Reaction between the (3,1) Isomer of $Ru_2(F_5ap)_4Cl$ and CN^-. Synthesis, Structural Determination, and Electrochemistry of $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ and Two Geometric Isomers of $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$

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Introduction

A number of diruthenium and dirhodium complexes bridged by four identical equatorial ligands have been synthesized and characterized over the last 20 years.[1−20] These compounds can be represented by a single structural formula in the case of symmetrical bridging ligands or by four different geometric isomers for complexes with unsymmetrical bridging ligands, as was recently demonstrated for $Ru_2(F_5ap)_4Cl$ and $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$, where F_5ap is the 2-(2,3,4,5,6-pentafluoroanilino)pyridinate anion.[20]

As part of our studies into the chemical reactivity of diruthenium and dirhodium complexes, we have often examined how the nature of the metal−axial ligand interaction and electrochemistry of diruthenium and dirhodium derivatives are affected by donor−acceptor properties and bonding symmetry (isomeric forms)[20] of the bridging ligands.[7−10,12−19] In several instances, we have observed that the two dimetal units could be linked by the same axial ligand to form a dimer of dimers.[21] In this regard, we attempted to bridge the (4,0) and (3,1) isomers of $Ru_2(F_5ap)_4Cl$[20] with cyanamide (NCN^{2-}) to form a dimer of dimers as was successfully done in the case of several related dirhodium derivatives.[21] Surprisingly, the reaction between the (3,1) isomer of $Ru_2(F_5ap)_4Cl$ and disodium cyanamide (Na_2NCN) did not yield a dimer of ruthenium dimers but rather gave a mixture of diruthenium derivatives with properties substantially different from those expected for simple axial ligation. It was believed that one of the new diruthenium derivatives was generated by a reaction between the (3,1) isomer of $Ru_2(F_5ap)_4Cl$ and CN^- ions resulting from the thermal decomposition of Na_2NCN. To confirm the assumption, the (3,1) isomer of $Ru_2(F_5ap)_4Cl$ and NaCN were reacted together. The reaction yielded the same diruthenium derivative as in the case of Na_2NCN addition, but two additional diruthenium complexes were also isolated. All three compounds possess a edge-sharing bioctahedral structure, and this paper reports their synthesis, structural characterization, and electrochemistry.

Experimental Section

Chemicals and Reagents. Dichloromethane (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. Analytical grade *n*-hexane (Mallinckrodt Chemical Co.) was used without further purification. Tetra-*n*-butylammonium perchlorate (TBAP, Fluka Chemical Co.) was twice recrystallized from absolute ethanol and dried in the oven at 40 °C. Sodium cyanide (NaCN) was purchased from Aldrich Chemical Co. and used as received. Nitrogen gas purchased from Trigas was of ultrahigh purity.

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. Cyclic voltammograms were obtained with an IBM model EC 225 voltammetric analyzer. The working electrode was a platinum button with a surface area of 0.19 mm^2. The reference electrode was a homemade saturated calomel electrode (SCE), and a platinum wire was used as the counter electrode. Electron spin resonance (ESR) spectra were recorded at 77 K on a modified Varian E-4 ESR spectrometer which was interfaced to a Tracor Northern TN-1710 signal averager. The g values were measured with respect to 1,1-diphenyl-2-picrylhydrazyl (DPPH) which has a g value of 2.0036 ± 0.0003. Elemental analysis was carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$ (Two Isomers) and $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$. Three different diruthenium compounds were obtained by reaction of the (3,1) isomer of $Ru_2(F_5ap)_4Cl$[20] with excess sodium cyanide. A mixture of 200 mg (0.15 mmol) of the (3,1) isomer of $Ru_2(F_5ap)_4Cl$ and 20 mg (0.40 mmol) of NaCN in 100 mL of fresh distilled THF was refluxed at 70 °C overnight. The reaction was carried out in air for the entire period and was monitored by thin-layer chromatography as the brown-green color of the reaction mixture gradually changed to green blue. The solution was evaporated under vacuum and the reaction mixture extracted by CH_2Cl_2 and H_2O. It was then separated on a silica gel column using CH_2Cl_2/hexane (1:8 v/v) as eluent. Three bands (green, purple, and blue) were collected and corresponded to $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ (**2**) and $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$ (isomers **1a**,**b**), respectively. The crude products were twice purified on a silica gel column using the same mixture of solvents as eluent. The compounds were obtained by removal of the solvents under vacuum using a rotary evaporator, but this procedure was done at room

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Table 1. Data Collection and Processing Parameters for the Investigated Compounds

	$Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$, **2**	$Ru_2(F_5ap)_4(\mu\text{-}CN)_2$, **1a**	$Ru_2(F_5ap)_4(\mu\text{-}CN)_2$, **1b**
space group	$P2_1/n$, monoclinic	$P2_1/n$, monoclinic	$P2_12_12_1$, orthorhombic
cell consts			
a, Å	11.853(5)	14.895(4)	13.603(4)
b, Å	27.644(9)	15.646(6)	17.882(7)
c, Å	15.144(6)	22.993(10)	21.316(9)
β, deg	107.77(3)	108.19(2)	
V, Å^3	4725	5091	5185
formula	$C_{46}H_{16}N_{10}F_{19}Ru_2{\cdot}C_6H_{14}$	$C_{46}H_{16}N_{10}F_{20}Ru_2{\cdot}2CH_2Cl_2$	$C_{46}H_{16}N_{10}F_{20}Ru_2{\cdot}2CH_2Cl_2$
fw	1358.06	1460.72	1460.72
Z	4	4	4
ρ_{calcd}, g/cm^3	1.91	1.91	1.87
μ, cm^{-1}	7.50	9.12	8.95
λ (Mo Kα), Å	0.710 73	0.710 73	0.710 73
temp, °C	−50	−50	−50
R^a	0.046	0.039	0.049
$R_w{}^b$	0.043	0.038	0.042

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

temperature for the blue compound in order to avoid its conversion to the green compound during warming of the solution. The yields of the three compounds were 30% (**2**), 15% (**1a**), and 10% (**1b**). Large clusters of fused crystals were obtained by a slow diffusion of hexane into benzene for the green and purple compounds. In the case of the blue compound, the solid obtained after removal of the solvents was rapidly dissolved in toluene/hexane (3:2 v/v) and the solution filtered with a small piece of cotton. The clear solution was degassed with nitrogen and stored in a refrigerator at ca. 3 °C. Crystal formation was observed after 10 days, but suitable crystals for X-ray analysis were collected only after 30 days.

Crystalline and powder forms of the sample were both used in the electrochemical and spectroscopic studies. Infrared spectra: $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ (**2**) (CsI pellet) 1995, 1713, 1599, 1505, 1453, 1427, 1327, 1304, 1262, 1154, 1018, 993, 874, 806, 762, 737 cm^{-1}; $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$ (isomer **1a**) (purple, CsI pellet) 2037, 1611, 1510, 1470, 1346, 1310, 1254, 1157, 1117, 1057, 1015, 991, 880, 862, 791, 770, 731 cm^{-1}; $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$ (isomer **1b**) (blue, CsI pellet) 2054, 1715, 1595, 1514, 1451, 1427, 1308, 1252, 1159, 1026, 1018, 995, 876, 791, 762, 608 cm^{-1}. Mass spectral data [m/e (fragment)]: 1273, $[Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)]^+$; 1292, $[Ru_2(F_5ap)_4(\mu\text{-}CN)_2]^+$. UV−vis: **2**, 1150, 820, and 680 nm; **1a**, 1020, 720, and 560 nm; **1b**, 1200 and 710 nm. Anal. Calcd for $C_{46}H_{16}N_{10}F_{19}Ru_2{\cdot}CH_2Cl_2$ (compound **2**): C, 41.56; H, 1.33; N, 10.32; F, 26.60. Found: C, 41.14; H, 1.24; N, 10.17; F, 25.34.

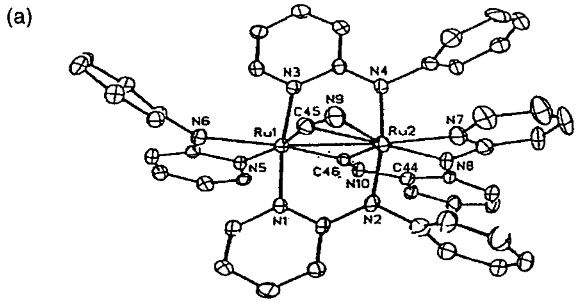
X-ray Crystallography. Single-crystal X-ray studies were performed at the University of Houston X-ray Crystallographic Center. Samples of each compound were mounted in a random orientation on a Nicolet R3m/V automatic diffractometer, and since the crystals were known to decompose outside the mother liquor, the samples were placed in a stream of dry nitrogen gas at −50 °C. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. The determination of the crystal systems, data collection procedures, and refinements were all carried out as described in the literature.[14a,18] Final cell constants, as well as other pertinent information to data collection and refinement of all three compounds, are listed in Table 1.

$Ru_2(F_5ap)_4(\mu\text{-}CN)_2$ (Isomer 1a) and $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ (2). X-ray crystal data were obtained with a very dark lilac multifaceted plate having approximate dimension 0.15 × 0.40 × 0.60 mm^3 for isomer **1a** and a dark green diamond shape plate having approximate dimension 0.55 × 0.45 × 0.15 mm^3 for compound **2**. The Laue symmetry was determined to be $2/m$, and from the systematic absences, the space group was shown unambiguously to be $P2_1/n$ for both compounds. The structures were solved by the SHELXTL direct methods program, which revealed the positions of most of the non-hydrogen atoms in the molecule. The remaining atoms in the structure were found in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor. A heavily disordered area of electron density corresponding to interstitial solvent was also found for **2**, but the exact identity of the solvent molecule could not be determined. Attempts to modelize the site with various rigid body groups failed to produce meaningful results. Eventually six unconstrained individual carbon atoms were refined, each with 50−100% occupancy. This is presumed to be heavily disordered hexane, but methylene chloride cannot be ruled out. For $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$, isomer **1a**, two molecules of methylene chloride from the crystallization solvent were located. After all shift/esd ratios were less than 0.1 (except for the disordered atoms), convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.9 e/Å^3 for **2** and 0.7 e/Å^3 for $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$.

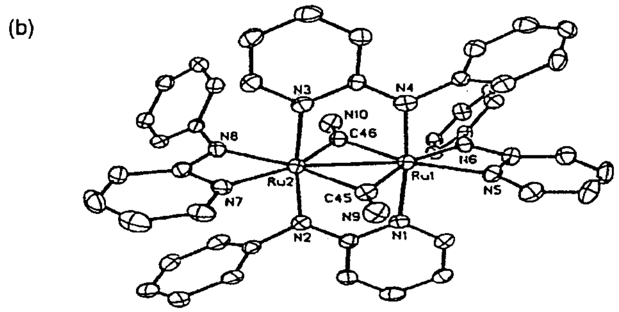
$Ru_2(F_5ap)_4(\mu\text{-}CN)_2$ (Isomer 1b). X-ray crystal data were measured on a very dark blue flat column having approximate dimension 0.12 × 0.18 × 0.50 mm^3. The Laue symmetry was determined to be mmm, and from the systematic absences, the space group was shown unambiguously to be $P2_12_12_1$. The structure was solved as described above and revealed the positions of most of the non-hydrogen atoms in the molecule. Two molecules of methylene chloride from the crystallization solvent were located and refined independently. The absolute configuration was determined by refinement of a parameter which multiplies Δf. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 1.5 e/Å^3.

Results and Discussion

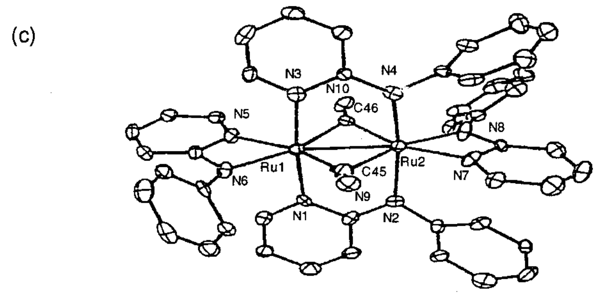
Three edge-sharing diruthenium complexes, **2**, **1a**, and **1b**, were isolated from the reaction between the (3,1) isomer of $Ru_2(F_5ap)_4Cl$ and excess NaCN. The exact mechanism by which the compounds are generated from the (3,1) isomer of $Ru_2(F_5ap)_4Cl$ is unknown at this time, but it is believed that both *mono*- and *bis*-CN adducts are generated in the early stage of the reaction. We are now trying to isolate and characterize these two adducts in order to obtain further evidence about the mechanism. Isomer **1b** is unstable both in solution and in the solid state and is converted over a period of hours at room temperature to $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$, **2**. The process involves the substitution of an ortho fluorine of the chelating F_5ap ligand bound to Ru(2) by one of the bridging cyanides to form a bridging isocyanide and the conversion of the remaining cyanide bridging ligand from a two electron (σ) donor to a four-electron ($\sigma-\pi$) donor. In addition to the rearrangement of the bridging cyanide ions, the oxidation state of the diruthenium unit changes from $Ru^{III}{}_2$ to either $Ru^{II}Ru^{III}$ or $Ru^{III}Ru^{IV}$,



Compound 2



Isomer 1a



Isomer 1b

Figure 1. Molecular structures of (a) $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$, **2**, and $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$, (b) isomer **1a** and (c) isomer **1b**. For purpose of clarity, the F atoms of the F_5ap groups have been omitted in the crystal structure of each compound.

depending on the electron distribution on the isocyanide moiety. It should be noted that the conversion from **1b** to **2** can be slowed at low temperature and this fact was used to obtain a crystal structure of compound **1b**. In contrast to the behavior of isomer **1b**, isomer **1a** is quite stable and does not undergo conversion to **2**.

Molecular Structure. Crystal structures of the three compounds are shown in Figure 1. The core atoms are labeled, but the hydrogen and fluorine atoms have been omitted for clarity. Selected bond distances and angles are listed in Tables 2 and 3. Each compound consists of a diruthenium unit with each metal ion in a distorted octahedral ligand environment. The two octahedra are fused on a common equatorial edge (edge-sharing), which is defined by the two carbon atoms C(45) and C(46). Two F_5ap ligands are chelated to the remaining equatorial positions of the bioctahedra, and the other two F_5ap ligands form two three-atom bridges across the axial binding sites. For the chelating F_5ap ligands, there is a cis arrangement of like donors (pyridyl nitrogens (N_p) and anilino nitrogens (N_a)) for isomer **1a** and a trans arrangement in isomer **1b**. Each ruthenium atom in isomer **1a** is bound axially to an anilino and pyridyl nitrogen while, in isomer **1b**, one ruthenium atom is bound axially to two anilino nitrogens and the second ruthenium atom is bound axially to two pyridyl nitrogens.

The bonds in the Ru−C bridge are symmetrical with respect to the Ru−Ru bond in isomer **1a** (Figure 1b), i.e., [(Ru(1)−C(45)] − [Ru(2)−C(45)] = 0.007 Å and [Ru(1)−C(46)] − [Ru(2)−C(46)] = 0.006 Å. Both Ru−C(45) bonds are trans to a Ru−N_p bond whereas both Ru−C(46) bond are trans to a Ru−N_a bond. This observation may explain the small but statistically significant difference between the two Ru−C bond lengths with the bridging CN groups; i.e., the average distance for the two Ru−C(45) bonds is 2.199 Å while that for the two Ru−C(46) bonds is 2.168 Å.

The electron distribution on the two metal centers in isomer **1b** (Figure 1) should be more polarized than in **1a** since Ru(1) is bound to three pyridyl and one anilino nitrogen and the Ru(2) atom to only one pyridyl and three anilino nitrogens. This polarization is reflected in the two Ru−C(45) bonds where [Ru(1)−C(45)] − [Ru(2)−C(45)] = 0.122 Å but not in the two Ru−C(46) bonds where [Ru(1)−C(46)] − [Ru(2)−C(46)] = 0.016 Å. It is not clear whether there is a relationship between the dissymmetry in the Ru−C(45) bonds and the instability of **1b** with respect to conversion to compound **2**.

The Ru−Ru distance of 2.580 Å in isomer **1a** is virtually identical to that in isomer **1b** (see Table 2). These two values can also be compared to a Ru−Ru distance of 2.573 Å reported for $Ru_2(ap)_6(PMe_2Ph)_2$, a complex which contains a single Ru−Ru bond.[22] Shaik et al.[23] have presented a broad overview of the edge-sharing bioctahedral molecules from a theoretical point of view. Each Ru(III) in this structural type should have an electronic configuration expressed as $t_{2g}{}^5$ if one assumes that the complexes have octahedral symmetry. These t_{2g}(or dπ) orbitals of the two metal atoms can overlap to form σ-, π-, and δ-bonding orbitals along with σ^*-, π^*-, and δ^*-antibonding orbitals. This bonding model differs from that of the tetracarboxylate type diruthenium complexes[23] which have two π and two π^* metal-centered orbitals. The maximum value for the Ru−Ru bond order in d^5-d^5 edge-sharing compounds is 1.0 on the basis of an electronic configuration of $\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*2}$. The fact that a similar Ru−Ru bond distance is seen for $Ru_2(ap)_6(PMe_2Ph)_2$ and for the two $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$ isomers examined in this study suggests that there is a single bond between the two Ru atoms in each geometric isomer of $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$. This conclusion is further supported by the ESR and NMR spectra of the two compounds. Both $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$ isomers are ESR silent but show well-resolved ^1H NMR spectra characteristic of diamagnetic Ru(III,III) species.[20]

The most striking structural feature of $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$, **2**, is the unusual asymmetric nature of the bridging cyanide ligand (see Figure 1). The C(45)−N(9) cyanide ligand bridges the two ruthenium atoms in a σ, π-mode, giving a total of four electrons which are σ-bonded to Ru(1) and weakly η^2 π-bonded to Ru(2). The distance from the Ru(2) atom to the middle of the C(45)−N(9) bond is 2.211 Å. Similar examples of an asymmetrically bridging CN group have been reported[24] for $[Rh_2(\mu\text{-}CN)(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ and $[Mn_2H(CN)(CO)_4(dppm)_2]$. Curtis et al. have also discussed criteria which allow distinction between the 2 electron (σ) and 4 electron (σ−π) donor behavior of bridging CO and CN groups.[25] The σ−π mode is characterized by an essentially invariant M−C−N bond

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Table 2. Selected Bond Lengths (Å)[a]

$Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$, **2**		$Ru_2(F_5ap)_4(\mu\text{-}CN)_2$, **1a**		$Ru_2(F_5ap)_4(\mu\text{-}CN)_2$, **1b**	
Ru(1)−Ru(2)	2.647(1)	Ru(1)−Ru(2)	2.580(1)	Ru(1)−Ru(2)	2.581(1)
Ru(1)−N(1)	2.118(6)	Ru(1)−N(1)	2.072(4)	Ru(1)−N(1)	2.074(8)
Ru(1)−N(3)	2.119(6)	Ru(1)−N(4)	2.011(4)	Ru(1)−N(3)	2.062(8)
Ru(1)−N(5)	2.108(6)	Ru(1)−N(5)	2.050(5)	Ru(1)−N(5)	2.053(8)
Ru(1)−N(6)	2.127(6)	Ru(1)−N(6)	2.057(4)	Ru(1)−N(6)	2.057(9)
Ru(1)−C(45)	1.980(10)	Ru(1)−C(45)	2.195(5)	Ru(1)−C(45)	2.129(12)
Ru(1)−C(46)	1.933(8)	Ru(1)−C(46)	2.171(7)	Ru(1)−C(46)	2.165(10)
N(9)−C(45)	1.173(13)	N(9)−C(45)	1.138(8)	N(9)−C(45)	1.138(8)
Ru(2)−N(2)	2.029(7)	Ru(2)−N(2)	2.016(4)	Ru(2)−N(2)	2.035(8)
Ru(2)−N(4)	2.042(7)	Ru(2)−N(3)	2.081(4)	Ru(2)−N(4)	2.027(8)
Ru(2)−N(7)	2.062(7)	Ru(2)−N(7)	2.062(4)	Ru(2)−N(7)	2.057(8)
Ru(2)−N(8)	2.052(7)	Ru(2)−N(8)	2.054(5)	Ru(2)−N(8)	2.035(9)
Ru(2)−N(9)	2.371(8)	Ru(2)−C(45)	2.202(7)	Ru(2)−C(45)	2.251(10)
Ru(2)−C(45)	2.202(8)	Ru(2)−C(46)	2.165(5)	Ru(2)−C(46)	2.187(11)
Ru(2)−C(46)	2.043(8)	N(10)−C(46)	1.143(8)	N(10)−C(46)	1.140(14)
N(10)−C(46)	1.227(11)				

[a] Individual (not average) values.

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

$Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$, **2**		$Ru_2(F_5ap)_4(\mu\text{-}CN)_2$, **1a**		$Ru_2(F_5ap)_4(\mu\text{-}CN)_2$, **1b**	
Ru(1)−Ru(2)−N(2)	86.2(2)	Ru(1)−Ru(2)−N(2)	85.7(1)	Ru(1)−Ru(2)−N(2)	86.2(2)
Ru(1)−Ru(2)−N(4)	86.0(2)	Ru(1)−Ru(2)−N(3)	87.2(1)	Ru(2)−Ru(1)−N(3)	87.2(2)
Ru(1)−Ru(2)−N(7)	166.3(2)	Ru(1)−Ru(2)−N(7)	150.7(1)	Ru(1)−Ru(2)−N(7)	147.2(2)
Ru(1)−Ru(2)−N(8)	129.3(2)	Ru(1)−Ru(2)−N(8)	146.0(1)	Ru(1)−Ru(2)−N(8)	149.2(3)
C(45)−Ru(1)−C(46)	104.6(3)	Ru(1)−C(45)−Ru(2)	71.9(2)	Ru(1)−C(45)−Ru(2)	72.2(3)
Ru(1)−C(45)−N(9)	161.6(7)	Ru(1)−Ru(2)−C(45)	53.9(1)	Ru(1)−Ru(2)−C(45)	51.7(3)
Ru(1)−C(46)−N(10)	142.6(6)	Ru(1)−Ru(2)−C(46)	53.6(2)	Ru(1)−Ru(2)−C(46)	53.2(3)
N(1)−Ru(1)−N(3)	172.4(2)	Ru(1)−C(45)−N(9)	144.5(5)	Ru(1)−C(45)−N(9)	150.3(9)
N(1)−Ru(1)−N(5)	91.6(2)	Ru(1)−C(46)−N(10)	143.1(5)	N(1)−Ru(1)−N(3)	173.8(3)
N(1)−Ru(1)−N(6)	94.9(2)	N(1)−Ru(1)−N(4)	172.2(2)	N(1)−Ru(1)−N(5)	92.6(3)
N(5)−Ru(1)−N(6)	61.7(2)	N(1)−Ru(1)−N(5)	91.5(2)	N(1)−Ru(1)−N(6)	90.8(3)
Ru(1)−Ru(2)−C(45)	47.1(3)	N(1)−Ru(1)−N(6)	92.2(2)	N(3)−Ru(1)−N(5)	90.8(3)
Ru(1)−Ru(2)−C(46)	46.5(2)	N(4)−Ru(1)−N(6)	95.6(2)	C(45)−Ru(1)−C(46)	109.8(4)
Ru(1)−C(45)−Ru(2)	78.3(3)	C(45)−Ru(1)−C(46)	107.6(2)	Ru(2)−Ru(1)−N(1)	87.2(2)
N(8)−Ru(2)−C(46)	82.8(3)	Ru(2)−Ru(1)−N(1)	87.5(1)	Ru(1)−Ru(2)−N(4)	86.5(2)
Ru(2)−Ru(1)−N(1)	85.9(2)	Ru(2)−Ru(1)−N(4)	85.9(1)	Ru(2)−Ru(1)−N(5)	147.9(2)
Ru(2)−Ru(1)−N(3)	86.5(2)	Ru(2)−Ru(1)−N(5)	151.0(1)	Ru(2)−Ru(1)−N(6)	149.7(2)
Ru(2)−Ru(1)−N(5)	140.4(2)	Ru(2)−Ru(1)−N(6)	145.4(1)	Ru(1)−C(46)−Ru(2)	72.8(3)
Ru(2)−Ru(1)−N(6)	157.9(2)	Ru(1)−C(46)−Ru(2)	73.0(2)	Ru(2)−Ru(1)−C(45)	56.1(3)
C(45)−Ru(2)−C(46)	93.6(3)	Ru(2)−Ru(1)−C(45)	54.2(2)	Ru(2)−Ru(1)−C(46)	54.0(3)
Ru(2)−C(45)−N(9)	83.3(6)	Ru(2)−Ru(1)−C(46)	53.4(1)	Ru(2)−C(45)−N(9)	135.7(9)
Ru(2)−C(46)−N(10)	133.8(6)	Ru(2)−C(45)−N(9)	143.6(5)	Ru(2)−C(46)−N(10)	145.6(9)
N(2)−Ru(2)−N(4)	172.1(3)	Ru(2)−C(46)−N(10)	143.9(5)	N(2)−Ru(2)−N(4)	169.1(3)
N(2)−Ru(2)−N(7)	95.5(3)	N(2)−Ru(2)−N(3)	172.0(2)	N(2)−Ru(2)−N(7)	90.1(3)
N(4)−Ru(2)−N(7)	92.1(3)	N(2)−Ru(2)−N(7)	91.6(2)	N(2)−Ru(2)−N(8)	94.4(4)
N(7)−Ru(2)−N(8)	64.3(3)	N(2)−Ru(2)−N(8)	96.0(2)	N(7)−Ru(2)−N(8)	63.5(3)
Ru(2)−Ru(1)−C(45)	54.6(2)	N(7)−Ru(2)−N(8)	63.3(2)	C(45)−Ru(2)−C(46)	104.7(4)
Ru(2)−Ru(1)−C(46)	50.1(2)	C(45)−Ru(2)−C(46)	107.5(2)	Ru(1)−Ru(2)−C(45)	51.7(3)
Ru(1)−C(46)−Ru(2)	83.4(3)	Ru(1)−Ru(2)−C(45)	53.9(1)		
C(44)−N(10)−C(46)	126.3(7)				

[a] Individual (not average) values.

angle with the asymmetry parameter α, which is defined as $\alpha = (d_2 - d_1)/d_1$ (d_2 and d_1 are the long and short M−C distances, respectively). The Ru(1)−C(45)−N(9) angle of 161.6(7)° (see Table 3) as well as the low asymmetry parameter α (α = 0.112), suggests that the cyanide group of $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ bridges the two ruthenium atoms in a $\sigma-\pi$ fashion.

Another interesting feature in the structure of $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ relates to the bond angles and bond distances associated with the two ruthenium ions and the C(46)−N(10) isocyanide ligand that is formed during the conversion of **1b** to **2**. The C(46)−N(10) bond length for the isocyanide group in **2** is 1.227 Å, which is more consistent with the bond length of a CN double bond rather than with the length of a triple bond. For example, the length of the triple bond of the C(46)−N(10) cyanide ligand in **1b** is 1.140 Å. The bridging isocyanide carbon is also asymmetric with respect to the two Ru−C bond distances, i.e., Ru(1)−C(46) = 1.933 Å and Ru(2)−C(46) = 2.043 Å. In addition, the C(46)−N(10)−C(44) bond angle of 126.3° is at the lower end of the range of values reported for bridging isocyanide groups.[26]

Electrochemistry. Cyclic voltammograms of the three investigated diruthenium compounds in CH_2Cl_2 containing 0.1 M TBAP are illustrated in Figure 2, and a summary of the redox potentials is given in Table 4. Both reductions and oxidation of isomers **1a**,**b** involve the Ru_2 core. The reductions (processes 2 and 3 in Figure 2) are assigned to the Ru_2^{6+}/Ru_2^{5+} and Ru_2^{5+}/Ru_2^{4+} couples, respectively, while the oxidation (process 1 in Figure 2) corresponds to a conversion of the Ru_2^{6+} to the Ru_2^{7+}

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(26) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193−233.

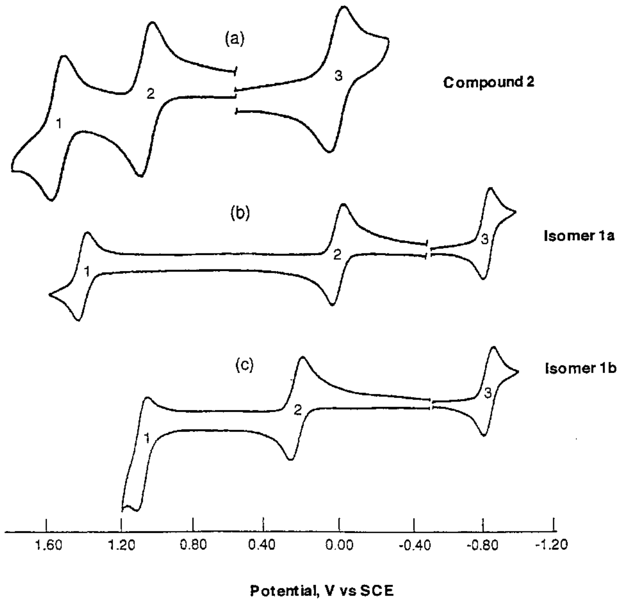

Figure 2. Cyclic voltammograms of the three compounds in CH_2Cl_2 containing 0.1 M TBAP. Data were obtained at a scan rate of 0.1 V/s using a platinum button electrode.

Table 4. Half-Wave Potentials (V vs SCE) for the Three Diruthenium Complexes in CH_2Cl_2 Containing 0.1 M TBAP

compd	oxidation		reduction	
2	1.45	0.95	−0.01	
1a		1.30	0.08	−0.81
1b		1.10	0.22	−0.82

core, consistent with what has been reported for other edge-sharing bioctahedral diruthenium(III) complexes.[27]

Oxidation State of the Ru_2 Core. The oxidation state of the Ru_2 core in the two $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$ derivatives, **1a**,**b**, is Ru_2^{6+} as indicated by well-resolved ^1H and ^{19}F NMR spectra of the compounds. The oxidation state of the Ru_2 core in $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ could be either Ru_2^{5+} or Ru_2^{7+} depending upon the formal charge on the isocyanide carbon (0 or −2). The 126.3° for the C(44)−N(10)−C(46) bond angle and the 1.227 Å for the C(46)−N(10) bond distance are both consistent with a carbon−nitrogen double bond. These data also support both an sp^2 hybridization for the carbon atom and a lone pair on the isocyanide nitrogen. For a neutral isocyanide bridging ligand, the CN group should behave as a two-electron donor ligand and the Ru_2 core can be described as Ru_2^{5+}. The well-resolved ESR spectrum of $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ at 77 K is illustrated in Figure 3. It shows a rhombic signal with three g values ($g_1 = 2.116$, $g_2 = 2.040$, and $g_3 = 1.953$) and resembles ESR spectra[8,18] of $[Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2]^-$ and $[Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2]^-$, two compounds which have been unambiguously assigned as diruthenium(II,III) complexes. The hyperfine splitting arising from the Ru isotopes of ^{99}Ru ($I = {}^5/_2$, 12.7%) and ^{101}Ru ($I = {}^5/_2$, 17.1%) has been documented in the literature.[20] The ESR spectrum of $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ is thus characteristic of compounds having a single unpaired electron,[28] and this suggests an electronic configuration of $\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*2}\sigma^{*1}$ for the Ru_2 core of the compound.

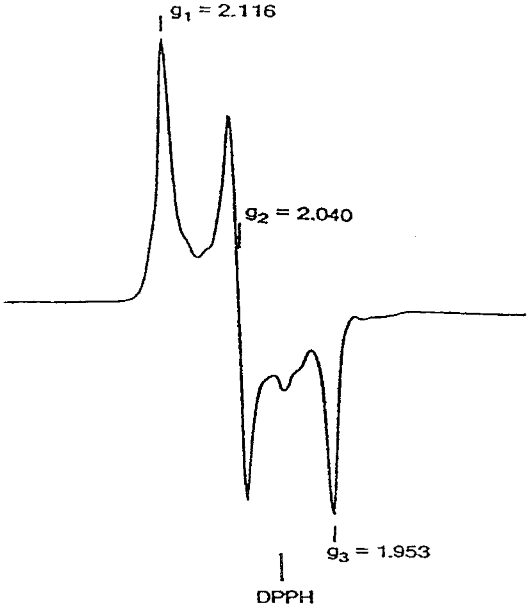

Figure 3. ESR spectrum of $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$, **2**, in CH_2Cl_2 at 77 K.

As indicated in Table 4, $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$, **2**, undergoes two reversible one-electron oxidations and a reversible one-electron reduction. The data (Figure 2a) do not support a Ru_2^{7+} oxidation state assignment for $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ since the assignment of Ru_2^{7+} for the diruthenium core of this compound would imply either the electrochemical generation of Ru_2^{8+} and Ru_2^{9+} cores or oxidation of the ligands, both of which are highly unlikely.

On the other hand, assignment of the metal core as Ru_2^{5+} would easily account for the results illustrated in Figure 2a. Indeed, the three electrode processes of $Ru_2(F_5ap)_3[\mu\text{-}(o\text{-}NC)F_4ap](\mu\text{-}CN)$ and $Ru_2(F_5ap)_4(\mu\text{-}CN)_2$ would then correspond to the reactions shown in Scheme 1, where steps 1−3 represents the three observed redox processes.

Scheme 1

$$Ru_2^{7+} \underset{(1)}{\xrightleftharpoons{+\,e^-}} Ru_2^{6+} \underset{(2)}{\xrightleftharpoons{+\,e^-}} Ru_2^{5+} \underset{(3)}{\xrightleftharpoons{+\,e^-}} Ru_2^{4+}$$

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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 molecules and molecular packing diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Cotton, F. A.; Torralba, R. C. *Inorg. Chem.* **1991**, *30*, 2196.