Isomer Effect on the Structure and Chemical Reactivity of Diruthenium Complexes. Synthesis and Characterization of the (4,0), (3,1), and (2,2) Trans Isomers of $Ru_2(F_5ap)_4Cl$ 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

John L. Bear,* Yulan Li, Baocheng Han,† Eric Van Caemelbecke, and Karl M. Kadish*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Received March 8, 1996⊗

The syntheses and characterization of the (4,0), (3,1), and (2,2) trans isomers of $Ru_2(F_5ap)_4Cl$ and $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ are reported where F_5ap is the 2-(2,3,4,5,6-pentafluoroanilino)pyridinate anion. The (4,0), (3,1), and (2,2) trans isomers of $Ru_2(F_5ap)_4Cl$ were separated on a silica gel column following the reaction between $Ru_2(CH_3COO)_4Cl$ and molten HF_5ap under argon. The (4,0), (3,1), and (2,2) trans isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ were obtained by reaction of their respective isomer of $Ru_2(F_5ap)_4Cl$ with $LiC{\equiv}CC_6H_5$ in THF at room temperature. The three isomers of $Ru_2(F_5ap)_4Cl$ and $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ were characterized by ^1H and ^{19}F NMR, ESR, and IR spectroscopy, mass spectrometry and electrochemistry. Each $Ru^{II}Ru^{III}$ isomer of $Ru_2(F_5ap)_4Cl$ is paramagnetic and undergoes two oxidations and one reduction in CH_2Cl_2, 0.1 M TBAP while each Ru^{III}_2 isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ is diamagnetic and undergoes one oxidation and two reductions under the same solution conditions. All of the redox processes are reversible and involve metal-centered one-electron transfers. The singly reduced products of the (4,0), (3,1), and (2,2) trans isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ were electrogenerated and display ESR signals consistent with the presence of a single unpaired electron. Molecular structures of the three isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ were also determined. The (4,0) isomer crystallizes in the monoclinic space group $P2_1/c$ with $a = 23.436(6)$ Å, $b = 20.640(6)$ Å, $c = 23.504(6)$ Å, $\beta = 105.82(2)°$, and $Z = 8$, while the (3,1) isomer crystallizes in the monoclinic space group $P2_1/n$ with $a = 15.621(3)$ Å, $b = 16.427(3)$ Å, $c = 21.166(5)$ Å, $\beta = 93.91(2)°$, and $Z = 4$. The (2,2) trans isomer crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.819(5)$ Å, $b = 13.390(4)$ Å, $c = 17.827(5)$ Å, $\alpha = 85.04(2)°$, $\beta = 72.66(2)°$, $\gamma = 68.47(2)°$, and $Z = 2$. The average Ru−Ru bond distances in the (4,0), (3,1), and (2,2) trans isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ are 2.450(1), 2.475(1), and 2.473(1) Å, respectively.

Introduction

Several dimetal complexes bridged by four identical equatorial ligands have been synthesized and characterized over the last two decades.[1−29] The bridging ligands in these complexes vary from slightly basic,[1−11] in the case of carboxylates and sulfate, to strongly basic,[12−29] in the case of 2-anilinopyridinate and *N,N′*-diphenylformamidinate and can be classified into two categories, symmetrical[1−10,14−20] and unsymmetrical.[11−13,21−29] Dimetal complexes bridged by four symmetrical ligands are represented by a single structural formula, but four different geometric isomers are possible for dimetal complexes containing four unsymmetrical bridging ligands. This is schematically shown in Chart 1, where the solid and open circles represent two different types of donor atoms.

---

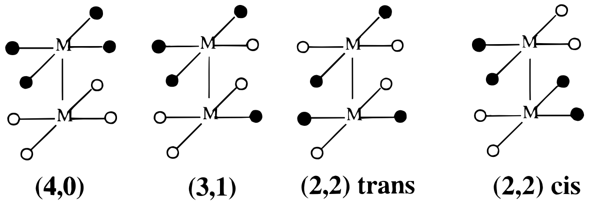
† Present address: Department of Chemistry, University of Wisconsin, Whitewater, Whitewater, WI 53190.

⊗ Abstract published in *Advance ACS Abstracts*, October 1, 1997.

(1) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388.
(2) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285.
(3) Kuz'menko, I. V.; Zhilyaev, A. N.; Fomina, T. A.; Porai-Koshits, M. A.; Baranovskii, I. B. *Russ. J. Inorg. Chem.* **1989**, *34*, 1457.
(4) Cotton, F. A.; Datta, T.; Labella, L.; Shang, M. Y. *Inorg. Chim. Acta* **1993**, *203*, 55.
(5) Aquino, M. A. S.; Macartney, D. H. *Inorg. Chem.* **1987**, *26*, 2696.
(6) Drew, M. G. B.; Higgins, P.; McCann, G. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1385.
(7) Holder, A. J.; Schröder, M.; Stephenson, T. A. *Polyhedron* **1987**, *6*, 461.
(8) Clark, D. L.; Green, J. C.; Redfern, C. M.; Quelch, G. E.; Hillier, I. H.; Guest, M. F. *Chem. Phys. Lett.* **1989**, *154*, 326.
(9) Matsubayashi, G.-E.; Yokoyama, K.; Tanaka, T. *J. Chem. Soc., Dalton Trans.* **1988**, 3059.
(10) Cogne, A.; Grand, A.; Rey, P.; Subra, R. *J. Am. Chem. Soc.* **1989**, *111*, 3230.
(11) Best, S. P.; Clark, R. J. H.; Nightingale, A. J. *Inorg. Chem.* **1990**, *29*, 1383.
(12) Best, S. P.; Chandley, P.; Clark, R. J. H.; McCarthy, S.; Hursthouse, M. B.; Bates, P. A. *J. Chem. Soc., Dalton Trans.* **1989**, 581.
(13) Seeber, R.; Piu, P.; Piraino, P.; Zanello, P. *Inorg.Chim. Act.* **1989**, *155*, 27.
(14) Cotton, F. A.; Ren, T. *Inorg. Chem.* **1995**, *34*, 3190.
(15) Cotton, F. A.; Matusz, M. *J. Am. Chem. Soc.* **1988**, *110*, 5761.
(16) Cotton, F. A.; Ren, T. *Inorg. Chem.* **1991**, *30*, 3675.
(17) Le, J. C.; Chavan, M. Y.; Chau, L. K.; Bear, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 7195.
(18) Bear, J. L.; Han, B. C.; Huang, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 1175.
(19) Bear, J. L.; Han, B. C.; Huang, S. R.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 3012.
(20) Bear, J. L.; Li, Y. L; Han, B. C.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 1395.
(21) Charkravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 172.
(22) Malinski, T.; Chang, D.; Feldmann, F. N.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1983**, *22*, 3225.
(23) Chavan, M. Y.; Feldmann, F. N.; Lin, X. Q.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 2373.
(24) Chakravarty, A. R.; Cotton, F. A. *Inorg. Chim. Acta* **1986**, *113*, 19.
(25) Cotton, F. A.; Ren, T.; Eglin, J. L. *Inorg. Chem.* **1991**, *30*, 2552.
(26) (a) Yao, C.-L.; Park, K. H.; Khokhar, A. R.; Jun, M.-J.; Bear, J. L. *Inorg. Chem.* **1990**, *29*, 4033. (b) Bear, J. L.; Liu, L.-M.; Kadish, K. M. *Inorg. Chem.* **1987**, *26*, 2927.
(27) Bear, J. L.; Yao, C. L.; Liu, L. M.; Capdevielle, F. J.; Korp, J. D.; Albright, T. A.; Kang, S. K.; Kadish, K. M. *Inorg. Chem.* **1989**, *28*, 1254.
(28) Bear, J. L.; Liu, L. M.; Kadish, K. M. *Inorg. Chem.* **1987**, *26*, 2927.
(29) Li, Y. L.; Han, B. C.; Bear, J. L.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4175.

S0020-1669(96)00265-0 CCC: $14.00

Chart 1



The isomer with four equivalent donor atoms on each metal atom is designated as the (4,0) isomer while that with three equivalent donor atoms on each metal is designated as the (3,1) isomer.[26-28] The notations of (2,2) trans and (2,2) cis indicate that these geometrical isomers have two equivalent donor atoms on each metal in trans and cis arrangements, respectively.[26-28]

The energy and ordering of the metal-centered molecular orbitals of diruthenium complexes are highly dependent on the donor/acceptor properties of the bridging and axial ligands. For this reason, a large number of diruthenium complexes containing bridging and axial ligands which vary significantly in their σ and π donor/acceptor properties have been synthesized and studied in recent years.[1,2,15,16,18-22,27,29] Diruthenium complexes with unsymmetrical ligands such as anilinopyridine (ap) and 2-(2,3,4,5,6-pentafluoroanilino)pyridinate (F_5ap) have been synthesized, but little is known on how the bonding orientations of these ligands would affect the reactivity and stucture of these complexes. For this reason, the synthesis and characterization of geometric isomers containing the diruthenium unit in a +6, +5, or +4 oxidation state are of interest.

Each $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ derivative can theoretically exist in four geometric isomer forms due to the unsymmetrical F_5ap bridging ligand (see Chart 1). The synthesis and preliminary characterization of the (4,0) isomer have been reported,[29] and we now describe the syntheses and characterization of the (3,1) and (2,2) trans isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$. A more detailed description of the synthetic procedure and characterization of the (4,0) isomer is also presented in this paper in addition to new data on the (4,0), (3,1), and (2,2) trans isomers of $Ru_2(F_5ap)_4Cl$, the starting compounds used in synthesis of the three isolated isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$.

Both series of diruthenium compounds were characterized by ^1H and ^{19}F NMR, ESR, and IR spectroscopy, mass spectrometry and electrochemistry. Molecular structures of the (4,0), (3,1), and (2,2) trans isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ were also determined by single-crystal X-ray diffraction.

Experimental Section

Chemicals and Reagents. 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. 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 2-methyl-2-propanoxide, 2-bromopyridine, 2,3,4,5,6-pentafluoroaniline, lithium phenylacetylide, $RuCl_3{\cdot}3H_2O$, and 1,4-phenylene diisocyanide, purchased from Aldrich Chemical Co., were used as received.

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 with *m*-nitrobenzyl alcohol (NBA) as the liquid matrix. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

^1H NMR spectra were recorded on a QE-300 FT NMR spectrometer while ^{19}F NMR spectra were obtained with a NT-200 spectrometer. IR spectra were obtained on an IBM Model IR/32 FTIR spectrometer. ESR spectra were recorded with an IBM ER 100D spectrometer. The *g* values were calculated with respect to the diphenylpicrylhydrazyl radical (DPPH) which has a signal at $g = 2.0036 \pm 0.0003$.[30] Magnetic susceptibility measurements were carried out at room temperature with a Johnson Matthey Model MSG-1 magnetic susceptibility balance which was calibrated with $Hg[Co(NCS)_4]$.

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, and a homemade saturated calomel electrode (SCE) was used as the reference electrode. The counter electrode was a platinum wire. Controlled-potential electrolysis was carried out with a BAS Model SP-2 potentiostat. An "H" type cell was used for bulk electrolysis. Two cylindrically shaped platinum gauze electrodes, separated by a fine-fritted disk, served as the working and counter electrodes, respectively.

HF_5ap. A 0.25 mL (ca. 2.5 mmol) portion of 2-bromopyridine was added to 5.0 equiv of sodium 2-methyl-2-propanoxide in 100 mL of THF under an argon atmosphere. The solution was refluxed overnight, after which 10.0 g (ca. 54.6 mmol) of 2,3,4,5,6-pentafluoroaniline was added and the solution refluxed for another 10 h. The mixture was then extracted by using CH_2Cl_2 and H_2O. The organic layer was collected, and anhydrous $CaCl_2$ was added. The solution was filtered, and the crude product was recovered after removal of the solvent. Pure 2-(2,3,4,5,6-pentafluoroanilino)pyridine, HF_5ap, was obtained by sublimation at 110 °C under a pressure of 5×10^{-3} Torr. The yield of the product was extremely variable and ranged between 5 and 70% despite what appeared to be constant reaction conditions. This problem of variable ligand yield is not understood and still under investigation. Mass spectral data (*m/e*, fragment): 260.5, $[HF_5ap]^+$. NMR data in CD_2Cl_2 (δ, ppm): 8.14 (d, 1H), 7.58 (t, 1H), 6.85 (t, 1H), 6.66 (d, 1H), 6.20 (s, b, 1H), (s = singlet; d = doublet; t = triplet; b = broad).

(4,0), (3,1), and (2,2) Trans Isomers of $Ru_2(F_5ap)_4Cl$.[31] $Ru_2(CH_3COO)_4Cl$ (0.18 g, ca. 0.4 mmol) and molten HF_5ap (4.00 g, ca. 15.4 mmol) were stirred under an argon atmosphere at 140 °C for 20 min. Excess HF_5ap ligand was sublimed off under vacuum at 110 °C and the residue twice chromatographed on a silica gel column, using CH_2Cl_2 and then acetone/*n*-hexane (1:9) as eluent. Three bands, which were yellow, brown, and green were collected, and these corresponded to the (4,0), (3,1), and (2,2) trans isomers of $Ru_2(F_5ap)_4Cl$, respectively. The crude products were washed using methanol and recrystallized three times using acetone/*n*-hexane (2:8). Only the (4,0) isomer of $Ru_2(F_5ap)_4Cl$ was characterized in detail, and the data are as follows. Infrared spectrum (CsI pellet), cm^{-1}: 1660.9 (w), 1558.7 (m), 1460.3 (s), 1420.2 (s), 1380.4 (s), 1288.6 (m), 1230.8 (m), 1124.6 (m), 1080.4 (w), 1003.7 (s), 972.2 (s), 854.6 (m), 780.4 (m), 742.7 (m), 718.6 (m), 682.9 (w), 634.7 (w), 588.4 (w), 511.2 (w) (s = strong; m = medium; w = weak). Mass spectral data (*m/e*, fragment): 1275.0, $[Ru_2(F_5ap)_4Cl]^+$; 1240.0, $[(Ru_2(F_5ap)_4]^+$; 1016.2, $[Ru_2(F_5ap)_3Cl]^+$; 980.4, $[(Ru_2(F_5ap)_3]^+$. Anal. Calcd for $C_{44}H_{16}N_8F_{20}Ru_2Cl$: C, 41.46; H, 1.26; N, 8.80; F, 29.84. Found: C, 41.55; H, 1.14; N, 8.77; F, 27.49.

(4,0) Isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)$ and $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$. A 4.0 mL (ca. 4.0 mmol) sample of $LiC{\equiv}CC_6H_5$ was added to 0.10 g (ca. 0.08 mmol) of $Ru_2(F_5ap)_4Cl$ in 100 mL of deaerated THF. The solution was stirred overnight at room temperature as its color changed from yellow-brown to red. The reaction mixture was then exposed to air and the solvent evaporated under vacuum. The residue was purified on a silica gel column using CH_2Cl_2/*n*-hexane (1:9) as eluent. A red and a blue band were observed on the column. The red band was collected and the solvent evaporated under vacuum. The solid was then recrystallized from CH_2Cl_2/*n*-hexane (2:8), and $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)$ was recovered in an isolated yield of 40%. Crystals suitable for X-ray single-crystal analysis were obtained by slow diffusion of *n*-hexane into a THF solution of the (4,0) isomer of

---

(30) Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: Philadelphia, PA, 1977; p 324.

(31) The (2,2) cis isomer of $Ru_2(F_5ap)_4Cl$ was apparently present in the reaction mixture, but we could not isolate an adequate amount of product to further characterize this compound. The low yield for the (2,2) cis isomer of $Ru_2(F_5ap)_4Cl$ is not yet understood.

$\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)}$. Infrared spectrum (CsI pellet), cm^{-1}: 1660.9 (w), 1554.8 (w), 1466.1 (s), 1423.6 (s), 1385.1 (m), 1334.9 (w), 1286.7 (m), 1265.5 (w), 1223.0 (w), 1126.6 (w), 993.5 (s), 970.3 (s), 858.4 (m), 765.8 (m), 740.8 (m), 723.4 (m), 681.0 (w), 588.4 (w), 509.3. Anal. Calcd for $\mathrm{C_{52}H_{21}N_8F_{20}Ru_2}$: C, 46.60; H, 1.57; N, 8.36; F, 28.38. Found: C, 46.65; H, 1.65; N, 8.08; F, 28.36.

The blue band was also collected and the solvent evaporated under vacuum. Pure $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$ was obtained in an isolated yield of 40% after elution with $\mathrm{CH_2Cl_2}$/*n*-hexane (2:8) and further purification on an alumina column using pure $\mathrm{CH_2Cl_2}$. Dark-green crystals suitable for X-ray analysis were obtained by recrystallization in a 9:1 mixture of $\mathrm{CH_2Cl_2}$ and benzene. Infrared spectrum (CsI pellet), cm^{-1}: 1545.2 (m), 1454.5 (s), 1367.7 (m), 1325.2 (m), 1115.0 (w), 956.8 (s), 833.4 (m), 727.3 (m), 665.5 (w), 513.1 (w). Anal. Calcd for $\mathrm{C_{60}H_{26}N_8F_{20}Ru_2}$: C, 50.07; H, 1.93; N, 7.63; F, 26.31. Found: C, 50.00; H, 1.81; N, 7.78; F, 26.39.

(3,1) and (2,2) Trans Isomers of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$. Both isomers were obtained using reaction conditions similar to those described above for preparation of the (4,0) isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$. To 0.1 g (0.08 mmol) of the (3,1) or (2,2) trans isomer of $\mathrm{Ru_2(F_5ap)_4Cl}$ in 100 mL of deaerated THF was added 2.0 mL (2.0 mmol) of $\mathrm{LiC{\equiv}CC_6H_5}$.

The mixture containing the (3,1) isomer was stirred at room temperature for 8 h as the color of the solution changed from yellow-brown to red. The solvent was then removed under vacuum and the residue purified on a silica gel column using $\mathrm{CH_2Cl_2}$/*n*-hexane (3:7) as eluent. A red and a blue band were observed on the column. The red band was collected and, after evaporation of the solvent under vacuum, gave the pure (3,1) isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)}$ in a 7% isolated yield. The blue band was also eluted from the column and the solvent evaporated under vacuum. The solid residue was further purified on an alumina column using $\mathrm{CH_2Cl_2}$ as eluent and gave pure $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$ in a 60% isolated yield after evaporation of the solvent.

The (2,2) trans isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$ was isolated in a yield of 85% using a procedure similar to that described above for the (3,1) isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$. The only difference was that the mixture was stirred for 4 h rather than 8 h as the color of the solution changed from green to red. Infrared spectrum for the (3,1) isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$ (CsI pellet), cm^{-1}: 2093.0 (w), 1606.9 (m), 1512.4 (s), 1468.0 (s), 1423.6 (m), 1340.7 (w), 1307.9 (w), 1026.3 (s), 995.4 (s), 723.2 (w), 756.2 (m), 6932.5 (w). Infrared spectrum for the (2,2) trans isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$ (CsI pellet), cm^{-1}: 2093.0 (m), 1608.8 (s),1512.4 (s), 1469.9 (s), 1423.6 (m) 1342.6 (m), 1307.9 (m), 1286.7 (w), 1155.5 (w), 1024.3 (s), 1012.8 (s), 995.4 (s), 864.2 (m), 765.2 (s), 692.5 (w).

X-ray Crystallography of the (4,0), (3,1), and (2,2) Trans Isomers. Single-crystal X-ray crystallographic studies were performed at the University of Houston X-ray Crystallographic Center. Since the material was subject to a slow decomposition, the sample was placed in a stream of dry nitrogen gas at −50 °C in a random orientation on 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, are summarized in Table 1. Intensities were measured using an ω scan technique, with a scan rate dependent 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, indicating that the crystal does not decompose during the data collection. During data reduction, Lorentz and polarization corrections were applied to the intensity data, but because of the small linear absorption coefficient, absorption corrections were not applied.

The structures were solved by the SHELXTL direct methods program which revealed the positions of many of the atoms in the asymmetric unit. Remaining non-hydrogen atoms 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 for all of them. 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 0.6, 0.7, or 0.5 e/Å^3 for the (4,0), (3,1), or (2,2) trans isomer, respectively. All calculations were made using the Nicolet SHELXTL PLUS (1987) series of crystallographic programs.

Table 1. Crystal Data and Data Collection and Processing Parameters of the (4,0), (3,1), and (2,2) Trans Isomers of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$

	(4,0)	(3,1)	(2,2) trans
space group	$P2_1/c$ (monoclinic)	$P2_1/n$ (monoclinic)	$P\bar{1}$ (triclinic)
a, Å	23.436(6)	15.621(3)	12.819(5)
b, Å	20.640(6)	16.427(3)	13.390(4)
c, Å	23.504(6)	21.166(5)	17.827(5)
α, deg			85.04(2)
β, deg	105.82(2)	93.91(2)	72.66(2)
γ, deg			68.47(2)
V, Å^3	10939	5459	2716
mol formula	$\mathrm{C_{60}H_{26}N_8F_{20}Ru_2}$	$\mathrm{C_{60}H_{26}N_8F_{20}Ru_2}$	$\mathrm{C_{60}H_{26}N_8F_{20}Ru_2}$
fw	1441.08	1441.08	1441.08
Z	8	4	2
ρ, g/cm^3	1.75	1.77	1.76
μ, cm^{-1}	6.55	6.62	6.60
λ (Mo Kα), Å	0.710 73	0.710 73	0.710 73
data coll range (2θ), deg	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 45$	$4 \le 2\theta \le 50$
temp, °C	−50	−50	−50
R^a	0.039	0.031	0.027
$R_w{}^b$	0.036	0.024	0.028

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

For the (4,0) isomer, all the carbons of the F$_5$ap ligand were refined isotropically in order to reduce the number of variables to a manageable value. One of the phenyl groups (C(53) to C(60)) was also found to be disordered over two positions, with this being modeled by using ideal rigid-body phenyl groups. The variation in the location of C(53) was too small to separate, and therefore it was refined common to both orientations. The occupancy factors refined to 62% for the C(54) to C(60) orientation and 38% for C(54′) to C(60).

The Laue symmetry of the (4,0) isomer was determined to be 2/*m*, and from the systematic absences, the space group was shown to be unambiguously $P2_1/c$. For the (3,1) and (2,2) trans isomers, the Laue symmetries were determined to be 2/*m* and $\bar{1}$, respectively. From the systematic absences, the space groups were shown to be unambiguously $P2_1/n$ for the (3,1) isomer and either $P1$ or $P\bar{1}$ for the (2,2) trans isomer. Successful refinement in $P\bar{1}$ showed it to be the correct setting.

Results and Discussion

Synthesis and Reaction. The affinities of the three isomers of $\mathrm{Ru_2(F_5ap)_4Cl}$ for $\mathrm{LiC{\equiv}CC_6H_5}$ are different under the same experimental conditions. For example, the formation of the (4,0) isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)}$ or $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$ from the (4,0) isomer of $\mathrm{Ru_2(F_5ap)_4Cl}$ could be easily controlled by changing the amount of $\mathrm{LiC{\equiv}CC_6H_5}$, but this was not the case for the (3,1) or (2,2) trans isomer. The (4,0) isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$ was the major product in the presence of a large excess of $\mathrm{LiC{\equiv}CC_6H_5}$ (>100 equiv), while the (4,0) isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)}$ was the major product when only 2−5 equiv of $\mathrm{LiC{\equiv}CC_6H_5}$ was used. On the other hand, when stoichometric amounts (1:1) of $\mathrm{LiC{\equiv}CC_6H_5}$ and the (3,1) isomer of $\mathrm{Ru_2(F_5ap)_4Cl}$ were used, the major product isolated was the (3,1) isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$ and only 7% of the (3,1) isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)}$ was obtained. No (2,2) trans isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)}$ could be obtained by a reaction between the (2,2) trans isomer of $\mathrm{Ru_2(F_5ap)_4Cl}$ and $\mathrm{LiC{\equiv}CC_6H_5}$. Only the (2,2) trans isomer of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$ and the parent complex $\mathrm{Ru_2(F_5ap)_4Cl}$ were isolated from the reaction mixture. It is not clear at present whether this is due to kinetic or thermodynamic effects, but the ease of adding two σ-bonded axial ligands to the $\mathrm{Ru_2}^{5+}$ core of $\mathrm{Ru_2(F_5ap)_4Cl}$ follows the order (4,0) < (3,1) < (2,2) trans.

Molecular Structures of the (4,0), (3,1), and (2,2) Trans Isomers of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$. Selected bond lengths and bond angles for the three isomers of $\mathrm{Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2}$

Table 2. Selected Bond Lengths (Å) for the (4,0), (3,1), and (2,2) Trans Isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$

(4,0) isomer[a]		(3,1) isomer		(2,2) trans isomer	
Ru(1)−Ru(2)	2.441(1)	Ru(1)−Ru(2)	2.475(1)	Ru(1)−Ru(2)	2.473(1)
Ru(1)−N(1)	2.069(6)	Ru(1)−N(1)	2.003(4)	Ru(1)−N(1)	2.147(2)
Ru(2)−N(2)	2.030(6)	Ru(2)−N(2)	2.147(4)	Ru(2)−N(2)	1.979(3)
Ru(1)−N(3)	2.030(8)	Ru(1)−N(3)	2.018(5)	Ru(1)−N(3)	2.159(2)
Ru(2)−N(4)	2.110(7)	Ru(2)−N(4)	2.087(4)	Ru(2)−N(4)	1.982(2)
Ru(1)−N(5)	2.036(6)	Ru(1)−N(5)	2.125(4)	Ru(1)−N(5)	2.012(2)
Ru(2)−N(6)	2.115(6)	Ru(2)−N(6)	1.970(4)	Ru(2)−N(6)	2.120(2)
Ru(1)−N(7)	2.123(7)	Ru(2)−N(7)	2.054(4)	Ru(2)−N(7)	2.016(2)
Ru(2)−N(8)	2.032(7)	Ru(1)−N(8)	2.085(4)	Ru(1)−N(8)	2.120(2)
Ru(1)−C(45)	1.955(12)	Ru(1)−C(45)	1.987(6)	Ru(1)−C(45)	1.990(3)
Ru(2)−C(53)	1.951(11)	Ru(2)−C(53)	1.979(6)	Ru(2)−C(53)	2.001(3)
C(45)−C(46)	1.212(17)	C(45)−C(46)	1.208(8)	C(45)−C(46)	1.201(4)
C(46)−C(47)	1.446(17)	C(46)−C(47)	1.445(8)	C(46)−C(47)	1.440(4)
C(53)−C(54)	1.211(28)	C(53)−C(54)	1.220(8)	C(53)−C(54)	1.204(4)
C(54)−C(55)	1.451(28)	C(54)−C(55)	1.425(8)	C(54)−C(55)	1.446(4)
C(53)−C(54′)	1.238(45)				
C(54′)−C(55′)	1.478(44)				

[a] Data for molecule 2 of the (4,0) isomer are included in the Supporting Information.

Table 3. Selected Bond Angles (deg) for the (4,0), (3,1), and (2,2) Trans Isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$

(4,0) isomer[a]		(3,1) isomer		(2,2) trans isomer	
Ru(2)−Ru(1)−N(1)	84.7(2)	Ru(2)−Ru(1)−N(1)	97.5(1)	Ru(2)−Ru(1)−N(1)	80.3(1)
Ru(2)−Ru(1)−N(3)	91.0(3)	Ru(2)−Ru(1)−N(3)	92.7(1)	Ru(2)−Ru(1)−N(4)	95.9(1)
N(1)−Ru(1)−N(3)	89.7(3)	N(1)−Ru(1)−N(3)	90.5(2)	N(1)−Ru(1)−N(4)	88.6(1)
Ru(2)−Ru(1)−N(5)	91.1(3)	Ru(2)−Ru(1)−N(5)	78.6(1)	Ru(2)−Ru(1)−N(5)	97.2(1)
N(1)−Ru(1)−N(5)	175.9(3)	N(1)−Ru(1)−N(5)	175.4(2)	N(1)−Ru(1)−N(5)	176.1(1)
N(3)−Ru(1)−N(5)	90.4(3)	N(3)−Ru(1)−N(5)	87.4(2)	N(4)−Ru(1)−N(5)	88.6(1)
Ru(2)−Ru(1)−N(7)	83.8(2)	Ru(2)−Ru(1)−N(8)	81.7(1)	Ru(2)−Ru(1)−N(8)	79.0(1)
N(1)−Ru(1)−N(7)	89.8(3)	N(5)−Ru(1)−N (8)	90.7(2)	N(1)−Ru(1)−N (8)	93.7(1)
N(3)−Ru(1)−N(7)	174.8(3)	N(3)−Ru(1)−N(8)	174.2(2)	N(4)−Ru(1)−N(8)	173.9(1)
N(5)−Ru(1)−N(7)	89.7(3)	N(5)−Ru(1)−N(8)	91.0(2)	N(5)−Ru(1)−N(8)	88.8(1)
Ru(2)−Ru(1)−C(45)	170.6(3)	Ru(2)−Ru(1)−C(45)	163.5(2)	Ru(2)−Ru(1)−C(45)	160.6(1)
N(1)−Ru(1)−C(45)	89.7(4)	N(1)−Ru(1)−C(45)	95.9(2)	N(1)−Ru(1)−C(45)	87.8(1)
N(3)−Ru(1)−C(45)	96.5(4)	N(3)−Ru(1)−C(45)	96.8(2)	N(4)−Ru(1)−C(45)	99.2(1)
N(5)−Ru(1)−C(45)	94.4(3)	N(5)−Ru(1)−C(45)	88.4(2)	N(5)−Ru(1)−C(45)	95.4(1)
N(7)−Ru(1)−C(45)	88.7(4)	N(8)−Ru(1)−C(45)	88.6(2)	N(8)−Ru(1)−C(45)	86.6(1)
Ru(1)−Ru(2)−N(2)	88.3(2)	Ru(1)−Ru(2)−N(2)	78.3(1)	Ru(1)−Ru(2)−N(2)	95.1(1)
Ru(1)−Ru(2)−N(4)	82.9(2)	Ru(1)−Ru(2)−N(4)	81.8(1)	Ru(1)−Ru(2)−N(3)	79.7(1)
N(2)−Ru(2)−N(4)	90.2(3)	N(2)−Ru(2)−N(4)	93.6(2)	N(2)−Ru(2)−N(3)	88.6(1)
Ru(1)−Ru(2)−N(6)	82.8(2)	Ru(1)−Ru(2)−N(6)	95.0(1)	Ru(1)−Ru(2)−N(6)	79.0(1)
N(2)−Ru(2)−N(6)	171.2(3)	N(2)−Ru(2)−N(6)	171.2(2)	N(2)−Ru(2)−N(6)	172.0(1)
N(4)−Ru(2)−N(6)	88.6(3)	N(4)−Ru(2)−N(6)	91.3(2)	N(3)−Ru(2)−N(6)	95.5(1)
Ru(1)−Ru(2)−N(8)	89.6(2)	Ru(1)−Ru(2)−N(7)	93.1(1)	Ru(1)−Ru(2)−N(7)	97.41(1)
N(2)−Ru(2)−N(8)	91.6(3)	N(2)−Ru(2)−N(7)	88.0(2)	N(2)−Ru(2)−N(7)	87.4(1)
N(4)−Ru(2)−N(8)	172.3(3)	N(4)−Ru(2)−N(7)	174.1(2)	N(3)−Ru(2)−N(7)	174.9(1)
N(6)−Ru(2)−N(8)	88.5(3)	N(6)−Ru(2)−N(7)	86.4(2)	N(6)−Ru(2)−N(7)	88.1(1)
Ru(1)−Ru(2)−C(53)	172.2(3)	Ru(2)−Ru(1)−C(53)	163.0(1)	Ru(2)−Ru(1)−C(53)	160.9(1)
N(2)−Ru(2)−C(53)	96.6(3)	N(2)−Ru(2)−C(53)	87.2(2)	N(2)−Ru(2)−C(53)	99.7(2)
N(4)−Ru(2)−C(53)	91.1(4)	N(4)−Ru(2)−C(53)	90.4(2)	N(3)−Ru(2)−C(53)	88.7(1)
N(6)−Ru(2)−C(53)	92.1(3)	N(6)−Ru(2)−C(53)	100.3(2)	N(6)−Ru(2)−C(53)	87.2(1)
N(8)−Ru(2)−C(53)	96.2(4)	N(7)−Ru(2)−C(53)	95.3(2)	N(7)−Ru(2)−C(53)	95.2(1)
Ru(1)−C(45)−C(46)	177.7(9)	Ru(1)−C(45)−C(46)	171.8(5)	Ru(1)−C(45)−C(46)	174.6(2)
C(45)−C(46)−C(47)	176.6(11)	C(45)−C(46)−C(47)	176.3(7)	C(45)−C(46)−C(47)	173.2(3)
Ru(2)−C(53)−C(54)	173.6(12)	Ru(2)−C(53)−C(54)	174.3(5)	Ru(2)−C(53)−C(54)	172.3(3)
C(53)−C(54)−C(55)	173.4(23)	C(53)−C(54)−C(55)	178.7(6)	C(53)−C(54)−C(55)	177.7(4)
Ru(2)−C(53)−C(54′)	166.4(23)				
C(53)−C(54′)−C(55′)	166.4(36)				

[a] Data for molecule 2 of the (4,0) isomer are included in the Supporting Information.

are summarized in Tables 2 and 3, and their crystal structures are presented in Figures 1 and 2. All intramolecular bond lengths and angles as well as other structural data for the (4,0) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)$ are given in the Supporting Information.

The X-ray structure of the (4,0) isomer consists of two independent molecules located in general positions (see Figure 1). The geometry of each Ru atom is nearly octahedral, with one set of four pyridyl nitrogens (for Ru(1) or Ru(3)), and another set of four anilino nitrogens (for Ru(2) or Ru(4)), forming the equatorial planes. The Ru−Ru−C angle is distinctly nonlinear, having an average value of 171.4° for molecule 1 and 167.7° for molecule 2. Other crystallographic differences between the two molecules can also be noted. For example, the variations in bond lengths and angles involving Ru(3) and Ru(4) (molecule 2) are more pronounced than those involving Ru(1) and Ru(2) (molecule 1). Also, the N−Ru−Ru−N torsion angles show a wider variation in molecule 2 than in molecule 1.

The coordination of each Ru atom is essentially octahedral in both the (3,1) and (2,2) trans isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ (see Figure 2), and only a single molecule of each

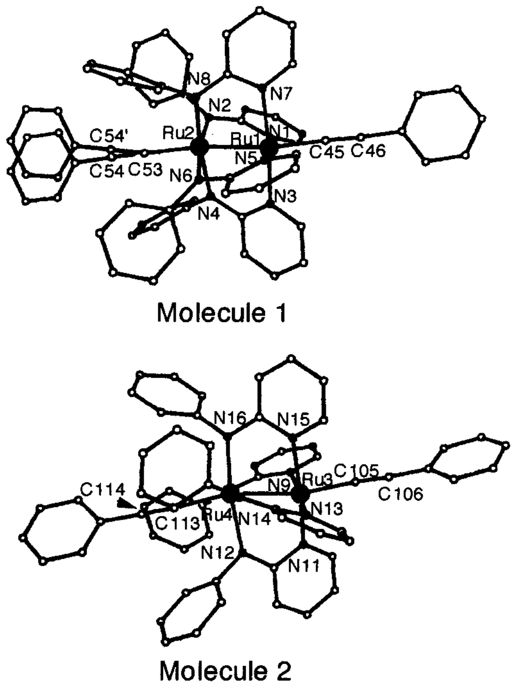
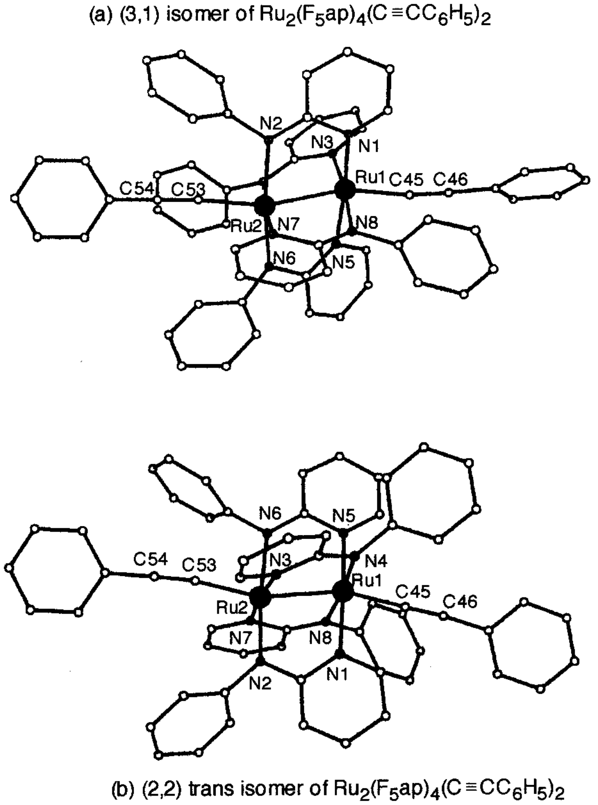


Figure 1. View of the (4,0) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ with the H and F atoms omitted in molecule 1 and molecule 2 but with both orientations of the disordered axial phenyl ring being shown.


(a) (3,1) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$

(b) (2,2) trans isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$

Figure 2. Views of (a) the (3,1) isomer and (b) the (2,2) trans isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ with H and F atoms omitted.

isomer is present in the crystal. In the (3,1) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$, (Figure 2a), either three pyridyl and one anilino nitrogens or one pyridyl and three anilino nitrogens form the equatorial planes of each ruthenium while in the (2,2) trans isomer (Figure 2b) these planes are formed by two pyridyl and two anilino nitrogens in a trans arrangement. Again, the Ru−Ru−C units are not linear in either the (3,1) or the (2,2) trans isomer, with values averaging 163.3° for the (3,1) and 160.8° for the (2,2) trans isomer. The four N−Ru−Ru−N individual torsion angles are quite different from each other in the (3,1) isomer, ranging from 10.3 to 18.5°. The N(1)−Ru−Ru−N(2) and N(3)−Ru−Ru−N(4) torsion angles average 12.7°, while the N(5)−Ru−Ru−N(6) and N(7)−Ru−Ru−N(8) values average 15.5°. On the basis of steric hindrance alone, one would have expected to see the $-C{\equiv}CC_6H_5$ axial ligands of the (3,1) isomer bend closer to the pyridyl groups than the anilino rings, but the opposite is observed.

In all three isomers, there is a 50:50 mixture of left-handed and right-handed molecules in the crystal with respect to the N−Ru−Ru−N torsion angles. Each Ru atom has two long Ru−N bonds and two short ones. This fact is illustrated by comparing the Ru−N_p bond lengths (N_p = pyridyl nitrogen) to the Ru−N_a bond lengths (N_a = anilino nitrogen) for the four F_5ap equatorial ligands in the (2,2) trans isomer. The Ru−N_a bond lengths are shorter than the Ru−N_p bond lengths for *only* two of the F_5ap ligands (see Table 2).

The crystal structures of the three compounds also reveal the following interesting geometric features:

(i) Three arrangements of bridging ligands are obtained for $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$, suggesting that each parent compound of $Ru_2(F_5ap)_4Cl$ should also have the corresponding (4,0), (3,1), or (2,2) trans arrangement.

(ii) The Ru−Ru bond distance in the (2,2) trans isomer is 2.473(1) Å, which is comparable to the value of 2.475(1) Å in the (3,1) isomer, and both values are slightly longer than the 2.441(1) and 2.460(1) Å values in the two molecules of the (4,0) isomer (see Table 2). These Ru−Ru bond distances are all significantly shorter than the 2.556(1) Å Ru−Ru distance in $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$. However, as compared to the Ru−Ru bond distances of several Ru_2^{4+}, Ru_2^{5+}, and Ru_2^{6+} complexes,[19] these bond distances are still much longer than expected for a Ru_2^{6+} complex of this structural type.

(iii) For each isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$, the smallest Ru−Ru−N and N−Ru−C bond angles are observed for the longest Ru−N bond lengths. This is illustrated in the case of the (3,1) isomer by the following data: The Ru(1)−N(5) bond length is longer than the Ru(1)−N(1) bond length (see Table 2), and subsequently the Ru(2)−Ru(1)−N(5) and the C(45)−Ru(1)−N(5) bond angles are both smaller than their respective Ru(2)−Ru(1)−N(1) and C(45)−Ru(1)−N(1) bond angles (see Table 3).

(iv) The deviation from linearity for the average Ru−Ru−C bond angles in the three geometric isomers follows the order (2,2) trans, 160.8° < (3,1), 163.3° < (4,0), 171.4° (or 167.7°) The three isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ are also ordered in the same way if one compares the steric hindrance between the phenyls of the equatorial ligands and the axial ligand and/or the polarization of the Ru−Ru bond. The fact that the average Ru−Ru−C bond angle differs from 180° results from electronic effects rather than a steric hindrance between the axial and equatorial ligands.[19]

(v) The arrangement of the equatorial ligands in the (4,0), (3,1), and (2,2) trans isomers leads to a severe twist in geometry of the structure, with the average N−Ru−Ru−N torsion angles being 19.9° for the (4,0), 14.4° for the (3,1), and 8.35° for the (2,2) trans isomer.

(vi) Suprisingly, in the case of the (4,0) isomer, the two axial phenylacetylide ligands have nearly the same geometries. For instance, the same distances are seen between C(45) and C(46)

Table 4. ^{1}H and ^{19}F NMR Chemical Shifts (δ, ppm)[a] of the (4,0), (3,1), and (2,2) Trans Isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ in CD_2Cl_2

isomer	^{1}H NMR			^{19}F NMR	
(4,0)	9.85 (4H, d)	5.92 (2H, d)	4.85 (2H, d)	−134.0 (4F, d)	−158.3 (4F, t)
	8.18 (4H, t)	5.66 (1H, t)	4.54 (4H, d)	−143.2 (4F, d)	−158.5 (4F, t)
	8.10 (2H, t)	5.12 (1H, t)	4.11 (4H, t)	−153.8 (4F, t)	
	8.03 (2H, t)				
(3,1)	9.83 (1H, d)	7.35 (2H, d)	6.79 (2H, d)	−136.3 (2F, q)	−155.7 (1F, t)
	9.57 (2H, d)	7.29 (2H, t)	6.66 (2H, t)	−139.2 (2F, q)	−157.2 (1F, t)
	9.23 (1H, d)	7.27 (2H, d)	6.59 (2H, d)	−140.7 (2F, t)	−159.2 (2F, t)
	7.41 (4H, t)	7.05 (4H, t)	6.45 (1H, d)	−143.9 (2F, t)	−160.4 (2F, t)
	7.38 (2H, d)	6.85 (1H, t)	6.35 (1H, t)	−154.8 (2F, t)	−160.8 (4F, q)
(2,2)	9.31 (4H, d)	7.09 (2H, t)	6.65 (4H, d)	−145.2 (8F, d)	−163.6 (8F, t)
	7.34 (8H, m)	6.90 (4H, d)	6.55 (4H, t)	−159.1 (4F, t)	

[a] s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.

(1.212 Å) and between C(53) and C(54) (1.211 Å) (Table 2), while the Ru(2)−Ru(1)−C(45) and Ru(1)−Ru(2)−C(53) units have almost the same angles (see Table 3). This could also suggest that electronic effects play an important role in the structure.

^{1}H and ^{19}F NMR Characterization. Well-defined ^{1}H and ^{19}F NMR spectra are obtained for the three isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$, indicating that the compounds are all diamagnetic. A summary of ^{1}H and ^{19}F NMR data is presented in Table 4. Ten distinct ^{1}H NMR resonances are seen for the (4,0) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$. The four occurring at 9.85, 8.18, 4.54, and 4.11 ppm show an integration representative of four H's and can be assigned to the four nonequivalent pyridyl protons of the equatorial ligands. Due to the different electronic environment created by the totally polar arrangement of the four equatorial ligands in the (4,0) isomer, chemical shifts of the protons on each of the phenyl rings in the axial ligand of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ differ from one another, thus appearing in pairs.

The magnitude of the related chemical shifts in the ^{1}H NMR spectrum of the (3,1) and (2,2) trans isomers is similar to that found in the ^{1}H NMR spectrum of the (4,0) isomer. The ^{1}H NMR spectrum of the (3,1) isomer shows nine doublets and six triplets while that of the (2,2) trans isomer exhibits three doublets and two triplets. The NMR data clearly indicate that the four bridging F_5ap ligands, as well as the two $-C{\equiv}CC_6H_5$ axial ligands, are identical in the (2,2) trans isomer, giving four nonequivalent pyridyl protons and three nonequivalent axial phenyl protons. The two equatorial ligands in the trans position of the (3,1) isomer are equivalent but the other two equatorial ligands and the two axial ligands are not equivalent in this compound.

The three isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ were also characterized by ^{19}F NMR. The ^{19}F NMR spectrum of the (4,0) isomer shows five peaks at −134.0, −143.2, −153.8, −158.3, and −158.5 ppm. This implies that the fluorine atoms of the pentafluorophenyl ring are nonequivalent due to restricted rotation, which is also observed in the X-ray structure. As illustrated in Table 4, the ^{19}F NMR spectrum of the (3,1) isomer shows more resonances than the spectrum of the (4,0) or (2,2) trans isomer. Also, the ^{19}F NMR spectrum of the (2,2) trans isomer displays only three peaks with a ratio of 1:2:2, which indicates that there is a free rotation of the pentafluorophenyl rings, thus making the two ortho and two meta fluorines equivalent.

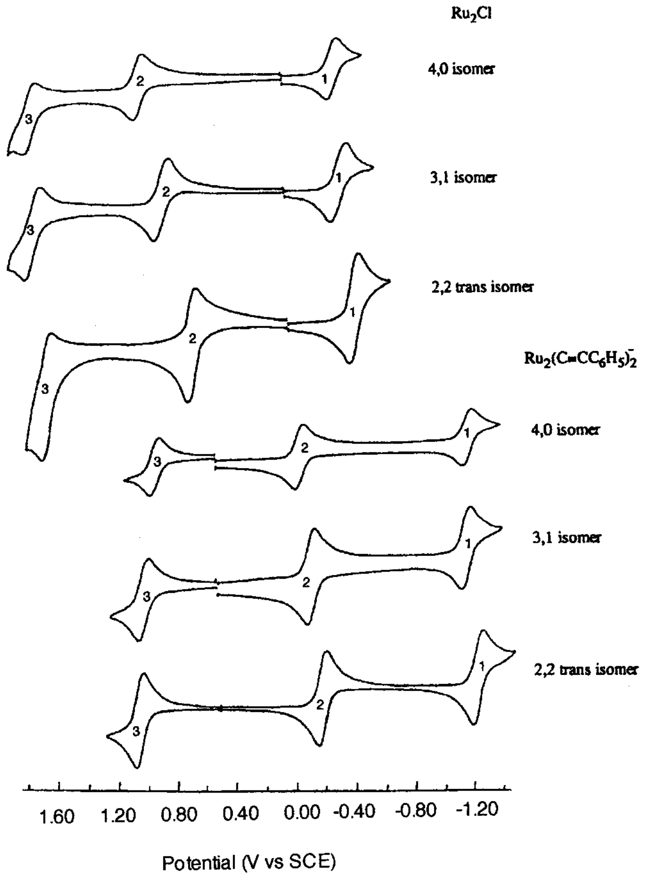


Figure 3. Cyclic voltammograms of each investigated isomer of $Ru_2(F_5ap)_4Cl$ and $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ in CH_2Cl_2 containing 0.1 M TBAP. Scan rate = 0.1 V/s.

Electrochemistry. Four oxidation states are possible for each of the six investigated compounds. A stepwise interconversion between the compounds with Ru_2^{7+}, Ru_2^{6+}, Ru_2^{5+}, or Ru_2^{4+} cores can be accomplished by the redox reactions shown in (1)−(3).

$$Ru_2^{5+} + e \rightleftharpoons Ru_2^{4+} \tag{1}$$

$$Ru_2^{6+} + e \rightleftharpoons Ru_2^{5+} \tag{2}$$

$$Ru_2^{7+} + e \rightleftharpoons Ru_2^{6+} \tag{3}$$

Cyclic voltammograms of the three isomers of $Ru_2(F_5ap)_4Cl$ and $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ in CH_2Cl_2 are shown in Figure 3, and a summary of half-wave potentials for each electrode reaction is given in Table 5. Each complex undergoes three reversible reactions. The three isomers of $Ru_2(F_5ap)_4Cl$ undergo two one-electron oxidations (reactions 2 and 3) and a single one-electron reduction (reaction 1) while the three isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ undergo a single one-electron oxidation

Table 5. Half-Wave Potentials of Investigated Compounds in CH_2Cl_2, 0.1 M TBAP

compd	isomer	$E_{1/2}$, V vs SCE[a] Ru_2^{7+}/Ru_2^{6+} (reaction 3)	Ru_2^{6+}/Ru_2^{5+} (reaction 2)	Ru_2^{5+}/Ru_2^{4+} (reaction 1)
$Ru_2(F_5ap)_4Cl$	(4,0)	1.68	0.95	−0.35
	(3,1)	1.61	0.78	−0.35
	(2,2) trans	1.59	0.63	−0.45
$Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$	(4,0)	0.90	−0.05	−1.18
	(3,1)	1.00	−0.14	−1.20
	(2,2) trans	1.04	−0.18	−1.21
$Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)$	(4,0)		0.80	−0.53

[a] See Figure 3 for labeling of reactions 1−3.

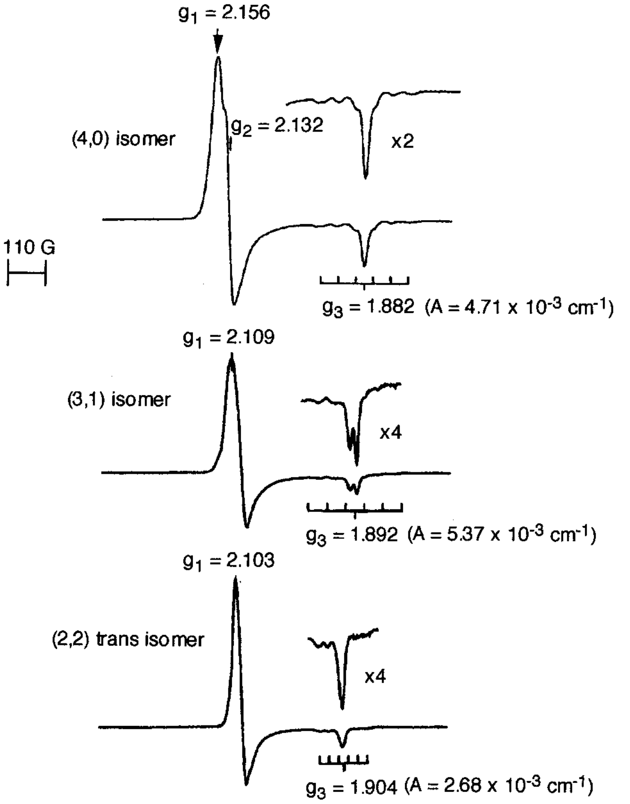


Figure 4. ESR spectra (77 K) in CH_2Cl_2, 0.2 M TBAP of the electrogenerated (4,0), (3,1), and (2,2) trans isomers of $[Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2]^-$.

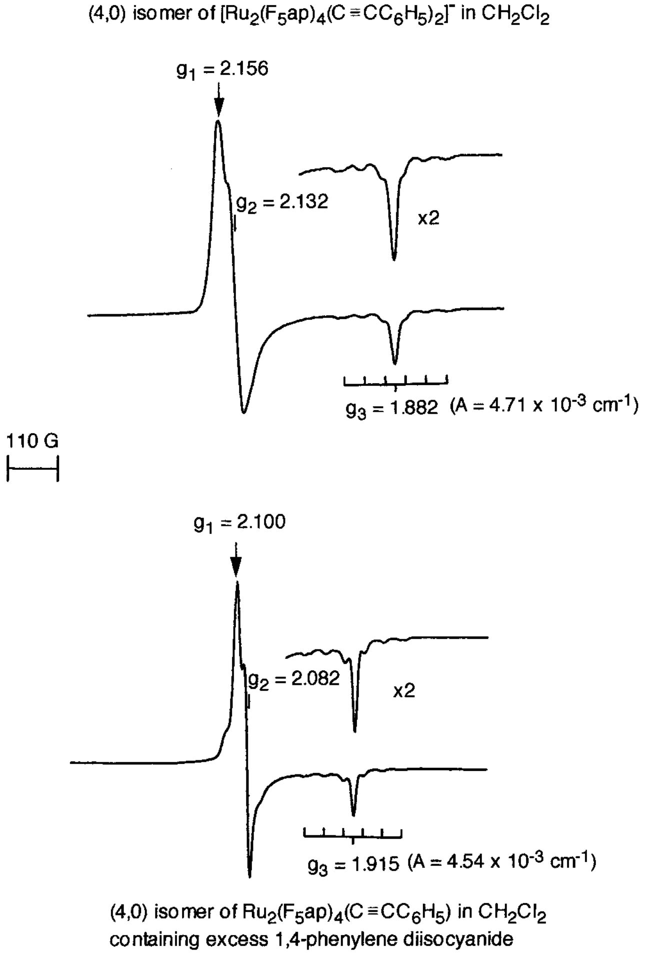


Figure 5. ESR spectra (77 K) of the electrogenerated (4,0) isomer of $[Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2]^-$ in CH_2Cl_2, 0.1 M TBAP and $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)$ in CH_2Cl_2 containing excess 1,4-phenylene diisocyanide.

(reaction 3) and two one-electron reductions (reactions 2 and 1) under the same solution conditions.

By comparing the cyclic voltammograms of the monochloro and bis(phenylacetylide) compounds, one can illustrate how the metal-centered molecular orbitals (HOMO and LUMO) are sensitive to the donor/acceptor properties and number of axial ligands. The average difference in $E_{1/2}$ between the monochloro and the corresponding bis(phenylacetylide) compound is 0.65 V for reaction 3, 0.91 V for reaction 2, and 0.81 V for reaction 1. Thus, the Ru_2^{6+}/Ru_2^{5+} process has the largest variation in half-wave potentials while the Ru_2^{6+}/Ru_2^{7+} process has the smallest.

The $E_{1/2}$ of a given electrode reaction is also dependent upon the type of isomer with the largest variation being seen in the case of the Ru^{6+}/Ru^{5+} reaction of the monochloro compound (reaction 2). As seen in Table 5, the $E_{1/2}$ for the first oxidation of $Ru_2(F_5ap)_4Cl$ shifts cathodically by 170 mV upon going from the (4,0) to the (3,1) isomer and by another 150 mV upon going from the (3,1) to the (2,2) trans isomer. This contrasts with reactions 1 and 3 of $Ru_2(F_5ap)_4Cl$ where $E_{1/2}$ shifts by only *ca.* 100 mV upon going from the (4,0) to the (2,2) trans isomer (see Table 5). A small isomer effect on $E_{1/2}$ is also seen for all three electrode reactions of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ (see $E_{1/2}$ values in Table 5).

ESR of Electrogenerated $[Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2]^-$. $Ru_2(F_5ap)_4Cl$ contains three unpaired electrons as evidenced by the fact that the solid compound has a room-temperature magnetic moment of 3.94 μ_B. This result is consistent with a ground state electronic configuration of $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$. The three isomers of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ are unambiguously diamagnetic (as shown by their well-defined ^1H and ^{19}F NMR spectra), and no ESR signals could be observed between room temperature and 77 K. This is not the case, however, for the singly reduced products of the (4,0), (3,1), or (2,2) trans isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2$ in CH_2Cl_2, 0.1 M TBAP which can be electrogenerated by bulk electrolysis of the neutral isomers at −0.60 V under argon.

The 77 K ESR spectrum of each $[Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2]^-$ isomer is shown in Figure 4. Interestingly, the (4,0) isomer of $[Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2]^-$ exhibits a rhombic signal while the (3,1) and (2,2) trans isomers both show an axial signal. However, all ESR spectra in Figure 4 are characteristic of species containing one rather than three unpaired electrons since, in the latter case, either no signal or a broad and ill-resolved ESR spectrum is observed.[1,32]

As shown in Figure 4, the g_3 component in the ESR spectrum of each isomer consists of two signals which arise from the two isotopes of the ruthenium atoms. One isotope has a spin constant of $^5/_2$ (29.8%) and has a six-line hyperfine splitting, while the other has a spin constant of 0 (70.2%) and appears as a singlet. The singlet signal is the most intense owing to the natural abundance of the isotope population of the ruthenium atoms. Interestingly, the most intense signal in the g_3 component of the (3,1) isomer of $[Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2]^-$ does not appear as a single peak, as is the case of the (4,0) or (2,2) trans isomer (see Figure 4), but rather is split into two closely-spaced peaks of unequal magnitude. The origin of the splitting is not known, but a similar splitting is also seen in at least one dirhodium complex where the single unpaired electron can be either localized on one rhodium atom or delocalized over the two rhodium metals.[28]

It should also be pointed out that all but one previously reported Ru_2^{5+} complex of the structural type investigated in this study have three unpaired electrons. The only exception is $Ru_2[(p\text{-tolyl})NNN(p\text{-tolyl})]_4(CH_3CN)(BF_4)$ ((*p*-tolyl)NNN(*p*-tolyl) = di-*p*-tolyltriazenate) which is ESR silent from room temperature to 77 K[33] but has one unpaired electron and an electronic configuration of $\sigma^2\pi^4\delta^2\pi^{*3}$. The lack of an ESR signal for this species is due to an extremely fast relaxation time when the unpaired electron is in an orbital doublet, i.e. when the ground state is an orbitally degenerate ^2E_g state.

Several experiments were performed in order to determine whether correlations might exist between the nature of the axial ligand and the magnetic properties of the diruthenium(II,III) complexes. For instance, it was observed that addition of more than 100 equiv of 1,4-phenylene diisocyanide to a CH_2Cl_2 solution of the (4,0) isomer of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)$ leads to an ESR spectrum (77 K) which is similar to that of $[Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)_2]^-$ (see Figure 5). On the other hand, no ESR spectrum was observed when methanol, CH_3CN, or F^-, was added to a CH_2Cl_2 solution of $Ru_2(F_5ap)_4(C{\equiv}CC_6H_5)$. The 1,4-phenylene diisocyanide ligand is similar to the acetylide ion in that both are good σ donors and π acceptors. This is not the case for CH_3OH, CH_3CN, and F^-, which are mainly σ donors. Our data thus imply that the Ru_2^{5+} species should show an ESR spectrum only if each ruthenium ion were complexed by an axial ligand which is both a good σ donor and a good π acceptor.

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 Dr. J. D. Korp for X-ray crystallography.

Supporting Information Available: Tables of data collection parameters, atomic coordinates, 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 (72 pages). Ordering information is given on any current masthead page.

IC9602658

---

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

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