Synthesis and Characterization of Formyl and Hydroxymethyl Complexes Derived from Isomeric Cations: *cis*-Ru(N−N)(η^2-tpy)$(CO)_2^{2+}2PF_6^-$ (N−N = 2,2′-Bipyridine, 4,4′-Dimethyl-2,2′-bipyridine; tpy = 2,2′:6′,2″-Terpyridine)

Dorothy H. Gibson,* Jose G. Andino, Srinivas Bhamidi, Bradley A. Sleadd, and Mark S. Mashuta

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

Received June 14, 2001

High-yield syntheses of the novel cations *cis*-Ru(N−N)(η^2-tpy)$(CO)_2^{2+}2PF_6^-$ (**2a**,**b**: N−N = 2,2′-bipyridine, tpy = 2,2′:6′,2″-terpyridine; **5a**,**b**: N−N = 4,4′-dimethyl-2,2′-bipyridine) have been developed. Compounds **2a** and **5a** are produced from reactions of *cis*-Ru(tpy)$(CO)_2(CH_3CN)^{2+}2PF_6^-$ (**9**) with the appropriate bipyridine. Their linkage isomers, **2b** and **5b**, are produced by thermolysis of **2a** and **5a**. Procedures are described for the sodium borohydride reductions of **2a**,**b** and **5a**,**b** to the corresponding formyl (**3a**,**b** and **6a**,**b**) and hydroxymethyl (**4a**,**b** and **7a**,**b**) derivatives. Compounds **2a**, **2b**, **5b**, and **4a** have been characterized by X-ray crystallography. The possible intermediacy of some of these compounds in catalytic reductions of CO_2 leading to glyoxylic or glycolic acid is discussed.

Introduction

Ruthenium and rhenium complexes containing chelating bipyridyl (bpy) and related ligands have been studied by electrochemists and photochemists for many years[1] and are effective as catalysts for the reduction of CO_2 to formate and CO primarily, with formaldehyde being generated in small amounts in some reactions.[2] Recently, Tanaka and co-workers[3] have observed the C_2 products glyoxylic acid, H(O)C−C(O)OH, and glycolic acid, $HOCH_2$−C(O)OH, in addition to CH_2O, formic acid and methanol from electrocatalytic reactions involving Ru(bpy)(tpy)$(CO)^{2+}2PF_6^-$ (bpy = 2,2′-bipyridine, tpy = 2,2′:6′,2″-terpyridine) with CO_2 in aqueous ethanol media. Except for reports of low yields of ethylene,[4] oxalate derivatives,[5] and ethanol,[6] this represents a significant departure for catalytic reductions of CO_2. It is recognized that electrocatalytic processes cannot provide routes to large-scale CO_2 conversion; solar energy-based processes are preferred. However, electron transfer reactions involving polypyridyl compounds can frequently be accomplished via charge-separated states generated photochemically.[1n] Effective catalysts must be coupled to photovoltaic devices capable of delivering electrons.

Rhenium or ruthenium polypyridine complexes with C_1 ligands, formyl complexes, M−CHO, hydroxymethyl complexes, $M-CH_2OH$, and metallocarboxylic acids, M−COOH, are the types of compounds suggested as intermediates in the catalytic reactions, but were little

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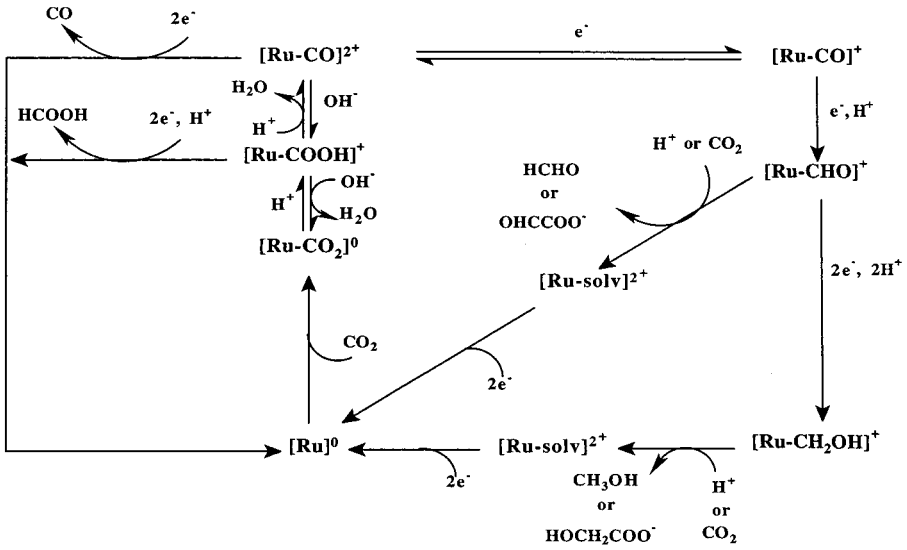
10.1021/om010520i CCC: $20.00
Publication on Web 10/13/2001

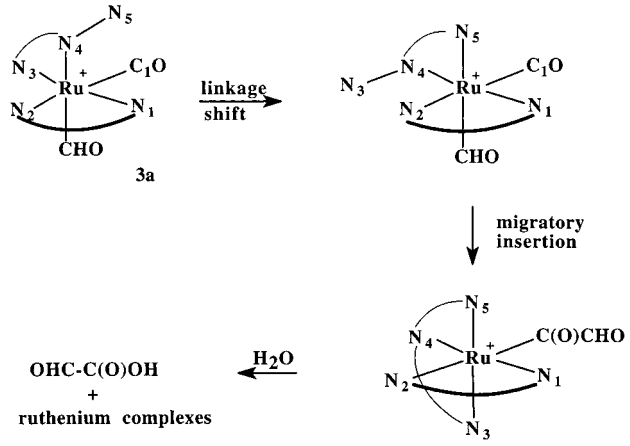
Scheme 1



[Ru-CO]+2 = Ru(bpy)(tpy)(CO)+2

known until recently.[7] In hopes of increasing the understanding of the catalytic processes and improving them, we have concentrated on the synthesis of these classes of compounds with both rhenium and ruthenium and studies of their reaction characteristics. Most recently, we have turned our attention to C_1 ruthenium complexes bearing both bipyridine and terpyridine ligands. The catalytic cycle proposed by the Tanaka group[3] (Scheme 1) for the production of C_2 compounds includes several steps which are currently without precedent in organometallic chemistry. In particular, while insertions of carbon dioxide into electron-rich metal carbon bonds are well known,[8] there have been no reports of CO_2 insertions into metal−carbon bonds of the M−CHO or M−CH_2OH types that are required in the latter stages of the cycle in Scheme 1 leading to C_2 products. Thus, we have tried to define a possible route to these products from other intermediates which could be formed from the same starting material, Ru(bpy)(η^3-tpy)(CO)$^{2+}$2PF_6^- (**1**), under the conditions of the catalytic reactions. A more likely route to the C_2 products seems possible through the two isomeric dicarbonyl cations with a bidentate tpy ligand, *cis*-Ru(bpy)(η^2-tpy)$(CO)_2^{2+}$2PF_6^- (**2a**,**b**), which could be generated in the electrocatalytic reactions from **1** and CO_2 as the result of reverse water-gas shift chemistry.[9] A synthesis of cation **2b** was reported several years ago by Thomas et al.[10] Although it was recognized that two isomers were possible, its linkage isomer,[11] **2a**, has not been identified previously. Assuming that catalytic

Scheme 2



N_1-N_2 = 2,2'-bipyridine; N_3-N_4-N_5 = 2,2':6',2''-terpyridine

reductions of these cations would provide a single product in each case, the formyl and hydroxymethyl complexes, Ru(bpy)(η^2-tpy)(CO)(CHO)$^+PF_6^-$ (**3a**,**b**) and Ru(bpy)(η^2-tpy)(CO)(CH_2OH)$^+PF_6^-$ (**4a**,**b**), respectively, would be formed. Some of these compounds could be the precursors to the observed C_2 products as suggested with the sequence of reactions beginning with the isomer identified as **3a** (the stereochemistry of this isomer is discussed in section 2 below) in Scheme 2 and leading, eventually, to glyoxylic acid (similar reactions from **4a** may yield glycolic acid). Since the exact catalytic sequence is currently unknown, all of the complexes are of interest. The critical steps of carbon−carbon bond formation needed in our proposed paths, by CO insertion, are precedented for hydroxymethyl complexes[12] and for acyl complexes[13] (although not specifically for formyl complexes). Also, there is recent precedent for migratory CO insertion driven by an η^2-

(8) (a) Darensbourg, D. J.; Fisher, M. B.; Schmidt, R. E., Jr.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297. (b) Darensbourg, D. J.; Kudaroski, R. *J. Am. Chem. Soc.* **1984**, *106*, 3672. (c) Shi, M.; Nicholas, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 5057.

(9) (a) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139. (b) Torrent, M.; Solá, M.; Frenking, G. *Chem. Rev.* **2000**, *100*, 439.

(10) Cation **2b** was prepared previously (Thomas, N. C.; Fischer, J. *J. Coord. Chem.* **1990**, *21*, 119); the protonated form of the phenanthroline analogue was characterized by X-ray crystallography.

(11) The term "linkage isomerization" has been applied previously to describe the fluxional behavior of Re(η^2-tpy)$(CO)_3$Cl; see: Civetello, E. R.; Dragovitch, P. S.; Karpishin, T. B.; Novick, S. G.; Bierach, G.; O'Connell, J. F.; Westmoreland, T. D. *Inorg. Chem.* **1993**, *32*, 237. In that context, compounds **2a**,**b** (and **5a**,**b**) are described as linkage isomers.

(12) (a) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353. (b) Vaughn, G. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1473. (c) There is one further hydroxymethyl complex that inserts CO, but the reaction pathway may involve radical species. See: van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887.

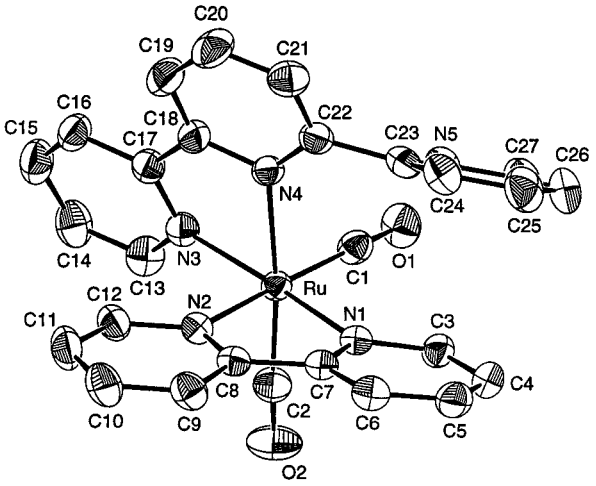


Figure 1. ORTEP drawing of **2a** with thermal ellipsoids shown at the 50% probability level.

coordinated terpyridine.[14] Linkage isomerization for η^2-terpyridine (as shown in Scheme 2) has been demonstrated previously.[11,15] Finally, hydrolytic cleavage of the metal−acyl bond would yield glyoxylic acid; such hydrolysis reactions also have precedent.[14] The present work describes the synthesis and structural characterizations of **2a**,**b**, the characterizations of **3a**,**b** and **4a**,**b** (including the structural characterization of **4a**), and the synthesis and characterizations of the related compounds with a dmbpy (4,4′-dimethyl-2,2′-bipyridine) ligand instead of bpy: **5a**,**b** (**5b** has been structurally characterized), **6a**,**b**, and **7a**,**b**, respectively.

Results and Discussion

1. Synthesis and Characterization of the Dicarbonyl Cations, *cis*-Ru(bpy)(η^2-tpy)$(CO)_2^{2+}2PF_6^-$ (2a, b) and *cis*-Ru(dmbpy)(η^2-tpy)$(CO)_2^{2+}2PF_6^-$ (5a,b). The starting material for the synthesis of all four cations is derived from *cis*-Ru(tpy)$(CO)_2Cl^+PF_6^-$ (**8**), which we reported previously.[7i] Treatment of this compound with $AgBF_4$ in acetone,[16] followed by acetonitrile then by anion exchange, provided a compound formulated as *cis*-Ru(tpy)$(CO)_2(CH_3CN)^{2+}2PF_6^-$ (**9**) on the basis of elemental analysis and spectral data (see Experimental Section). Reaction of **9** with 2,2′-bipyridine afforded the dicarbonyl cation **2a** in high yield. Compound **2a** has been characterized by elemental analysis, spectral data, and X-ray structure determination.[17] The ORTEP diagram for **2a** is shown in Figure 1; crystallographic data are summarized in Table 1. Selected bond distances and bond angles are shown in Table 2. Compound **2a** exhibits slightly distorted octahedral geometry about the ruthenium center and shows two cis carbonyl ligands and a bidentate terpyridine ligand; the central nitrogen atom of the terpyridine ligand is trans to a carbonyl ligand in this isomer.[18] The distortion is also evidenced by the trans N(1)−Ru−N(3) bond angle which is significantly less, at 168.1(1)°, than 180° and by a greatly enlarged C(1)−Ru−N(1) bond angle of 98.0(2)°. Both of these appear to be caused by the compressed chelate angles of 77.8(1)° involving N(1)−Ru−N(2) and 77.7(1)° involving N(3)−Ru−N(4).

Compound **2a** can be converted to its linkage isomer, **2b**, by refluxing in acetone solution for 3 h followed by precipitation; prolonged reflux in acetone, beyond this time, will lead to significant conversion of **2b** to cation **1**. Compound **2b** was characterized by elemental analysis, spectral data, and X-ray crystallography.[17] The ORTEP diagram for **2b** is shown in Figure 2; crystallographic data are summarized in Table 1. Selected bond distances and bond angles are shown in Table 3. Compound **2b** also exhibits distorted octahedral geometry about the metal center and shows two cis carbonyl ligands and a bidentate terpyridine ligand. This isomer is easily distinguished from **2a** because the central nitrogen of the terpyridine is trans to a nitrogen of the bpy ligand rather than to CO as in **2a**. The trans N(1)−Ru−N(4) atoms are not linear, with a bond angle of 168.9(2)°. The bond angles in the cation bear a close similarity to those in the cation of Ru(phen)(η^2-tpy-H)$(CO)_2^{3+}3PF_6^-$, in which the pendant pyridine had been protonated.[10] The analogous trans N−Ru−N bond angle [N(12)−Ru−N(19)] in that cation was 167.4(1)°. The plane of the pendant pyridine ligand in **2b** is approximately parallel to a terminal carbonyl [C(2)−O(2)].

In similar fashion, the reaction of **9** with 4,4′-dimethyl-2,2′-bipyridine afforded **5a**, *cis*-Ru(dmbpy)(η^2-tpy)$(CO)_2^{2+}2PF_6^-$.[18] The compound was characterized by elemental analysis and spectral data.[19] Conversion of **5a** to its linkage isomer **5b** was accomplished by refluxing **5a** in CH_2Cl_2 solution for 48 h. Compound **5b** was characterized by elemental analysis, spectral data, and X-ray structure determination, which shows the same orientation of carbonyl and tpy ligands as does **2b**. The ORTEP diagram for **5b** is shown in Figure 3; crystallographic data are summarized in Table 1. Selected bond distances and bond angles are shown in Table 4. Compound **5b** also exhibits distorted octahedral geometry about the metal center and shows cis carbonyl ligands and a bidentate tpy ligand. As in **2b**, the middle nitrogen of the tpy ligand is trans to another nitrogen, and this trans N(1)−Ru−N(4) angle is greatly distorted from linearity at 165.8(2)°. Again, the pendant pyridine group is approximately parallel to a terminal carbonyl group [C(2)−O(2)].

Compounds **2a** and **2b** can be easily distinguished by examination of their ^{1}H NMR spectral data. Both compounds show two low-field doublets; in **2a** these

(13) (a) Sheridan, J. B.; Johnson, J. R.; Handwerker, B. M.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2404. (b) Geoffroy, G. L.; Sheridan, J. B.; Bussmer, S. L.; Kelley, C. *Pure Appl. Chem.* **1989**, *61*, 1723.

(14) Groen, J. H.; de Zwart, A.; Vlaar, M. J. M.; Ernsting, J. M.; van Leeuwen, P. W. N. M.; Vrieze, K.; Kooijman, H.; Smeets, W. J. J.; Spek, A. L.; Budzelaar, P. H. M.; Xiang, Q.; Thummel, R. P. *Eur. J. Inorg. Chem.* **1998**, 1129.

(15) (a) Abel, E. W.; Dimitrou, V. S.; Long, N. J.; Orrell, K. G.; Osbourne, A. G.; Sik, V.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Dalton Trans.* **1993**, 291.

(16) Our previous efforts to remove Cl^- from **8** by treatment with $AgBF_4$ were unsuccessful,[7i] possibly due to hydrolyzed reagent.

(17) Because of the pendant pyridine ligand in these complexes, each compound exists as a pair of enantiomers. The structure of only one enantiomer has been solved in each case.

(18) We have not been able to find precedent for the naming of compounds such as these which would specify the position of the pendant pyridine in **2a**,**b** or **5a**,**b**. We suggest the prefix *cis,syn-N* for **2a** (or **5a**) to indicate that the pendant pyridine is near to coordinated nitrogen; similarly, we suggest the prefix *cis,syn-C* to specify that the pendant pyridine in **2b** (or **5b**) is near to coordinated CO.

(19) Recently, a mixture of the two cations has been synthesized but could not be separated into the components: Fletcher, N. C.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1998**, 2293.

Table 1. Crystal Data and Refinement Parameters for 2a, 2b, 5b, and 4a

	2a	2b	5b	4a
empirical formula	$C_{27}H_{19}N_5O_2P_2F_{12}Ru$	$C_{27}H_{19}N_5O_2P_2F_{12}Ru\cdot 0.75(CH_3CH_2)_2O$	$C_{29}H_{23}N_5O_2P_2F_{12}Ru\cdot (CH_3)_2CO$	$C_{27}H_{22}N_5O_2PF_6Ru\cdot 0.5CH_3CN$
fw	836.48	876.5	922.58	713.55
cryst syst	triclinic	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$
a, Å	12.686(4)	12.798(4)	12.838(2)	12.6412(10)
b, Å	13.613(4)	14.334(5)	14.798(3)	16.6584(10)
c, Å	10.071(3)	11.184(3)	19.803(4)	15.4015(10)
a, deg	110.28(2)	98.44(2)	90	90
b, deg	104.73(2)	96.15(2)	90	112.513(10)
g, deg	97.43(3)	67.63(3)	90	90
V, Å^3	1532(1)	1873(1)	3762(2)	2996.1(4)
Z	2	2	4	4
D_{calcd}, mg/m^3	1.813	1.553	1.622	1.582
μ, mm^{-1}	0.726	0.600	0.602	0.650
θ range, deg	2.0−25.0	2.0−25.0	2.06−25.0	2.13−25.0
no. of reflns measd	5627	6898	3693	5509
no. of unique reflns (R_{int})	5377 (0.009)	6561 (0.023)	3691 (0.054)	5256 (0.028)
GOF	3.09	6.77	1.06	1.09
R, R_w ($I > 3\sigma I$)	0.045, 0.069	0.067, 0.082		
R1, wR2 (all)			0.065, 0.097	0.066, 0.137

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

Bond Distances			
C(1)−Ru	1.905(5)	N(3)−Ru	2.081(4)
C(2)−Ru	1.887(5)	N(4)−Ru	2.158(4)
N(1)−Ru	2.092(4)	C(1)−O(1)	1.148(6)
N(2)−Ru	2.118(4)	C(2)−O(2)	1.131(6)
Bond Angles			
Ru−C(1)−O(1)	176.7(4)	N(1)−Ru−N(2)	77.8(1)
Ru−C(2)−O(2)	175.8(5)	N(1)−Ru−N(3)	168.1(1)
C(1)−Ru−N(1)	98.0(2)	N(3)−Ru−N(4)	77.7(1)
C(1)−Ru−N(2)	175.4(2)	C(1)−Ru−C(2)	88.9(2)
C(2)−Ru−N(4)	173.7(2)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for 2b

Bond Distances			
C(1)−Ru	1.908(9)	N(3)−Ru	2.101(6)
C(2)−Ru	1.906(8)	N(4)−Ru	2.107(6)
N(1)−Ru	2.082(6)	C(1)−O(1)	1.126(9)
N(2)−Ru	2.124(6)	C(2)−O(2)	1.117(8)
Bond Angles			
Ru−C(1)−O(1)	176.8(7)	N(1)−Ru−N(2)	78.7(2)
Ru−C(2)−O(2)	174.5(7)	N(1)−Ru−N(4)	168.9(2)
C(1)−Ru−N(2)	173.7(3)	N(3)−Ru−N(4)	78.1(2)
C(2)−Ru−N(3)	175.8(3)	C(1)−Ru−C(2)	91.7(3)
C(2)−Ru-N(4)	99.6(3)		

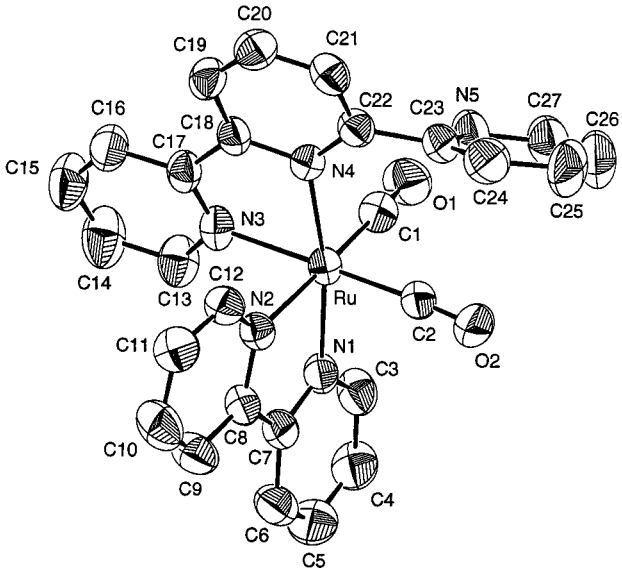


Figure 2. ORTEP drawing of **2b** with thermal ellipsoids shown at the 50% probability level.

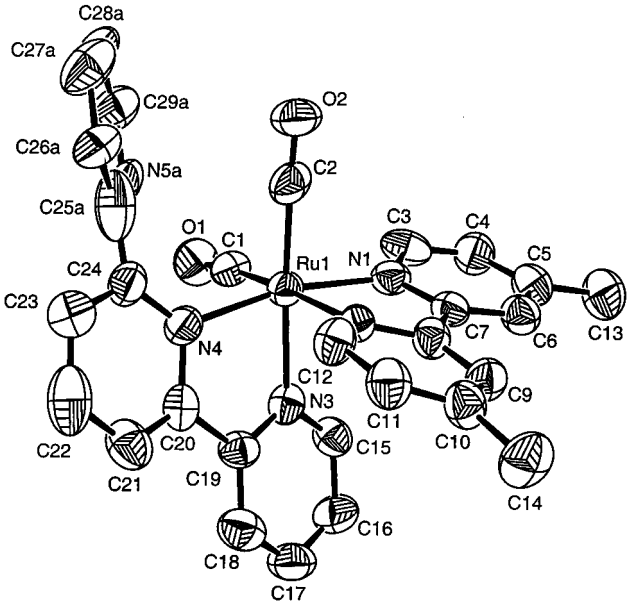


Figure 3. ORTEP drawing of **5b** with thermal ellipsoids shown at the 50% probability level.

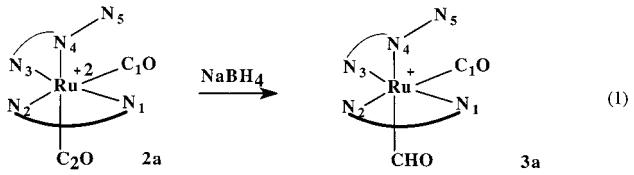
resonances are separated by approximately 0.4 ppm, whereas the doublets are closely spaced in **2b** with a separation of approximately 0.2 ppm. Compounds **5a** and **5b** can be distinguished in a similar fashion.

2. Synthesis and Characterization of the Formyl Complexes, Ru(bpy)(η^2-tpy)(CO)(CHO)$^+$PF$_6^-$ (3a,b) and Ru(dmbpy)(η^2-tpy)(CO)(CHO)$^+$PF$_6^-$ (6a,b). Treatment of cation **2a** in dry MeOH with a molar equiv of $NaBH_4$ in diglyme quickly afforded a yellow precipitate, which was purified and then characterized by elemental analysis and spectral means. The use of MeOH as a reaction solvent is important because it is necessary to precipitate the labile formyl complex from solution as quickly as possible, as observed with other such compounds.[20] The properties of the single product are in agreement with its formulation as Ru(bpy)(η^2-tpy)(CO)(CHO)$^+$PF$_6^-$ (**3a**). The IR spectrum showed the terminal carbonyl at 1948 cm^{-1} and the $\nu_{C=O}$ at characteristically low frequency (1621 cm^{-1}); NMR spectral

Table 4. Selected Bond Distances (Å) and Angles (deg) for 5b

Bond Distances			
C(1)−Ru	1.889(9)	N(3)−Ru	2.095(7)
C(2)−Ru	1.888(9)	N(4)−Ru	2.095(6)
N(1)−Ru	2.066(6)	C(1)−O(1)	1.141(9)
N(2)−Ru	2.102(5)	C(2)−O(2)	1.149(9)
Bond Angles			
Ru−C(1)−O(1)	175.6(7)	N(1)−Ru−N(2)	77.7(2)
Ru−C(2)−O(2)	175.6(8)	N(1)−Ru−N(4)	165.8(2)
C(1)−Ru−N(1)	99.1(3)	N(3)−Ru−N(4)	78.9(3)
C(1)−Ru−N(2)	173.9(3)	C(1)−Ru−C(2)	92.1(3)
C(2)−Ru−N(3)	176.3(3)		

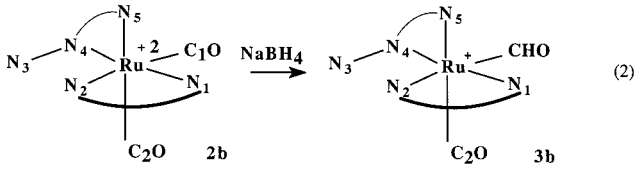
data showed a low-field singlet at δ 13.35 for the formyl proton and a low-field resonance at δ 259.53 for the formyl carbon, as are typical for such complexes.[7l,20] The NMR spectral data were obtained at low temperature because of the (typically) labile behavior of the compound in solution.[20] Compound **3a** could not be characterized by X-ray crystallography, but the structural arrangement of the ligands is likely to be analogous with that of the corresponding hydroxymethyl complex, **4a** (see below), which was prepared by borohydride reduction of the same cation. Thus, we expect that the CO group in **2a** which has been reduced is the one trans to the middle nitrogen of the tpy ligand, as shown in eq 1.



(1)

N_1-N_2 = 2,2'-bipyridine; N_3-N_4-N_5 = 2,2':6',2''-terpyridine

Reaction of **2b** with $NaBH_4$ in diglyme at 0 °C with MeOH as solvent again afforded a single formyl complex, **3b**, which was characterized through elemental analyis and spectral data. The IR spectrum showed the terminal carbonyl group at 1958 cm^{-1} and the formyl carbonyl at 1597 cm^{-1}; NMR spectral data showed the formyl proton as a singlet at δ 13.73 and the formyl carbon appeared at δ 265.40. Again the NMR spectral data were obtained at −10 °C because of the lability of the compound in solution. The stereochemistry of **3b** has not yet been established, but for steric reasons, we expect that **3b** has the geometry suggested in eq 2.



(2)

N_1-N_2 = 2,2'-bipyridine; N_3-N_4-N_5 = 2,2':6',2''-terpyridine

Compound **6a** was prepared from **5a** in the same manner described for **3a**,**b**. The compound was characterized by elemental analysis and by spectral data. The IR spectrum showed the terminal carbonyl at 1952 cm^{-1} and the formyl carbonyl at 1612 cm^{-1}; NMR spectral data, obtained at low temperature, showed the formyl proton at δ 13.38, and the formyl carbon appeared at δ 259.65. The stereochemistry of **6a** is not known with certainty, but is tentatively assigned as analogous to that of **3a**, with the formyl group being trans to the middle nitrogen of the terpyridine ligand because of the similarity in synthetic methodology (see eq 1).

Compound **6b** was obtained in similar manner and was characterized by elemental analysis and by spectral data. The IR spectrum showed the terminal carbonyl at 1950 cm^{-1} and the formyl carbonyl at 1592 cm^{-1}; NMR spectral data, obtained at low temperature, showed the formyl proton at δ 13.76, and the formyl carbon appeared at δ 265.98. Its structure has not been established, but is expected to be analogous to the one suggested for **3b** (see eq 2).

In most cases, we used approximately 1:1 molar ratios of $NaBH_4$ to cation in preparing the formyl complexes. However, since the number of hydride equivalents per mole of $NaBH_4$ is four, it is possible to use less less than an equimolar amount to convert the cation to the formyl complex. This was necessary with cation **3a**. After several trials, we settled on the procedure in the Experimental Section, which afforded the formyl complex quickly, in high yield, and without contamination by the hydroxymethyl complex (**4a**). Compounds **3a**,**b** and **6a**,**b** are significantly more labile in solution than their bis-bipyridine[7c,h] or bis-phenantroline[7l] analogues, and it is necessary to isolate them quickly.

3. Synthesis and Characterization of Hydroxymethyl Complexes, Ru(bpy)(η^2-tpy)(CO)(CH_2OH)$^+$-PF_6^- (4a,b) and Ru(dmbpy)(η^2-tpy)(CO)(CH_2OH)$^+$-PF_6^- (7a,b). Treatment of **2a**, in CH_3CN/H_2O, with excess $NaBH_4$ in diglyme afforded compound **4a**, which has been characterized by elemental analysis, spectral data, and X-ray crystallography. The IR spectrum showed ν_{OH} 3227 cm^{-1} as a broad peak and ν_{CO} at 1927 cm^{-1}. In CD_3CN, NMR spectra showed the methylene protons appeared as a singlet at δ 4.17 and the methylene carbon appeared at δ 63.62. In CD_3OD, the diastereotopic methylene protons appeared as a pair of doublets centered at δ 4.39 similar to those of the bis-bipyridine analogue.[7d] The hydroxyl proton could not be identified in spectra taken in either solvent. This is not unusual; $IrH(CH_2OH)(PMe_3)_4$[21] did not show a resonance for the hydroxyl proton in spectra recorded in CD_2Cl_2, but did show this proton when the spectrum was recorded in pyridine-d_5. The variable behavior is likely due to variations in line broadening resulting from hydrogen bonding. The ORTEP diagram for **4a** is shown in Figure 4; crystallographic data are summarized in Table 1. Selected bond distances and bond angles are shown in Table 5. Compound **4a** exhibits distorted octahedral geometry about the ruthenium center and shows the new hydroxymethyl group cis to the CO ligand. Also, the carbonyl that was reduced is the one trans to the middle nitrogen of the terpyridine ligand. The σ-donor hydroxymethyl group exerts a strong trans effect on the Ru−N(4) bond. At 2.250(4) Å, this ruthenium−nitrogen bond is more than 0.1 Å longer than the other Ru−N bonds in the molecule; this effect has been observed previously in ruthenium complexes with polypyridine ligands.[22] A PLUTO diagram (Figure 5), taken

(20) (a) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (b) Gibson, D. H.; Mandal, S. K.; Owens, K.; Richardson, J. F. *Organometallics* **1987**, *6*, 2624. (c) Gibson, D. H.; Owens, K.; Mandal, S. K.; Franco, J. O.; Sattich, W. E. *Organometallics* **1989**, *8*, 498.

(21) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580.

(22) See ref 7i and references therein.

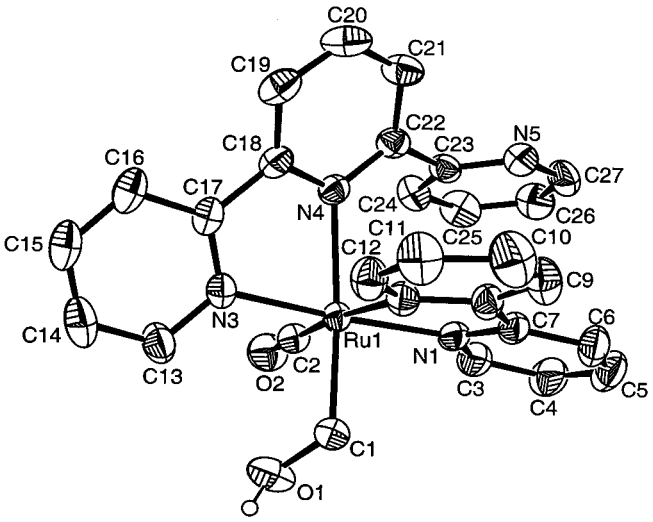


Figure 4. ORTEP drawing of **4a** with thermal ellipsoids shown at the 50% probability level.

Table 5. Selected Bond Distances (Å) and Angles (deg) for 4a

	Bond Distances		
C(1)−Ru	2.089(5)	N(3)−Ru	2.084(4)
C(2)−Ru	1.827(5)	N(4)−Ru	2.250(4)
N(1)−Ru	2.061(4)	C(1)−O(1)	1.422(6)
N(2)−Ru	2.135(4)	C(2)−O(2)	1.160(6)
	Bond Angles		
Ru−C(1)−O(1)	115.2(3)	N(1)−Ru−N(4)	100.62(14)
Ru−C(2)−O(2)	178.7(4)	N(2)−Ru−N(4)	81.91(14)
C(1)−Ru−N(4)	165.14(19)	N(3)−Ru−N(4)	76.40(14)
C(2)−Ru−N(2)	173.73(18)	C(1)−Ru−C(2)	89.5(2)
N(1)−Ru−N(3)	171.61(16)		

from the packing diagram for **4a**, illustrates the strong intermolecular hydrogen bonding between the hydroxyl proton of one molecule and the nitrogen of a pendant pyridine ligand in a second cation in an adjacent unit cell; the N−H bond distance is 2.08(3) Å.

Similar treatment of **2b** with excess $NaBH_4$ in acetonitrile/water afforded hydroxymethyl complex **4b**, which was characterized by elemental analysis and spectral data. The IR spectrum showed ν_{OH} bands at 3607 (s) and 3424 (br) cm^{-1}. In CD_3CN, ^1H NMR spectra showed the diastereotopic methylene protons as a broad singlet at δ 4.63 and a triplet at δ 4.31; the hyroxyl proton was visible at δ 3.39 as a broad singlet. The methylene carbon appeared at δ 62.64. In CD_3OD, the methylene protons showed a pattern similar to that in CD_3CN. In DMSO-d_6 they showed as a multiplet at δ 4.23 and a broad singlet at δ 4.15; the hydroxyl proton appeared as a broadened singlet at δ 3.78. The complexity of the resonances for the methylene protons may be a reflection of a preferred orientation of the hydroxyl group which makes the dihedral angles between the hydroxyl proton and each methylene proton different. We do not have structural data for **4b**, so the exact arrangement of ligands is not known; we assume that the carbonyl and hydroxymethyl groups remain cis since the two carbonyl groups in **2b** are cis.

Reaction of **5a** in acetonitrile with excess $NaBH_4$ in water afforded hydroxymethyl complex **7a**, which was characterized by elemental analysis and spectral data. The IR spectrum showed ν_{OH} as a sharp peak at 3584 cm^{-1} and ν_{CO} at 1920 cm^{-1}. The ^1H NMR spectrum showed the methylene protons as a doublet at δ 4.15.

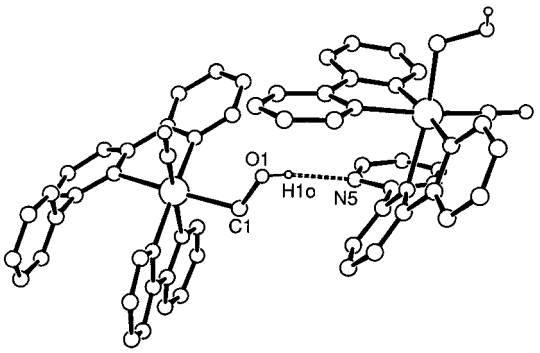


Figure 5. PLUTO diagram showing hydrogen bonding between adjacent molecules in **4a**.

The methylene carbon appeared at δ 63.41. In CD_3OD, however, the diastereotopic methylene protons appeared as a pair of doublets centered at δ 4.25. The hydroxyl proton could not be identified in ^1H NMR spectra. We assign the structure, tentatively and based on the similarities in synthetic methodology for cations **2a** and **5a**, as being analogous to that of **4a** (see Figure 4) with the hydroxymethyl ligand trans to the middle nitrogen of the terpyridine ligand.

Similarly, treatment of **5b** with excess $NaBH_4$ in acetonitrile/water afforded hydroxymethyl complex **7b**, which was characterized by elemental analysis and spectral data. The IR spectrum showed ν_{OH} as a broad band at 3327 cm^{-1} and ν_{CO} at 1923 cm^{-1}. In CD_3CN, NMR spectral data showed the methylene protons as a broad singlet at δ 4.64 and a multiplet at δ 4.27 (much the same as **4b**); the methylene carbon appeared at δ 63.41. The hydroxyl proton could not be identified. Again, we are not able to assign the structure precisely. Tentatively, we assume that the hydroxymethyl group and the carbonyl ligand are cis since the two carbonyl groups in **5b** are cis; the orientation of the terpyridine ligand relative to these is not known.

The amount of $NaBH_4$ used to reduce cations **2a**,**b** and **5a**,**b** to the hydroxymethyl derivatives has varied widely. The preparations of these compounds described in the Experimental Section represent optimized procedures obtained after numerous trials. As with the formyl complexes, our goal has been to obtain each hydroxymethyl complex as quickly as possible (to prevent degradation) and in high yield. Compound **7b** was particularly difficult, but the use of a 10:1 ratio of $NaBH_4$ to the cation was necessary to ensure rapid, and complete, conversion of cation **5b**.

Work is in progress to determine the reaction characteristics of compounds **3a**,**b**, **4a**,**b**, **6a**,**b**, and **7a**,**b**. These compounds are the first formyl and hydroxymethyl complexes of a metal bearing a terpyridine ligand to be characterized; the pendant pyridine group in these η^2-tpy complexes is expected to have impact on the chemistry of the compounds. In particular, we will try to establish their propensity for CO insertion reactions, which may set the stage for hydrolytic cleavage leading to glyoxylic acid or glycolic acid.

Experimental Section

General Data. Reagent grade solvents dichloromethane, acetone, and acetonitrile were used as received. Diethyl ether was distilled from sodium benzophenone; methanol was dis-

tilled from calcium hydride. CD_3CN was obtained from Cambridge Isotope Laboratories. $AgBF_4$, NH_4PF_6, 2,2′-bipyridine, 2,2′:6′,2″-terpyridine, and 4,4′-dimethyl-2,2′-bipyridine were obtained from Aldrich. Spectral data were obtained on the following instruments: NMR, Varian Unity Inova 500 MHz; FTIR, Mattson RS1. Diffuse-reflectance data were obtained on the Mattson instrument with a DRIFTS accessory (Graseby Specac Inc., "Mini-Diff") as KCl dispersions. ^1H and ^{13}C NMR spectra were referenced to residual deuterated solvents. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Ru(tpy)(CH_3CN)($CO)_2$($PF_6)_2$ (9). To a solution of 2.28 g (4 mmol) of Ru(tpy)($CO)_2$Cl(PF_6) (**8**)[7i] in acetone (500 mL) was added $AgBF_4$ (0.853 g; 4.4 mmol) in the minimum amount of methanol. The solution was stirred at room temperature for 4 h, and then solvent was evaporated. The resulting brown solid was triturated with CH_3CN, and then the mixture was filtered to remove residual AgCl. The filtrate was concentrated to effect precipitation of the product. This product was dissolved in CH_3CN, and an aqueous solution of NH_4PF_6 (0.640 g; 4.00 mmol) was added. The light yellow solid product was obtained upon partial removal of acetonitrile. Yield: 2.45 g; 85%. The compound can be recrystallized from CH_3CN/ether.

Anal. Calcd for $C_{19}H_{14}F_{12}N_4O_2P_2Ru$: C, 31.63; H, 1.96. Found: C, 31.71; H, 1.91. IR (DRIFTS, KCl): ν_{CN} 2329 and 2302 cm^{-1}, ν_{CO} 2106 and 2058 cm^{-1}. ^1H NMR (CD_3CN): δ 8.74 (2H, d, J = 5.5 Hz), 8.55 (3H, m), 8.50 (2H, d, J = 8.0 Hz), 8.34 (2H, t, J = 8.0 Hz), 7.77 (2H, t, J = 5.5 Hz), 2.02 (3H, s). ^{13}C NMR (CD_3CN): δ 191.65 (CO), 187.79 (CO), 159.07 (2C), 158.21 (2 C, quat.), 155.92 (2C, quat.), 144.10 (1C), 142.84 (2C), 130.33 (2C), 126.96 (2C), and 125.94 (2C). Resonances for the coordinated CH_3CN are masked by the solvent.

***cis*-Ru(bpy)(η^2-tpy)($CO)_2$($PF_6)_2$ (2a).** Compound **9** (0.30 g, 0.36 mmol) was placed in a 500 mL Erlenmeyer flask along with 0.65 g (4.16 mmol) of 2,2′-bipyridine. Then 400 mL of CH_2Cl_2 was added, and the solution was stirred at room temperature for 7 h. A white solid separated and was isolated by filtration, mp >260 °C. Yield: 0.20 g, 80%.

Anal. Calcd for $C_{27}H_{19}F_{12}N_5O_2P_2Ru$: C, 38.76; H, 2.29. Found: C, 38.96; H, 2.34. IR (DRIFTS, KCl): ν_{CO} 2096 and 2036 cm^{-1}. ^1H NMR (CD_3CN): δ 9.17 (d), 8.78 (s), 8.62 (d), 8.49 (t), 8.42 (d), 8.27 (d), 8.17 (m, 3H), 8.05 (d), 7.99 (t), 7.92 (t), 7.62 (t), 7.57 (d), 7.45 (m, 2H), 7.23 (d), 7.17 (d), 7.12 (t). ^{13}C NMR (CD_3CN): δ 191.66, 191.04, 161.78, 157.91, 157.42, 157.24, 156.90, 155.98, 155.52, 155.20, 150.75, 149.51, 143.09, 142.97, 142.92, 141.35, 139.78, 131.51, 129.94, 129.71, 129.41, 128.00, 126.72, 125.83, 125.71, 125.20, 124.36.

***cis*-Ru(bpy)(η^2-tpy)($CO)_2$($PF_6)_2$ (2b).** Compound **2a** (1.00 g, 1.20 mmol) was dissolved in 50 mL of acetone and refluxed for 3 h. The solution was concentrated to approximately half of its original volume, then 25 mL of water was added. This mixture was chilled at 0 °C for 1 h to precipitate the white product; it was collected by filtration and dried, mp >260 °C. Yield: 0.72 g, 72%.

Anal. Calcd for $C_{27}H_{19}F_{12}N_5O_2P_2Ru$: C, 38.76; H, 2.29. Found: C 38.46; H, 2.29. IR (DRIFTS, KCl): ν_{CO} 2096, 2036 cm^{-1}. ^1H NMR (CD_3CN): δ 9.05 (d), 8.91 (s), 8.67 (d), 8.55 (t), 8.49 (t, 2H), 8.40 (t), 8.34 (d), 8.21 (t), 8.11 (m, 3H), 8.01 (d), 7.89 (t), 7.69 (t), 7.51 (t, 2H), 7.39 (d), 7.26 (d). ^{13}C NMR (CD_3CN): δ 191.78, 189.42, 164.00, 158.05, 157.69 (2 carbons), 156.59. 156.38, 155.48, 151.15, 150.60, 150.09, 143.44, 143.06, 142.91 (2 carbons), 139.76, 131.55, 130.77, 129.94, 129.59, 127.33, 126.90, 126.86, 126.39, 126.31, 126.02.

Ru(bpy)(η^2-tpy)(CO)(CHO)(PF_6) (3a). Compound **2a** (0.30 g, 0.36 mmol) was placed in a 25 mL Schlenk flask under N_2. Then, dry methanol (1.5 mL) was added, and the slurry was stirred. $NaBH_4$ (0.5 M in diglyme) (0.5 mL, 0.25 mmol) was added, and the mixture was stirred for 1 min. The mixture became clear, and then a yellow solid quickly separated and was collected by filtration and washed with H_2O. After drying on the funnel, the product was dissolved in CH_3CN (1 mL) under N_2 and at 0 °C. Then it was precipitated by adding 10 mL of cold H_2O. The yellow solid product was collected by filtration and dried under vacuum, mp 127 °C. Yield: 0.22 g, 89%.

Anal. Calcd for $C_{27}H_{20}F_6N_5O_2PRu$: C, 46.82; H, 2.19. Found: C, 46.78; H, 2.55. IR (DRIFTS, KCl): ν_{CO} 1948 cm^{-1}; $\nu_{C=O}$ 1621 cm^{-1}. ^1H NMR (CD_3CN, −10 °C): δ 13.35 (s, CHO); 9.13 (d), 8.51 (d), 8.33 (t), 8.26 (m, 3H), 8.21 (d), 8.05 (d), 8.00 (m, 2H) 7.78 (t), 7.75 (t), 7.67 (t), 7.46 (d, 2H), 7.31 (d), 7.28 (t), 7.19 (t), 7.03 (t). ^{13}C NMR (CD_3CN, −10 °C): δ 259.53 (*C*HO); 202.71 (CO); 161.78, 158.54, 156.83, 155.90 (2C), 155.18 (3C), 150.50, 148.10, 140.68, 140.37, 140.32, 137.72, 137.67, 128.10, 127.66, 127.57, 127.30, 126.40, 125.31, 124.13, 123.93, 123.78, 123.73.

Ru(bpy)(η^2-tpy)(CO)(CHO)(PF_6) (3b). Compound **2b** (0.20 g, 0.24 mmol) was placed in a 15 mL Schlenk tube under N_2 at 0 °C. Dry methanol (0.5 mL) was added, and the slurry was stirred. $NaBH_4$ (0.5 M in diglyme) (0.50 mL, 0.25 mmol) was added, and the mixture was stirred for 1 min. The mixture became clear briefly, and then a yellow solid separated and was collected by filtration, washed with H_2O, and dried under vacuum. Yield: 0.12 g, 71%. The product was dissolved in CH_3CN (1 mL) under N_2 and at 0 °C, then precipitated by adding 10 mL of cold H_2O; the yellow solid was collected by filtration and dried under vacuum, mp 130 °C.

Anal. Calcd for $C_{27}H_{20}F_6N_5O_2PRu$: C, 46.82; H, 2.19. Found: C, 46.85; H, 2.51. IR (DRIFTS, KCl): ν_{CO} 1958 cm^{-1}; $\nu_{C=O}$ 1597 cm^{-1}. ^1H NMR (CD_3CN, −10 °C): δ 13.73 (s, 1, CHO); 9.08 (d), 8.59 (d), 8.55 (d), 8.49 (d), 8.42 (d), 8.32 (d), 8.25 (m, 2H), 8.18 (t), 8.08 (t), 8.01 (t), 7.91 (t), 7.75 (d), 7.67 (t), 7.64 (d), 7.45 (t), 7.41 (t), 7.31 (t), 7.17 (d). ^{13}C NMR (CD_3CN, −10 °C): δ 265.40 (CHO), 199.29 (CO), 164.77, 160.00, 157.94, 157.41, 156.14, 154.70, 154.07, 152.20, 150.38, 148.27, 140.55, 140.10, 139.97, 139.38, 138.30, 129.00, 127.95, 127.87, 127.51, 125.81, 125.28, 125.20, 125.08, 124.77, 123.83.

Ru(bpy)(η^2-tpy)(CO)(CH_2OH)(PF_6) (4a). Compound **2a** (0.10 g, 0.12 mmol) was placed in a test tube. Then, CH_3CN (3 mL) and H_2O (3 mL) were added. To this solution, $NaBH_4$ (0.5 M in diglyme) (1 mL, 0.50 mmol) was added, and the mixture was stirred for 30 min. The red mixture, containing a small amount of black solid, was filtered, and the filtrate was concentrated under vacuum to precipitate the product. The red product was collected by filtration and dried under vacuum, mp 134 °C. Yield: 0.074 g, 89%.

Anal. Calcd for $C_{27}H_{22}F_6N_5O_2PRu$: C, 46.69; H, 3.19. Found: C, 46.87; H, 3.31. IR (DRIFTS, KCl): ν_{OH} 3277 (br) cm^{-1}, ν_{CO} 1927 cm^{-1}. ^1H NMR (CD_3CN): δ 9.41 (d), 8.49 (d, 2H), 8.30 (m, 3H), 8.21 (s, 2H), 8.13 (d, 2H), 7.96 (t), 7.71 (m, 2H), 7.55 (d), 7.43 (d), 7.24 (m, 2H), 7.16 (d), 6.94 (d), 4.17 (s, 2H). ^{13}C NMR (CD_3CN): δ 204.95, 162.14, 159.42, 157.23, 155.99, 155.56, 155.47, 155.19, 155.01, 150.43, 147.91, 139.90, 139.84, 139.66, 137.54, 136.10, 127.54, 127.47, 127.17, 127.10, 126.05, 125.18, 124.48, 123.48, 123.72, 123.12, 63.62.

Ru(bpy)(η^2-tpy)(CO)(CH_2OH)(PF_6) (4b). Compound **2b** (0.30 g, 0.36 mmol) was placed in a test tube. Then, CH_3CN (6 mL) and H_2O (3 mL) were added, and the mixture was chilled to 0 °C. A solution of $NaBH_4$ (0.068 g, 1.80 mmol) in 2 mL of water was then added, and the mixture was stirred for 1 h. The mixture became a clear red solution during this time. The cold solution was then concentrated, under vacuum, to force precipitation of the product. The orange product was collected by filtration, then dried under vacuum: 0.20 g, 83% yield. The residue was redissolved in 5 mL of acetone, then hexane (2 mL) was added to precipitate the orange solid product, mp 119 °C.

Anal. Calcd for $C_{27}H_{22}F_6N_5O_2PRu$: C, 46.69; H, 3.19. Found: C, 46.91; H, 3.28. IR (DRIFTS, KCl): ν_{OH} 3607 (sharp), 3424 (br); ν_{CO} 1931 cm^{-1}. ^1H NMR (CD_3CN): δ 8.68 (d), 8.64 (s, br), 8.43 (d), 8.37 (d), 8.34 (d), 8.23 (d), 8.14 (dd), 8.00 (t),

7.98 (t), 7.93 (t), 7.78 (d), 7.72 (s, br), 7.67 (d), 7.63 (t), 7.54 (t), 7.35 (s), 7.30 (d), 4.63 (s, br), 4.31 (t), 3.39 (s, br). ^{13}C NMR (CD_3CN): δ 201.85, 163.96, 160.40, 158.94, 157.03, 155.70, 154.84, 153.47, 151.17, 150.46, 148.25, 140.01, 139.69, 139.37, 139.25, 137.93, 129.24, 128.10, 127.96, 127.92, 126.01, 125.29, 125.13, 124.46 (two carbons), 124.02, 63.46.

***cis*-Ru(dmbpy)(η^2-tpy)$(CO)_2(PF_6)_2$ (5a).** To a solution of **9** (0.360 g, 0.5 mmol) in 25 mL of acetone was added 4,4′-dimethyl-2,2′-dipyridine (0.140 g, 0.75 mmol). The solution quickly turned red, but was allowed to stir for 4 h. Solvent was then removed, and the crude product was recrystallized from acetone/methanol (1:3), affording a white crystals, mp 263 °C (dec). Yield: 0.320 g, 72%.

Anal. Calcd for $C_{29}H_{23}F_{12}N_5O_2P_2Ru$: C, 40.29; H, 2.68. Found: C, 40.22; H, 2.77. IR (DRIFTS, KCl): ν_{CO} 2092, 2041 cm^{-1}. ^{1}H NMR (CD_3CN): δ 9.15 (d), 8.76 (d), 8.61 (d), 8.48 (t), 8.42 (d), 8.20 (t), 8.12 (s), 8.05 (s), 7.92 (t), 7.85 (d), 7.69 (t), 7.57 (d), 7.48 (t), 7.26 (d), 7.16 (d), 7.05 (d), 6.90 (d), 2.48 (s, 3H, CH_3), 2.45 (s, 3H, CH_3). ^{13}C NMR (CD_3CN): δ 191.58, 191.03, 161.16, 157.46, 156.68, 156.43, 155.97, 155.44, 155.18, 154.95, 154.14, 153.67, 150.19, 148.10, 142.60, 142.38, 138.85, 131.02, 129.79, 129.34 (two resonances), 127.39, 126.37, 125.92, 125.69, 124.58, 123.94, 21.06, 20.85.

***cis*-Ru(dmbpy)(η^2-tpy)$(CO)_2(PF_6)_2$ (5b).** A suspension of **5a** (0.216 g, 0.25 mmol) in 250 mL of CH_2Cl_2 was refluxed for 48 h under nitrogen and gave a clear solution. The solvent was removed under vacuum, and the residue was triturated with 5−10 mL of methanol, which effected precipitation of an off-white solid product, mp 255 °C (dec). Yield: 0.204 g, 94%.

Anal. Calcd for $C_{29}H_{23}F_{12}N_5O_2P_2Ru$: C, 40.29; H, 2.68. Found: C, 40.17; H, 2.81. IR (DRIFTS, KCl): ν_{CO} 2097, 2041 cm^{-1}. ^{1}H NMR (CD_3CN): δ 8.91 (d), 8.85 (d), 8.60 (d), 8.56 (t), 8.50 (d), 8.33 (s), 8.23 (t), 8.22 (s), 8.11 (m, 2H), 7.99 (d), 7.70 (m, 2H), 7.52 (t), 7.38 (d), 7.31 (d), 7.08 (d), 2.65 (s, 3H, CH_3), 2.45 (s, 3H, CH_3). ^{13}C NMR (CD_3CN): δ191.82, 189.67, 163.90, 158.02, 157.59, 156.49, 156.32, 156.28, 155.94, 155.87, 154.90, 151.03, 149.83, 149.50, 143.22, 142.78, 139.60, 131.36, 131.21, 130.22, 129.39, 127.38, 127.17, 126.63, 126.43, 126.18, 126.08, 21.52, 21.36.

Ru(dmbpy)(η^2-tpy)(CO)(CHO)(PF_6) (6a). To a stirred suspension of **5a** (0.086 g; 0.1 mmol) in 1 mL of dry methanol, at 0 °C and under nitrogen, was added $NaBH_4$ (0.5 M solution in diglyme: 200 μL, 0.1 mmol). The suspended solid turned green. After stirring the suspension for 2 min, the product was collected by filtration and washed with cold water. The solid was then dissolved in 3 mL of cold acetonitrile (−30 °C) and 15 mL of cold water was added to precipitate the product. The mixture was allowed to warm to room temperature, and the product was collected by filtration as bright yellow solid, mp 146 °C (dec). Yield: 0.058 g, 81%.

Anal. Calcd for $C_{29}H_{24}F_6N_5O_2PRu$: C, 48.33; H, 3.36. Found: C, 48.03; H, 3.37. IR (DRIFTS, KCl): ν_{CO} 1952, $\nu_{C=O}$ 1612 cm^{-1}. ^{1}H NMR (CD_3CN, −10 °C): δ 13.38 (s, 1H, CHO), 9.15 (d), 8.50 (d), 8.31 (m, 3H), 8.10 (d), 8.07 (s), 8.01 (t), 7.92 (s), 7.74 (t), 7.69 (t), 7.50 (d), 7.47 (d), 7.22 (t), 7.18 (d), 7.12 (d), 6.85 (d), 2.42 (s, 3H, CH_3), 2.43 (s, 3H, CH_3). ^{13}C NMR (CD_3CN, −10 °C): δ 259.65, 202.62, 161.58, 158.38, 156.72, 154.96 (3 resonances), 154.63, 153.02, 150.10 (2 resonances), 149.78, 147.15, 140.13, 140.02, 137.44, 128.60, 128.00, 127.38, 127.03, 126.14, 125.03, 124.32, 124.14, 124.06, 123.48, 21.02, 20.62.

Ru(dmbpy)(η^2-tpy)(CO)(CHO)(PF_6) (6b). To a stirred suspension of **5b** (0.086 g; 0.1 mmol) in 1 mL of dry methanol, at 0 °C and under nitrogen, was added $NaBH_4$ (0.5 M solution in diglyme: 200 μL, 0.1 mmol). After stirring for 2 min, the yellow product was collected by filtration and washed with cold water. The product was then dissolved in 5 mL of cold (−30 °C) acetonitrile, under nitrogen, and 20 mL of cold (0 °C) water was added to precipitate the product. This mixture was allowed to warm to room temperature, then the product was collected, washed with cold water, and finally dried under vacuum, mp 158 °C (dec). Yield: 0.052 g, 72%.

Anal. Calcd for $C_{29}H_{24}F_6N_5O_2PRu$: C, 48.33; H, 3.36. Found: C, 48.01.01; H, 3.48. IR (DRIFTS, KCl): ν_{CO} 1950, $\nu_{C=O}$ 1592 cm^{-1}. Anal. Calcd for $C_{29}H_{24}F_6N_5O_2PRu$: C, 48.33; H, 3.36. Found: C, 48.01; H, 3.48. ^{1}H NMR (CD_3CN, −30 °C): δ 13.76 (s, 1H, CHO), 8.85 (d), 8.58 (t), 8.56 (s), 8.50 (d), 8.39 (s), 8.26 (t), 8.20 (s), 8.09 (t), 8.01 (s), 7.91 (t), 7.74 (d), 7.61 (d), 7.49 (m, 2H), 7.32 (t), 7.25 (s), 7.16 (s), 2.55 (s, 3H, CH_3), 2.42 (s, 3H, CH_3). ^{13}C NMR (CD_3CN; −30 °C): δ 265.98, 199.13, 164.14, 159.53, 156.80, 155.59, 153.22, 153.16, 152.22, 151.76, 150.92 (2 resonances), 149.86, 147.55, 140.07, 138.80, 137.80, 128.46, 128.17, 127.73, 127.35, 125.49, 125.34, 124.73, 124.55, 124.26, 124.01, 20.74, 20.70.

Ru(dmbpy)(η^2-tpy)(CO)$(CH_2OH)(PF_6)$ (7a). To a solution of cation **5a** (0.173 g, 0.20 mmol) in CH_3CN (10 mL) was added $NaBH_4$ (0.076 g, 0.20 mmol) dissolved in 2 mL of water. The solution turned green immediately after the addition but gradually turned red. The mixture was allowed to stir for 2 h, then concentrated to about one-third of its original volume. Water (10 mL) was added dropwise to precipitate **7a** as a red solid, which was then collected by filtration and dried under vacuum. Yield: 0.112 g, 78%. An analytical sample was obtained by dissolving a sample of the compound in acetone, then layering the solution with hexane. A microcrystalline red solid formed quickly, mp 172 °C (dec).

Anal. Calcd for $C_{29}H_{26}F_6N_5O_2PRu$: C, 48.20; H, 3.63. Found: C, 48.29; H, 3.77. IR (DRIFTS, KCl): ν_{OH} 3584 (sharp), ν_{CO} 1920 cm^{-1}. ^{1}H NMR (CD_3CN): δ 9.42 (d), 8.47 (d), 8.32 (d), 8.25 (t), 8.09 (d), 7.99 (s), 7.96 (t), 7.84 (s), 7.72 (t), 7.58 (d), 7.45 (d), 7.21 (t), 7.10 (s), 7.06 (s), 6.76 (d), 4.17 (d), 2.41 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (CD_3CN, −10 °C): δ 204.95, 161.80, 159.22, 157.19, 155.80, 155.34 (2 resonances), 154.68, 154.42, 152.11, 150.01, 147.97, 147.01, 139.62, 139.33, 137.35, 128.23, 127.65, 127.27, 126.87, 125.89, 124.98, 124.52, 124.07, 123.54, 123.43, 63.33, 21.13, 20.69.

Ru(dmbpy)(η^2-tpy)(CO)$(CH_2OH)(PF_6)$ (7b). To **5b** (0.206 g, 0.24 mmol) in acetonitrile (15 mL) was added 0.091 g (2.4 mmol) of $NaBH_4$ in 2 mL of water at 0 °C. The orange-red solution was allowed to stir for 30 min. The ice bath was removed and the solution was stirred at room temperature for a further period of 2 h. Concentration of the solution to about one-third of the original volume followed by addition of 5 mL of water gave a bright red microcrystalline solid. The product was collected by filtration and dried under vacuum, mp 172 °C (dec). Yield: 0.125 g, 70%.

Anal. Calcd for $C_{29}H_{26}F_6N_5O_2PRu$: C, 48.20; H, 3.63. Found: C, 48.09; H, 3.72. IR (DRIFTS, KCl): ν_{OH} 3327 (br), ν_{CO} 1923 cm^{-1}. ^{1}H NMR (CD_3CN): δ 8.70 (d), 8.40 (m, 3H), 8.21 (s), 8.14 (t), 8.10 (s), 8.05 (t), 8.00 (t), 7.78 (d), 7.66 (d), 7.53 (m, 2H), 7.46 (d), 7.37 (t), 7.30 (d), 7.16 (d), 4.64 (br s, 1H), 4.27 (m, 1H), 2.55 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (CD_3CN, −10 °C): δ 202.22, 163.72, 160.39, 158.39, 156.95, 155.65, 154.51, 152.37 (2 carbons), 151.68, 150.45, 150.32, 148.16, 140.02, 139.39, 137.80, 129.26, 128.91, 128.65, 127.93, 126.07, 125.87, 125.25, 124.73, 124.46, 124.42, 63.67, 21.34, 21.27.

X-ray Crystal Structure of 2a and 2b. Crystal data and experimental details are given in Table 1. Data were collected on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator, using the $\omega-2\theta$ scan technique. Structures were solved by direct methods (SIR92[23]), and crystallographic computations utilized the teXsan crystallographic software package (Molecular Structure Corporation).[24]

A yellow-orange crystal of **2a**, grown by diffusing diethyl ether over a CH_3CN solution of the compound, was mounted

(23) Altomare, A.; Burla, M. C.; Camalli, G.; Cascarano, G.; Giacovazzo, C.; Gualiardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(24) *teXsan: Single-Crystal Structure Analysis Software*, Version 1.6; Molecular Structure Corp.: The Woodlands, TX 77381, 1993.

on a glass fiber, and data were collected at room temperature. The structure contains two disordered hexafluorophosphate anions. In the first PF_6^-, each fluorine atom (F7−F12) is located at three positions (a, b, and c), and these were refined isotropically at 33.3% occupancy. A "spinning top" configuration was used to model the disorder present in the second PF_6^- anion. Two full-occupancy F atoms (F1, F2) were refined anisotropically; four other sets of F atoms refined with isotropic thermal parameters at a quarter occupancy were used to complete the model. All other non-hydrogen atoms were refined with anisotropic thermal parameters. An empirical correction for absorption using ψ-scans was applied. Hydrogen atoms were located by difference maps and included as fixed contributions ($B = 1.2 \times$ attached atom). The final residuals for 472 parameters refined against 5373 unique data with $I > 3\sigma(I)$ were $R = 0.045$ and $R_w = 0.069$.

A yellow-orange crystal of **2b**, grown by slow diffusion of ether into an acetonitrile solution of the compound at −30 °C, was mounted on a glass fiber, and data were collected at room temperature. A partial, disordered ether solvate was present and modeled as three C−C−O−C−C groups, each of 25% occupancy; hydrogens of the solvate were excluded. The structure contains two disordered PF_6^- anions. In one anion, each fluorine is located at three positions; the disorder was modeled with three sets of F atoms (F1a−F6a, F1b−F6b, and F1c−F6c) having occupancies of 0.6, 0.2, and 0.2, respectively. The disorder in the second PF_6^- is similar; the disorder was modeled with three sets of fluorine atoms (F7a−F12a, F7b−F12b, and F7c−F12c) having occupancies of 0.4, 0.3, and 0.3, respectively. The phosphorus atoms were refined with anisotropic thermal parameters, while all fluorine atoms in this structure were refined isotropically. All other non-hydrogen atoms not involved in disorder were refined with anisotropic thermal parameters. An empirical correction for absorption using ψ-scans was applied. Hydrogen atoms were located by difference maps and included as fixed contributions ($B = 1.2 \times$ attached atom). The final residuals for 514 parameters refined against 6561 unique data with $I > 3\sigma(I)$ were $R = 0.067$ and $R_w = 0.082$.

X-ray Crystal Structure of 4a and 5b. Crystal data and experimental details are given in Table 1. Data were collected on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator, using the $\omega-2\theta$ scan technique. Structures were solved by direct methods[25] and refined[26] using the Bruker SHELXTL (version 5.1019) software package.[27] ORTEP diagrams for **4a** and **5b** were generated using ORTEP-3.[28]

Single crystals of **4a** were obtained by dissolving the complex in acetonitrile, adding water to the cloud point, and allowing the sample to stand for 2 days. A partial, disordered acetonitrile solvate was present and modeled as two C−C−N groups, each of 25% occupancy; hydrogens of the acetonitrile were excluded. The PF_6^- anion is disordered; each fluorine atom was located at three positions. One set was refined with anisotropic thermal parameters at 45% occupancy; the other two were refined isotropically at 35% and 20%, respectively. All other non-hydrogen atoms were refined with anisotropic thermal parameters. H atom positions were calculated and included as fixed contributions with ($U(H) = 1.2U_{eq}$ attached C atom) for the phenyl and methylene H's. The OH hydrogen atom in the hydroxy methyl group was located by a difference map and was assigned ($U(H) = 1.5U_{eq}$ attached O atom). An empirical correction for absorption using ψ-scans was applied. The final residuals for 432 parameters refined against 5256 unique data were R1 = 0.066 and wR2 = 0.137.

Single crystals of **5b** were obtained by dissolving the compound in acetone and layering with ether in a Schlenk tube. A full occupancy acetone solvate is present. The structure contains two disordered PF_6^- anions. In one anion, four full-occupancy fluorine atoms were refined anisotropically, while the other two F atoms (F5a, F5b and F6a, F6b) all had 50% occupancy. A "spinning top" configuration was used to model the disorder present in the second PF_6^- anion. Two full-occupancy F atoms (F7, F8) were refined anisotropically; two other sets of F atoms were refined with isotropic thermal parameters at a half-occupancy were used to complete the model. H atom positions were calculated and included as fixed contributions with ($U(H) = 1.2U_{eq}$ attached C atom) for the phenyl H's. For the methyl groups, the torsion angle that defines its orientation was not allowed to refine, and these atoms were assigned ($U(H) = 1.5U_{eq}$ attached C atom). An empirical correction for absorption using ψ-scans was applied. The final residuals for 432 parameters refined against 3691 unique data were R1 = 0.065 and wR2 = 0.097.

Acknowledgment. This work was supported by the United States Department of Energy, Division of Chemical Sciences, Office of Science. The X-ray equipment was purchased with assistance from the National Science Foundation (Grant No. CHE-9016978). We also thank Dr. Haiyang He for technical assistance.

Supporting Information Available: Tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances and bond angles, anisotropic thermal parameters, and hydrogen coordinates for **2a**,**b**, **4a**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010520I

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