.5(3)
N(3)−Ru(1)−N(7)	171.7(3)	N(10′)−Ru(3)−N(12′)	172.8(3)
N(1)−Ru(1)−C(53)	87.3(3)	N(9)−Ru(3)−C(95)	85.9(3)
Ru(2)−Ru(1)−C(53)	160.8(2)	Ru(3′)−Ru(3)−C(95)	160.0(3)
N(3)−Ru(1)−C(53)	102.5(3)	N(10′)−Ru(3)−C(95)	100.4(3)
N(5)−Ru(1)−C(53)	99.5(3)	N(11)−Ru(3)−C(95)	102.6(3)
N(7)−Ru(1)−C(53)	85.7(3)	N(12′)−Ru(3)−C(95)	86.6(3)
Ru(1)−Ru(2)−C(61)	158.5(3)		

$Ru_2(dpf)_4(CN)_2$, **4**

Ru(2)−Ru(1)−N(1)	80.9(2)	Ru(2)−Ru(1)−N(3)	92.4(3)
Ru(2)−Ru(1)−N(5)	92.4(3)	Ru(2)−Ru(1)−N(7)	79.3(2)
Ru(1)−Ru(2)−N(2)	90.9(2)	Ru(1)−Ru(2)−N(4)	79.8(2)
Ru(1)−Ru(2)−N(6)	80.6(2)	Ru(1)−Ru(2)−N(8)	93.0(3)
Ru(2)−Ru(1)−C(53)	159.7(3)	Ru(1)−Ru(2)−C(54)	160.8(3)
N(1)−Ru(1)−N(3)	89.9(3)	N(1)−Ru(1)−N(5)	173.3(4)
N(3)−Ru(1)−N(5)	90.3(3)	N(3)−Ru(1)−N(7)	171.5(4)
N(5)−Ru(1)−N(7)	88.5(3)	N(1)−Ru(1)−N(7)	90.3(2)
N(1)−Ru(1)−C(53)	86.2(3)	N(3)−Ru(1)−C(53)	103.4(4)
N(5)−Ru(1)−C(53)	100.3(4)	N(7)−Ru(1)−C(53)	85.1(3)
N(2)−Ru(2)−N(6)	171.5(3)	N(4)−Ru(2)−N(6)	90.4(2)
N(2)−Ru(2)−N(8)	90.4(3)	N(4)−Ru(2)−N(8)	172.8(3)
N(6)−Ru(2)−N(8)	88.8(3)	N(2)−Ru(2)−N(4)	89.3(2)
N(2)−Ru(2)−C(54)	101.1(4)	N(4)−Ru(2)−C(54)	85.4(3)
N(6)−Ru(2)−C(54)	87.4(4)	N(8)−Ru(2)−C(54)	101.7(3)
Ru(1)−C(53)−N(9)	174.2(8)	Ru(2)−C(54)−N(10)	177.4(10)

[a] Individual (not average) values.

Finally, the formation of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ from $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ can also be accomplished using a large excess of $LiC{\equiv}CC_6H_5$ in THF. This was verified in the present study.

The overall reactions given in eqs 1−3 are quite fascinating since it has long been assumed that the formation of the first ruthenium axial ligand bond deactivates the complex with respect to the addition of a second axial ligand bond, either due to steric hindrance and/or a *trans* effect.[2,27] It now appears that the formation of stable diruthenium(III,III) complexes depends primarily upon the donor properties of the bridging ligands, axial ligands, and the formation of the second axial ligand bond.

Molecular Structures. Selected bond lengths and bond angles for compounds **1**−**4** are summarized in Tables 2 and 3, and their crystal structures are presented in Figures 1−3. Complete intramolecular bond lengths and angles as well as other structural data are given as Supporting Information.

For compound **1**, the coordinations about Ru1 and Ru2 are essentially octahedral and square pyramidal, respectively, with four dpf nitrogens in each of the equatorial planes. The Ru1−N distance is 2.090 Å, which is significantly longer than Ru2−N distance of 2.044 Å. The Ru−Ru bond length of 2.339 Å is in the expected range for diruthenium(II,III) complexes of this structural type. The Ru2−Ru1−Cl bond angle is 180°. The N−Ru−Ru−N torsion angle is 14.6°, and there is a 50:50 mixture of left- and right-handed torsional twists in the crystal. The two dpf phenyl rings are twisted out of the bridging ligand plane by distinctly different amounts (C1−N1−C2−C3 = −74° and C1−N2−C8−C13 = −39°), as in the case of the parent complex having no axial ligand.

The unit cell of compound **2** contains two independent molecules having 2-fold internal symmetry. The two molecules possess radically different structural features. The Ru1−Ru2 bond distance of 2.369(1) Å is significantly shorter than the Ru3−Ru4 length of 2.431(1) Å. The coordination about Ru1 and Ru3 is essentially octahedral, with four nitrogens in the equatorial plane (Figure 1). The Ru1−N distance averages 2.114 Å, and the Ru3−N distance averages 2.090 Å. In both types of molecules, the axial ligand is bound nearly linearly to the Ru−Ru bond. The terminal phenyl is heavily disordered off of this axis, displaying a “wagging” type of motion. The

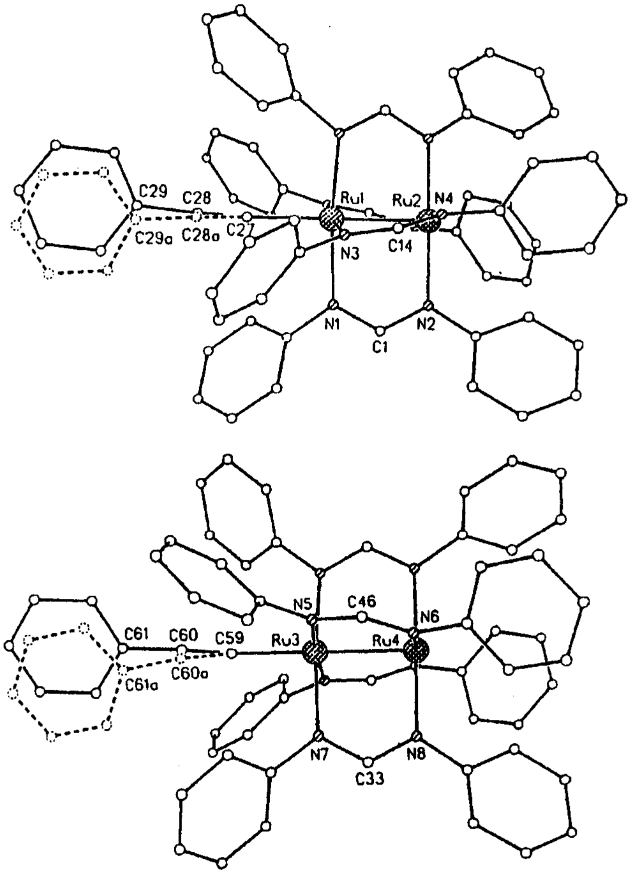

Figure 1. View of molecules 1 and 2 of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ with the core atoms labeled. Two representative orientations of the disordered axial ligand are shown.

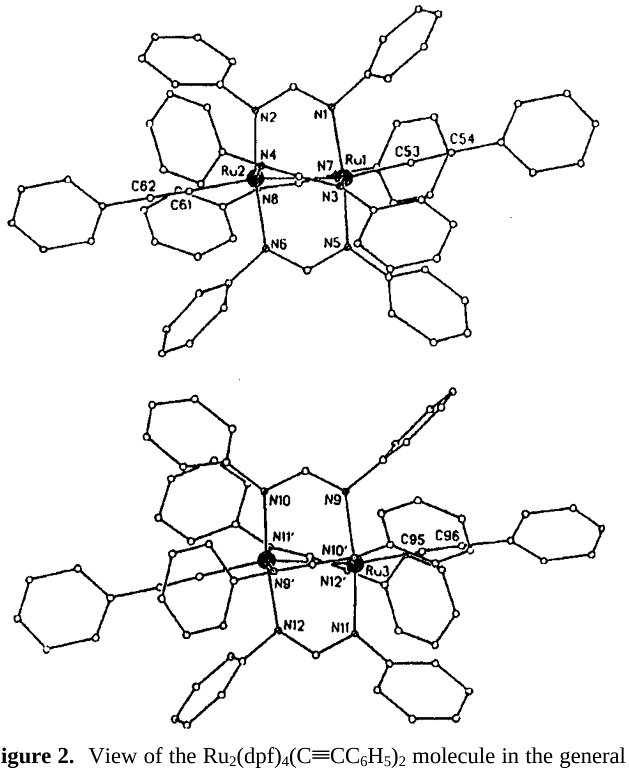

Figure 2. View of the $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ molecule in the general and special positions with the core atoms labeled.

Ru1−C and Ru3−C axial bond lengths are 2.037(7) and 2.018(7) Å, respectively. The coordination about Ru2 and Ru4 is square pyramidal, with four dpf nitrogens forming the base. The Ru2−N distance averages 2.048 Å, and the Ru4−N average is 2.052 Å. The molecule containing Ru1−Ru2 has an average N−Ru−Ru−N torsion angle modules of 15.3°, while that of the second molecule averages 8.9°. For both molecules, there is a 50:50 mixture of left- and right-handed torsional twists in the crystal.

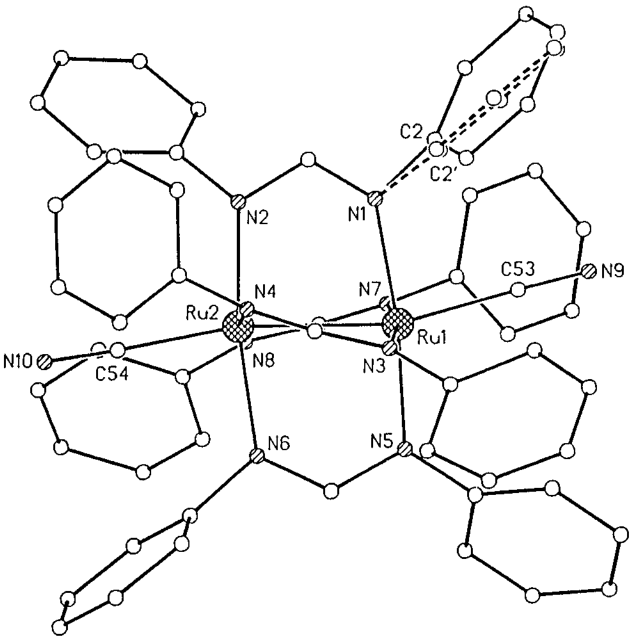

Figure 3. View of the $Ru_2(dpf)_4(CN)_2$ molecule.

In the unit cell of compound **3**, there are also two crystallographically different types of molecules which, similar to **2**, are distinguished by the orientations of the dpf phenyl rings. The molecule in the general position in the unit cell has different dpf phenyl arrangements on the Ru1 and Ru2 ends, while the molecule located around the 2-fold site necessarily has identical dpf arrangement on both Ru3 ends. The Ru3 arrangement is the mirror image of the Ru2 type.

Each Ru is in a distorted octahedral ligand environment (Figure 2), with four dpf nitrogens forming the equatorial plane. The Ru−N bond distances and the Ru−Ru−N bond angles are not all the same in compound **3**. There are two long bonds (average 2.100 Å) and two short ones (average 2.009 Å). The Ru−Ru−N bond angles are greater than 90° for the two short bonds (average 92.8) and less than 90° for the two long bonds (average 80.2). The Ru−Ru−C angle is distinctly nonlinear, averaging 159.8°C, and the average of Ru−Ru bond distances is 2.556 Å. The average N−Ru−Ru−N torsion angle is 13.7° in the Ru1/Ru2 molecule and 15.5° in the Ru3/Ru3′ molecule.

A comparison of the crystal and molecular structures of compounds **1**−**3** allows us to evaluate both the effect of substituting the phenylacetylide ion for an axial chloride and the effect of forming the second axial phenylacetylide bond with oxidation to the Ru_2^{6+} state. The crystal and molecular structure of **1** is consistent with that of other reported diruthenium(II,III) carboxylate type complexes with an axial chloride.[5] The replacement of chloride by phenylacetylide results in significant changes in both the crystal and molecular structure. For example, there are two independent molecules in the crystal of **2** having identical connectivities but radically different configurations. A significant difference between the two molecules is observed in the average N−Ru−Ru−N torsion angle modules (15.3° vs 8.9°), the Ru−Ru bond distances (2.369 Å vs 2.431 Å), and the Ru−C_{axial} bond distances (2.037 Å vs 2.018 Å).

The orientations of the dpf phenyl rings in the two molecules are essentially the same on Ru1 and Ru3, but the “slot” occupied by the various orientations of the axial phenyl is completely different. Given the distance of the axial phenyl from the dpf ligands, the orientations of these groups would not be expected to have much of an effect on one another. On Ru2 and Ru4, the orientations of the dpf phenyl rings are radically different. A 2-fold relation is present in both cases, but the phenyls on Ru2 all appear to lie parallel to one another, while on Ru4 the phenyls are clearly closer to the typical "edge-to face" arrangement found in the similar molecules.

In the crystal structure, the two different types of molecules are arranged in an alternating head-to-tail relationship along any given 2-fold axis. It is tempting to propose that the configuration of one molecule induces the complementary configuration on its vertical neighbors. However, this does not seem plausible since the only "communication" between adjacent molecules in this direction is the distal edge of a single phenyl ring. It is not reasonable to assume that the molecules would uniformly adopt different configurations in response to an identical steric neighbor. Also, the Ru1−Ru4 distance of 13.026 Å is quite similar to the Ru2−Ru3′ distance of 13.087 Å, indicating no preferred contact between the head or tail of either configuration. The only remaining molecular packing explanation would involve the contacts between dpf ligands on molecules of the neighboring 2-fold axes. Examination of the packing of the molecule in the unit cell does not show any obvious close contacts, although there may be subtle steric forces at work.

The crystal structure of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ (**3**) reveals several interesting and unusual geometric features. The average Ru−Ru bond distance is 2.556(1) Å, which is much longer than expected for a Ru_2^{6+} complex of this structural type.[2,8] For example, the parent molecule $Ru_2(dpf)_4Cl$ has a Ru−Ru bond distance of 2.339(1) Å and a theoretical bond order of 2.5 based on the generally accepted electronic configuration of $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$. Assuming a similar ordering of the Ru−Ru molecular orbitals, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ should have a bond order of 3. In addition, the crystal and molecular structures of the Ru_2^{6+} complex, $K_2[Ru_2(SO_4)_4(H_2O)_2]$, has a Ru−Ru bond distance of 2.303(1) Å.[20] This anionic complex has the basic carboxylate type structure except that the four three-atom bridging ligands are the highly charged $(SO_4)^{2-}$ ion. The $K_2[Ru_2(SO_4)_4(H_2O)_2]$ complex has a magnetic moment consistent with four unpaired electrons and a proposed electronic configuration of $\sigma^2\pi^4(\delta\pi^{*2}\delta^*)$, corresponding to a Ru−Ru bond order of 2.

The only diruthenium complexes with Ru−Ru bond distances comparable to that of $Ru_2(dpf)_4(CN)_2$ and $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ are the Ru_2^{6+} derivatives $Ru_2(C_5NH_4NH)_6(PMe_2Ph)_2$ (Ru−Ru = 2.573(2) Å),[18a] $Ru_2(C_6H_5)_2[3,5\text{-}(OCH_3)_2C_6H_3CONH]_2[(C_6H_5)_2POC(3,5\text{-}(OCH_3)_2C_6H_3)N]_2$ (Ru−Ru = 2.567(1) Å),[19] and $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$, (Ru−Ru = 2.650(1) Å).[17] For these complexes, a single net Ru−Ru σ bond has been proposed. The Ru−Ru bond distances for several diruthenium compounds are summarized in Table 4, and it is clear that the bond length for **3** is more consistent with a Ru−Ru single bond. One possible explanation is that the strong axial interaction by two phenylacetylide ions results in the energy of the Ru−Ru σ orbital being above that of the π^* orbital, giving an electronic configuration of $\pi^4\delta^2\pi^{*4}$.

Table 4. Comparison of Ru−Ru Distances in Selected Diruthenium Compounds

Ru−Ru oxidn state	compd	Ru−Ru dist (Å)	ref[c]
II−II	$Ru_2[(p\text{-tol})NC(H)N(p\text{-tol})]_4$	2.474(1)	8
	$Ru_2[(p\text{-tol})NNN(p\text{-tol})]_4$	2.417(2)	9
II−III	$Ru_2(PhNpy)_4Cl$	2.275(3)	5
	$Ru_2(PhNpy)_4(C{\equiv}CC_6H_5)$	2.319(2)	2
	$Ru_2(dpf)_4Cl$	2.339(1)	tw
	$Ru_2(dpf)_4(C{\equiv}CC_6H_5)$	2.400(1)[b]	tw
III−III	$Ru_2(CH_2CMe_3)_6$	2.311(3)	16
	$Ru_2(dpf)_4(CN)_2$	2.539(1)	tw
	$Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$	2.556(1)b	tw
	$Ru_2(R)_2(R'CONH)_2[R_2POC(R')N]_2$[a]	2.567(1)	19
	$Ru_2(C_5NH_4NH)_6(PMe_2Ph)_2$	2.573(2)	18a
	$Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$	2.650(1)	17

[a] $R = C_6H_5$, $R' = 3,5\text{-}(OCH_3)_2C_6H_3$. [b] Average value of two molecules in crystal structure (see Table 3 for individual metal−metal distances). [c] tw = this work.

Another unexpected feature of **3** is the high degree of distortion of the basic octahedral structure about each of the ruthenium ions. The Ru−Ru−C angle is distinctly nonlinear, averaging 159.8°. This is quite strange, since in this orientation the overlap between the sp-hybridized orbital from phenylacetylide and the σ orbitals from Ru−Ru molecular orbitals is not maximized. To our knowledge, all of the M−M−C (where M = Rh, Ru)[2,27−29] angles reported in the literature are nearly linear (deviation less than 3°). In addition, the Ru−N bonds are found to differ, with two long ones (average 2.100 Å) and two short ones (average 2.009 Å) on each Ru metal. The long Ru−N bonds are the ones adjacent to the dpf phenyl rings which are closest to the axial phenyl and flatten out against it. These longer bonds also show a compressed Ru−Ru−N angle (average 80.1°) compared to the short Ru−N bond (Ru−Ru−N angle average 92.7°). It is not clear whether the distortion is caused by electronic (some type of Jahn−Teller effect) or steric forces.

In an attempt to resolve this question, the complex $Ru_2(dpf)_4(CN)_2$ (**4**) was synthesized and structurally characterized. The molecular structure of $Ru_2(dpf)_4(CN)_2$ is shown in Figure 3 and is similar to that of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$. As is seen in Table 3, all of the bond angles for **4** are comparable with the corresponding ones found in **3**. Most importantly, the deviation from linearity in the Ru−Ru−C angles and the distortions in the equatorial planes are almost identical for both compounds. This indicates that the distortion of the octahedral symmetry observed for **3** and **4** is due to electronic effects. All of the important bond distances in **4** are reduced relative to those observed in **3**, although the coordinating atoms in the corresponding positions are the same (see Table 2): The Ru−Ru, Ru−C, and average Ru−N bond distances are reduced from 2.556, 1.987, and 2.055 Å for **3** to 2.539, 1.971, and 2.046 Å for **4**.[30] The shorter Ru−Ru bond distance in the cyano complex appears to aggravate the strain present in the five-membered rings, and the N−Ru−Ru−N angles increase from 14.6° (average) in **3** to 17.0° in **4**. The comparison of Ru−Ru and Ru−N bond lengths and N−Ru−Ru−N torsion angles for **1**−**4** are given in Table 5.

NMR Characterization of Compounds 3 and 4. The conventional ^{13}C NMR spectrum of compound **3** in $CDCl_3$ is shown in Figure 4a. There are 11 resonances for 11 different types of carbon atoms. This unambiguously indicates that the eight phenyl rings are magnetically equivalent under the experimental conditions. The peaks at 137.53, 127.50, and 46.46 ppm are of low intensity and can be tentatively assigned to three of the four quartet carbon atoms on the basis that quartet carbons generally have a short relaxation time, giving resonance

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[28] Bear, J. L.; Yao, C.-L.; Lifsey, R. S.; Korp, J. D.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 336.

[29] Huang, S. R.; Han, B. C.; Bear, J. L. Manuscript in preparation. In this paper, the $Rh_2(dpf)_4(C{\equiv}CC_6H_5)$ compound gives a Rh−Rh−C angle of 179°.

[30] Compounds **3** and **4** were analyzed at 22 and −50 °C, respectively. This difference in temperature, however, should not yield shorter bond distances.

Table 5. Comparison of Bond Distances and Torsion Angles for Investigated Compounds

Ru−Ru oxidn state	compd	Ru−Ru bond dist (Å)	av Ru−N bond dist (Å)	av N-Ru−Ru−N torsion angle (deg)
II−III	$Ru_2(dpf)_4Cl$	2.339(1)	2.090[a]	14.6
	$Ru_2(dpf)_4(C{\equiv}CC_6H_5)$	2.369(1),[b] 2.431(1)[c]	2.114,[a,b] 2.090[a,c]	15.3,[b] 8.9[c]
III−III	$Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$	2.553(1),[b] 2.558(1)[c]	2.100,[d] 2.009[e]	13.7,[b] 15.5[c]
	$Ru_2(dpf)_4(CN)_2$	2.539(1)	2.088,[d] 2.004[e]	17.0

[a] For the six-coordinated Ru atom. [b] Molecule 1. [c] Molecule 2. [d,e] Average values of two long and two short bonds, respectively..

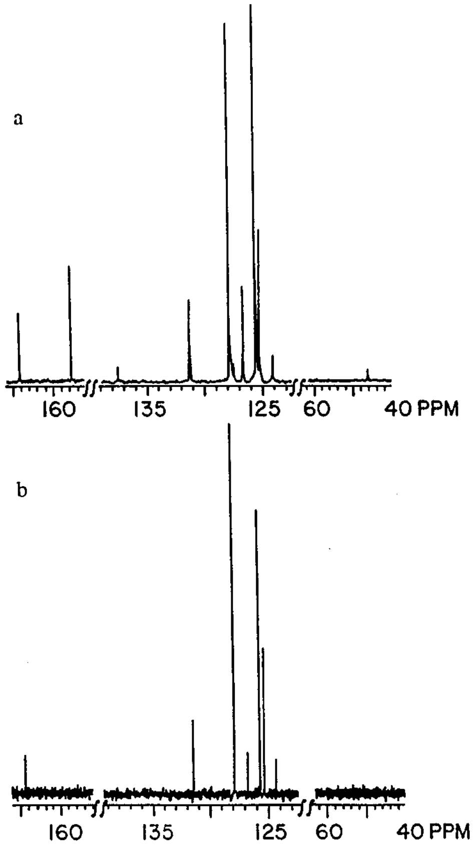


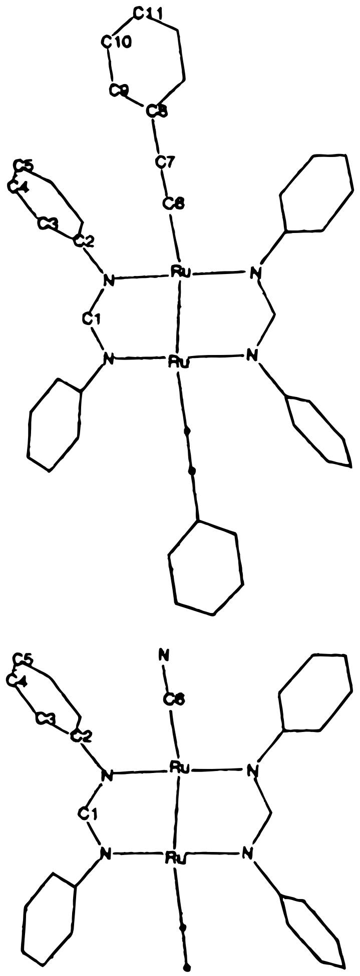
Figure 4. (a) Conventional and (b) DEPT ^{13}C NMR spectra of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ in $CDCl_3$.

peaks with low intensity. This assignment is confirmed by the DEPT (*D*istortionless *E*nhancement *P*olarization *T*ranslation) ^{13}C NMR spectrum in Figure 4b which was accumulated while all quartet carbons are simultaneously decoupled. The DEPT spectrum contains only seven resonances with the four “missing” peaks being the quartet carbons located at 155.55, 137.53, 127.50, and 46.46 ppm in Figure 4a.

The numbering of the carbons in $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ and $Ru_2(dpf)_4(CN)_2$ is shown in Chart 2.

The peaks at 168.61 and 155.55 ppm in Figure 4a are attributed to the four formamidinate carbon atoms labeled as C1 and to the eight carbons labeled as C2 which are on the dpf phenyl rings. This assignment is based on the NMR spectrum of the free Hdpf ligand which displays similar-shaped resonances at 149.85 and 145.25 ppm in the same solvent.[31] The 155.55 ppm peak due to a quartet carbon is not seen in Figure 4b. The acetylide carbon atoms directly attached to the Ru metal centers (C6) are highly shielded and appear at 46.46 ppm. The remaining C7 carbons of the acetylide group are subject to a ring current generated by the dpf and axial phenylacetylide phenyl rings and are observed at 137.53 ppm. The last quartet carbon has a resonance at 127.50 ppm and arises from the carbon atoms labeled as C8.

Chart 2



Resonances of phenyl carbon atoms usually appear in the range of 125−135 ppm,[32] and two distinct groups of peaks in this region are seen in Figure 4 for compound **3**. The first group contains three intense signals at 127.73, 125.57, and 125.21 ppm, while the second has three weak signals at 131.27, 126.70, and 124.19 ppm. The resonances in the former group are tentatively assigned to carbon atoms C3, C5, and C4 from the dpf phenyl rings, and those in the latter are assigned to C9, C10, and C11 from the axial phenylacetylide phenyl rings.

A similar analysis was carried out for compound **4**, which has six resonance peaks in the ^{13}C NMR spectrum. The values of δ are given in Table 6. The most downfield peak is at 169.51 ppm and is due to C1, while a peak at 155.00 ppm is assigned to C2. The resonances at 128.59, 126.52, and 125.13 ppm are attributed to C3, C5, and C4. The most upfield resonance at 20.44 ppm is due to C6 of the axial cyanide.

It should be noted that the distortion of the octahedral symmetry observed in the single crystals of compounds **3** and

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(31) Free dpf ligands show five resonances at 149.85, 145.25, 129.26, 123.22, and 119.09 ppm in $CDCl_3$.

(32) Drago, R. S. *Physical Methods in Chemistry;* W. B. Saunders: Philadephia, PA, 1977; pp 305.

Table 6. Chemical Shifts (ppm) of ^{13}C NMR Data for **3** and **4** in $CDCl_3$

carbon[a]	$Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$	$Ru_2(dpf)_4(CN)_2$
C1	168.61	169.51
C2	155.55	155.00
C3	127.73	128.59
C4	125.21	125.13
C5	125.57	126.52
C6	46.46	20.44
C7	137.53	
C8	127.50	
C9	131.27	
C10	126.70	
C11	124.19	

[a] See Chart 2 for the number of the carbons.

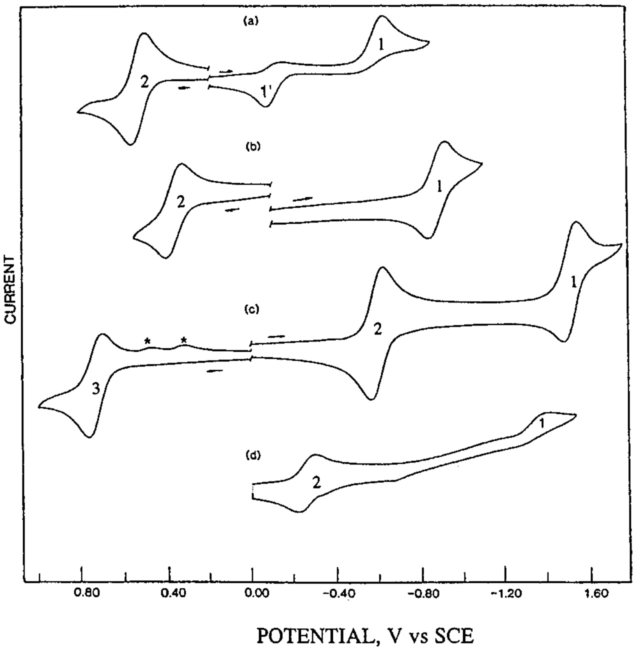

Figure 5. Cyclic voltammograms of (a) $Ru_2(dpf)_4Cl$, (b) $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$, (c) $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$, and (d) $Ru_2(dpf)_4(CN)_2$ in CH_2Cl_2, 0.1 M TBAP. Scan rate = 0.1 V/s. The redox reactions for processes 1−3 are designated in the text. Decomposition products of $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^+$ are indicated by **.

4 (Figures 2 and 3) is not seen under the NMR experimental conditions. This suggests that the eight phenyl rings spin rapidly in the solution resulting in magnetic equivalence of these phenyl rings.

The magnetic moments of compounds **1** and **2** are paramagnetic, and no NMR signals could be observed.

Electrochemistry. Four oxidation states are possible for the investigated compounds, and a stepwise interconversion between compounds with Ru_2^{7+}, Ru_2^{6+}, Ru_2^{5+}, or Ru_2^{4+} cores can be accomplished by the three redox reactions shown in eqs 4−6.

$$Ru_2^{5+} + e \rightleftharpoons Ru_2^{4+} \quad \text{(Rxn 1)} \tag{4}$$

$$Ru_2^{6+} + e \rightleftharpoons Ru_2^{5+} \quad \text{(Rxn 2)} \tag{5}$$

$$Ru_2^{7+} + e \rightleftharpoons Ru_2^{6+} \quad \text{(Rxn 3)} \tag{6}$$

Only one of the four investigated compounds can exist in all four oxidation states. This is shown by the cyclic voltammograms in Figure 5c. Compound **1**, which contains a Ru_2^{5+} center, undergoes a reversible one-electron oxidation at $E_{1/2}$ = 0.54 V (Rxn 2) and an irreversible reduction at E_{pc} = −0.63 V (Rxn 1). The latter reaction is coupled to a new reversible reduction at $E_{1/2}$ = −0.09 V (labeled as Rxn 1′). Rxn 1 in Figure 5a is associated with the conversion of $Ru_2(dpf)_4Cl$ to $Ru_2(dpf)_4$, while Rxn 1′ involves a reoxidation of $Ru_2(dpf)_4$ to $Ru_2(dpf)_4ClO_4$, where ClO_4^- comes from the supporting electrolyte which is present in a concentration 100 times that of the Cl^-. Thus, the overall reactions involving the first reduction and reoxidation of $Ru_2(dpf)_4Cl$ occur as shown in Scheme 1.

Scheme 1

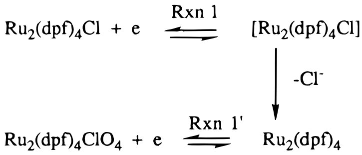

Table 7. Half-Wave Potentials (V vs SCE) of Investigated Compounds in CH_2Cl_2, 0.1 M TBAP[a]

initial oxidn state	compd	Ru_2^{7+}/Ru_2^{6+} (Rxn 3)	Ru_2^{6+}/Ru_2^{5+} (Rxn 2)	Ru_2^{5+}/Ru_2^{4+} (Rxn 1)
II,III	$Ru_2(dpf)_4Cl$		0.54	−0.64[b,c]
	$Ru_2(dpf)_4(C{\equiv}CC_6H_5)$		0.33	−0.89
III,III	$Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$	0.73	−0.61	−1.54
	$Ru_2(dpf)_4(CN)_2$		−0.25	−1.34[b]

[a] See Figure 5 for labeling of Rxns 1−3. [b] Cathodic peak potential, E_{pc}, for a scan rate of 0.1 V/s. [c] An additional reaction is seen at $E_{1/2}$ = −0.09 V (see Figure 5a) and is associated with reduction and reoxidation of $Ru_2(dpf)_4ClO_4$ which is generated in solution.

The electrochemistry of a similar diruthenium(II,III) compound, $Ru_2(DtolF)_4Cl$ (where DtolF = di-*p*-tolyformamidinate), has recently been reported.[33] No mechanism was given for the reduction or oxidation of this compound, but the similarity in its redox potentials to Rxns 1′ and 2 of compound **1** suggests that $Ru_2(DtolF)_4Cl$ is also converted to its ClO_4^- form in solutions of CH_2Cl_2 containing TBAP.

Compound **2**, which also contains a Ru_2^{5+} center, undergoes a reversible one-electron oxidation at $E_{1/2}$ = 0.33 V in CH_2Cl_2, 0.1 M TBAP (Rxn 2) and a reversible one-electron reduction at −0.89 V (Rxn 1) under the same solution conditions. Compound **3**, which contains a Ru_2^{6+} center, undergoes an oxidation at $E_{1/2}$ = 0.73 V (Rxn 3) and two reversible one-electron reductions at $E_{1/2}$ = −0.61 and −1.54 V (Rxns 2 and 1). The singly and doubly reduced forms of **3** are stable, but this is not the case for the electrooxidized Ru_2^{7+} which slowly decomposes to yield a species which is reduced at E_{pc} = 0.48 and 0.32 V for a scan rate of 0.1 V/s. The decomposition of the Ru_2^{7+} product can be slowed down at −70 °C, a condition under which the oxidation becomes reversible and the two rereduction peaks are no longer seen.

Compound **4**, which contains a Ru_2^{6+} core, displays a reversible one-electron reduction at −0.25 V (Rxn 2) and an irreversible reduction at E_{pc} = −1.34 V (Rxn 1). The latter reaction is coupled to an irreversible oxidation at E_{pa} = −0.65 V and can be assigned to an oxidation of $[Ru_2(dpf)_4(CN)]^-$ which is generated after the loss of one axial ligand from $[Ru_2(dpf)_4(CN)_2]^{2-}$. No oxidation processes for this compound are observed within the solvent potential window of about +1.7 V vs SCE.

A comparison of the cyclic voltammograms in Figure 5 and the $E_{1/2}$ values in Table 7 illustrates the sensitivity of the metal-centered molecular orbitals to the donor−acceptor properties and number of axial ligands. The 0.85 V difference in $E_{1/2}$ for Rxn 2 of compounds **2** and **3** mainly arises from the bonding of the second phenylacetylide ligand, since the difference in

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[33] Cotton, F. A.; Ren, T. *Inorg. Chem.* **1995**, *34*, 3190.

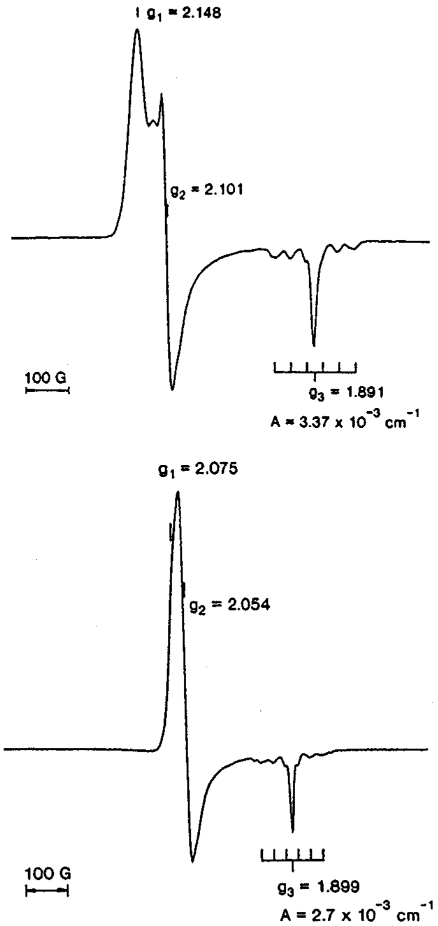

Figure 6. ESR spectra of (a) $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ in CH_2Cl_2, 0.1 M TBAP and (b) $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ in THF containing excess $CNCH_2C_6H_5$.

basicity between the axial ligands of $C{\equiv}CC_6H_5$ and Cl^- gives a value of $\Delta E_{1/2} = 0.21$ V for $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ and $Ru_2(dpf)_4Cl$. The electrochemical data clearly shows that $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ is thermodynamically more stable than $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$. This is due to the bonding of the second phenylacetylide ligand.

ESR of Electrochemically Generated $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ and $[Ru_2(dpf)_4(CN)_2]^-$. Compounds **1** and **2** have magnetic moments of 3.89 and 3.87 μ_B in the solid state at 297 K, indicating that the two compounds are paramagnetic and possess three unpaired electrons. No ESR signals for these compounds could be observed at temperatures as low as 77 K.

Compounds **3** and **4** are also ESR silent at room and low temperatures, consistent with their diamagnetism. However, the singly reduced forms of the complexes, $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ and $[Ru_2(dpf)_4(CN)_2]^-$, display rhombic signals in CH_2Cl_2, as shown in Figure 6a for the case $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$. Three **g** tensors are located at 2.148, 2.101, and 1.891 for $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ and 2.120, 2.090, and 1.908 for $[Ru_2(dpf)_4(CN)_2]^-$. The shapes of the signals are consistent with a species having a single unpaired electron rather than with one having three unpaired electrons, a condition under which either no ESR spectrum or a broad and ill-resolved ESR spectrum should be obtained.[4,34]

It should be pointed out that all but one previously reported Ru_2^{5+} complex of this structural type[2,4–7] have three unpaired electrons. The only exception is $Ru_2[(p\text{-tolyl})NNN(p\text{-tolyl})]_4(CH_3CN)\cdot BF_4$ which has one unpaired electron with an electronic configuration of $\sigma^2\pi^4\delta^2\pi^{*3}$ but is ESR silent down to 77 K.[35] This lack of an ESR signal has been attributed to extremely fast relaxation when the unpaired electron is in an orbital doublet, which means that the ground state is an orbitally degenerate ^2E_g state. This is not the case for $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$, whose ground-state electronic configuration is tentatively assigned as $\pi^4\delta^2\pi^{*4}\delta^{*1}$. In this configuration, only one electron rather than three occupies the δ^* orbital and gives a $S = {}^1/_2$ system.

The novel appearance of a $\mathbf{g}_3$ tensor in Figure 6a results from different nuclear spin constants of the ruthenium isotopes which are present in the radical anion complex. The fraction of the signal which displays hyperfine splitting (sextet, $A = 3.37 \times 10^{-3}$ cm^{-1} for $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ and $A = 2.97 \times 10^{-3}$ cm^{-1} for $[Ru_2(dpf)_4(CN)_2]^-$) is due to the isotopes ^{99}Ru ($I = {}^5/_2$, 12.7%) and ^{101}Ru ($I = {}^5/_2$, 17.1%). All other isotopes of ruthenium (72.2%) have a nuclear spin constant of zero, and therefore, only a single intense signal is observed. To our knowledge, no ESR spectrum reflecting a Ru isotope effect has ever been reported in the literature for a diruthenium complex.

All attempts to isolate a sufficiently stable diruthenium(III,IV) species, such as $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^+$, by bulk controlled-potential electrolysis either at low temperatures or in various solvents have to date been unsuccessful. Several decomposition products with a complicated cyclic voltammogram have always been obtained. The product of the second reduction of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$ also undergoes a chemical reaction in CH_2Cl_2 on the bulk electrolysis time scale. Compound **4**, on the other hand, does not form a diruthenium(III,IV) species within the solvent potential window.

As discussed above, compound **2**, which contains a Ru_2^{5+} core, has a magnetic moment of 3.87 μ_B in the solid state at 297 K, and no ESR signals could be observed for this compound at temperatures as low as 77 K. This, however, is not the case when excess $CNCH_2C_6H_5$ is added to a THF solution of compound **2**, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$, which results in formation of the bis-adduct, $Ru_2(dpf)_4(C{\equiv}CC_6H_5)(CNCH_2C_6H_5)$. The latter complex has an ESR spectrum resembling that of $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ and $[Ru_2(dpf)_4(CN)_2]^-$ as shown in Figure 6b. This implies that two of the three unpaired electrons in $Ru_2(dpf)_4(C{\equiv}CC_6H_5)$ pair to give the same electronic configuration as in $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ and $[Ru_2(dpf)_4(CN)_2]^-$. This also suggests that ESR spectra will be obtained for diruthenium(II,III) complexes containing two axial ligands possessing both σ donor and π acceptor properties.

Acknowledgment. The support of the Robert A. Welch Foundation (J.L.B., Grant E-918; K.M.K., Grant E-680) is gratefully acknowledged. We also acknowledge assistance with crystallography from Dr. J. D. Korp.

Supporting Information Available: Tables of data collection parameters, atomic coordinates and *U* values, anisotropic displacement parameters, H atom coordinates and isotropic displacement parameters, and all molecular bond lengths and angles, and figures showing various views (including space-filling views) of the molecule and molecular packing diagrams (60 pages). Ordering information is given on any current masthead page.

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(34) Smith, K. M. *Porphyrins and Metalloporphyrins;* Elsevier Scientific Publishing Co: New York, 1975; pp 582.

(35) Cotton, F. A.; Falvello, L. R.; Ren, T.; Vidyasagar, K. *Inorg. Chim. Acta* **1992**, *194*, 163.