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Synthesis of Heteroleptic Bis(diimine)carbonylchlororuthenium(II) Complexes from Photodecarbonylated Precursors

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The reactions of bidentate diimine ligands ($\mathbf{L}^2$) with binuclear $[\mathrm{Ru}(\mathbf{L}^1)(\mathrm{CO})\mathrm{Cl}_2]_2$ complexes [$\mathbf{L}^1 \neq \mathbf{L}^2 =$ 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (4,4′-$\mathrm{Me_2}$bpy), 5,5′-dimethyl-2,2′-bipyridine (5,5′-$\mathrm{Me_2}$bpy), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (4,7-$\mathrm{Me_2}$phen), 5,6-dimethyl-1,10-phenanthroline (5,6-$\mathrm{Me_2}$phen), di(2-pyridyl)ketone (dpk), di(2-pyridyl)amine (dpa)] result in cleavage of the dichloride bridge and the formation of cationic $[\mathrm{Ru}(\mathbf{L}^1)(\mathbf{L}^2)(\mathrm{CO})\mathrm{Cl}]^+$ complexes. In addition to spectroscopic characterization, the structures of the $[\mathrm{Ru(bpy)(phen)(CO)Cl}]^+$, $[\mathrm{Ru(4,4'\text{-}Me_2bpy)(5,6\text{-}Me_2phen)(CO)Cl}]^+$ (as two polymorphs), $[\mathrm{Ru(4,4'\text{-}Me_2bpy)(4,7\text{-}Me_2phen)(CO)Cl}]^+$, $[\mathrm{Ru(bpy)(dpa)(CO)Cl}]^+$, $[\mathrm{Ru(5,5'\text{-}Me_2bpy)(dpa)(CO)Cl}]^+$, $[\mathrm{Ru(bpy)(dpk)(CO)Cl}]^+$, and $[\mathrm{Ru(4,4'\text{-}Me_2bpy)(dpk)(CO)Cl}]^+$ cations were confirmed by single crystal X-ray diffraction studies. In each case, the structurally characterized complex had the carbonyl ligand *trans* to a nitrogen from the incoming diimine ligand, these complexes corresponding to the main isomers isolated from the reaction mixtures. The synthesis of $[\mathrm{Ru(4,4'\text{-}Me_2bpy)(5,6\text{-}Me_2bpy)(CO)(NO_3)}]^+$ from $[\mathrm{Ru(4,4'\text{-}Me_2bpy)(5,6\text{-}Me_2bpy)(CO)Cl}]^+$ and $\mathrm{AgNO_3}$ demonstrates that exchange of the chloro ligand can be achieved.

Introduction

Ruthenium(II) complexes of diimine ligands have attracted attention as photoredox catalysts for water splitting,[1] as candidates for use in molecular electronics[2−4] and as sensitizers for photovoltaic cells.[2,5−9] The photoluminescent and redox properties of mononuclear and polynuclear ruthenium complexes of diimine ligands have also been intensively studied.[1,10−13] Additionally, complexes with mixed diimine and carbonyl ligands have been investigated as catalysts for carbon dioxide reduction.[14−17] Despite the diversity of applications and the fact that redox properties and catalytic activity have been found to vary with the ligands present,[12,15] few strategies are available which enable the controlled sequential addition of different ligands to ruthenium(II).[12,18−20]

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Routinely, monocarbonyl complexes with two identical diimine ligands, $[Ru(\mathbf{L^1})_2(CO)Cl]^+$, have been used as catalysts for the reduction of carbon dioxide to carbon monoxide and formate,[14] and in the photochemical water−gas shift reaction.[21] These catalysts are commonly formed either by carbonylation of $[Ru(\mathbf{L^1})_2Cl_2]$ with carbon monoxide[15] or as side products in the synthesis of dichlorobis(bidentate)ruthenium(II) ($[Ru(\mathbf{L^1})_2Cl_2]$) complexes, arising from the decarbonylation of dimethylformamide.[22] The investigation of compounds containing dissimilar diimines has been limited by the lack of a convenient synthetic methodology. The development of a facile synthetic routes to $[Ru(\mathbf{L^1})(CO)Cl_2]_2$ dimers[23] has provided access to a family of compounds which are ideal precursors for an array of $[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]^+$ complexes, that could find application as catalysts,[14,21] and as precursors to heteroleptic tris(diimine) ruthenium(II) complexes of type $[Ru(\mathbf{L^1})(\mathbf{L^2})(\mathbf{L^3})]^{2+}$ complexes.[12,18]

We report a convenient synthesis of monocarbonylmonochlorobis(diimine)ruthenium(II) complexes, $[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]^+$ (where $\mathbf{L^1}$ and $\mathbf{L^2}$ are inequivalent diimine ligands), which involves addition of a diimine ligand to dinuclear carbonyldichloro(bidentate)ruthenium(II) complexes ($[Ru(\mathbf{L^1})(CO)Cl_2]_2$), obtained by photodecarbonylation of $[Ru(\mathbf{L^1})(CO)_2Cl_2]$[23a] or from $[Ru(CO)_3Cl_2]_2$.[23b−f] In terms of the preparation of $[Ru(\mathbf{L^1})(\mathbf{L^2})(\mathbf{L^3})]^{2+}$ complexes, this synthesis circumvents inefficiencies derived from the low yields often associated with the formation of triflate complexes and avoids the need to dispose of triflate wastes,[12,18b,24] which are an integral part of our existing synthesis.[12]

Results and Discussion

Synthesis and Spectroscopic Characterization. The $[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]^+$ complexes were generally prepared by reacting $[Ru(\mathbf{L^1})(CO)Cl_2]_2$ with an excess of a bidentate ligand ($\mathbf{L^2}$) in a suitable solvent (e.g. 2-methoxyethanol).

$$[Ru(\mathbf{L^1})(CO)Cl_2]_2 + \mathbf{L^2} \rightarrow 2[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]Cl \quad (1)$$

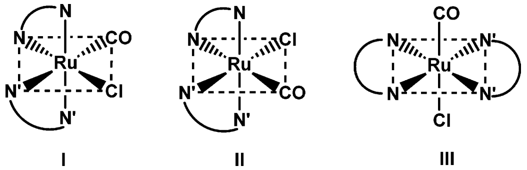

Figure 1. Three possible geometric isomers of $[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]^+$ ($\mathbf{L^1}$, $\mathbf{L^2}$ = symmetrical bidentate ligands).

In the formula $[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]^+$, the ligand attached to Ru in $[Ru(\mathbf{L^1})(CO)Cl_2]_2$ is given first followed by the ligand added to cleave this precursor. For example, $[Ru(\mathbf{bpy})(\mathbf{phen})(CO)Cl]^+$ was obtained by reacting $[Ru(\mathbf{bpy})(CO)Cl_2]_2$ with 1,10-phenanthroline and $[Ru(\mathbf{phen})(\mathbf{bpy})(CO)Cl]^+$ from the inverse reaction. The products were typically isolated as yellow solids by precipitation from aqueous solution as sparingly soluble hexafluorophosphate or perchlorate salts. Residual bidentate ligand coprecipitating with the product was removed either by washing with ether or a small amount of ethanol, or by dissolution of the product in an acetone/ethanol mixture and reprecipitation with ether. To facilitate comparison, analytical data have generally been obtained for the hexafluorophosphate salts. Representative UV−visible spectra of $[Ru(bpy)(phen)(CO)Cl]^+$ and $[Ru(phen)(bpy)(CO)Cl]^+$, recorded in dichloromethane (see Experimental Section), indicated the presence of strong charge-transfer transitions in the UV region. In comparison to related complexes of the type $[Ru(\mathbf{L^1})(\mathbf{L^2})X_2]$, where X is for example a halide or SCN^-, the presence of the carbonyl ligand in $[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]^+$ causes a lowering of the energy of the filled Ru(II) t_{2g} orbitals which contributes to a shift in charge-transfer transition into the UV region. Consequently, the monocarbonyl monochloride complexes are poor absorbers of visible light and unsuitable for application in, for example, the Graetzel solar cell.[5−9] In this context, their utility lies in the potential to be converted into photoactive dyes of type $[Ru(\mathbf{L^1})(\mathbf{L^2})(\mathbf{L^3})]^{2+}$.

Structural assignment of the $[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]^+$ complexes is complicated by the possibility that three geometric isomers may form, two *cis* (**I** and **II**) and one *trans* isomer (Figure 1). The infrared spectra of the bis-bidentate complexes show single strong $\nu(CO)$ bands, as well as strong absorptions around either 840 cm^{-1} or 1100 cm^{-1}, attributable respectively to $\nu(PF_6^-)$ or $\nu(ClO_4^-)$ of the counterions. Weak absorptions ca. 1600 and 1500 cm^{-1}, associated with the carbon−carbon and carbon−nitrogen stretching of the aromatic systems, and in the 730 → 900 cm^{-1} region, attributable to C−H out of plane bending, confirm the presence of the polypyridyl ligands. Since the three geometric isomers would be expected to exhibit single terminal $\nu(CO)$ and $\nu(Ru-Cl)$ stretches, infrared spectroscopy cannot be reliably used to establish which isomer is formed. The ^1H NMR spectra, however, can be used to discriminate between the *cis*-isomers (**I** or **II**) and the *trans*-isomer (**III**). In the *trans*-isomer, a σ_h plane of symmetry renders the environments of the two halves of each bidentate ligand equivalent. Thus, in a *trans*-isomer (**III**) of $[Ru(bpy)(phen)(CO)Cl]^+$ only eight signals are expected in the aromatic region of the

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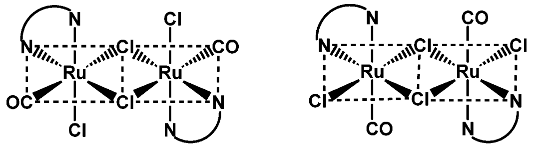
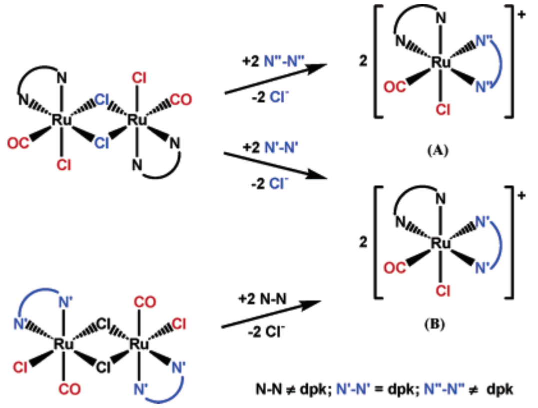


(a) N-N not dpk (b) N-N = dpk

Figure 2. Representations of the structures of $[Ru(N\text{-}N)(CO)Cl_2]_2$ based upon the X-ray determined structures of (a) N-N = phen and (b) N-N = dpk.

Scheme 1. Major Isomers (**A**) Formed by Cleavage of Dichloride Bridge in $[Ru(N\text{-}N)(CO)Cl_2]_2$ with a Diimine Ligand (N-N, N″-N″) ≠ dpk) and (**B**) Formed by Reaction of $[Ru(dpk)(CO)Cl_2]_2$ with a Diimine (N-N) and $[Ru(N\text{-}N)(CO)Cl_2]_2$ with dpk

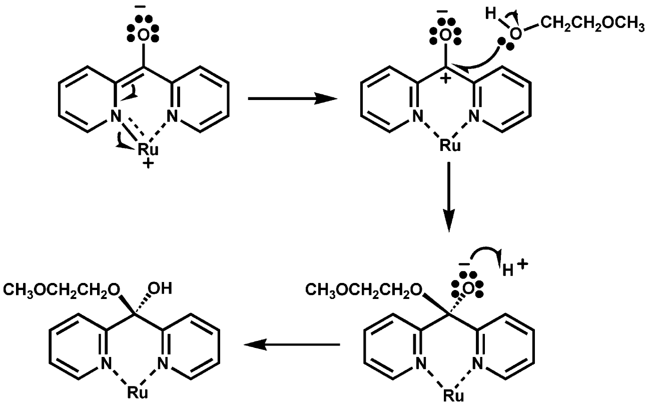


^{1}H NMR spectrum in contrast to the sixteen signals expected in the spectrum of either *cis*-isomer (**I** or **II**).

In predicting the likely geometry of the bis(bidentate) species, the stereochemistry of the reactant dimer must be considered (Figure 2). Assuming the X-ray determined structure of $[Ru(phen)(CO)Cl_2]_2$ to be the typical geometry of such a complex,[23a] a *trans*-isomer could be generated by substitution of a bridge Cl^- and a Cl^- *trans* to the coordinated diimine. However, the proton NMR spectra of all $[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]^+$ complexes are indicative of *cis*-configurations of the carbonyl and chloride ligands. This is not surprising, since the location of the two bidentate ligands in an equatorial plane might be expected to lead to some steric strain. Direct cleavage of the bridge and replacement by the incoming ligand should form a *cis*-isomer (Scheme 1), in which the incoming diimine ligand (N″-N″) has one nitrogen *trans* to the carbonyl and the other *trans* to a nitrogen of the original diimine ligand (i.e., Scheme 1, **A**). Since in $[Ru(\mathbf{L^1})(CO)Cl_2]_2$ ($\mathbf{L^1} \neq$ dpk) the diimine is *trans* to two chloride ligands,[23a] formation of the *cis*-isomer with the carbonyl *trans* to the first diimine ligand (Figure 1, **II**) would require rearrangement. The observation of two *cis*-isomers in the NMR spectra of these compounds is indicative of some rearrangement, although invariably one isomer clearly predominates.

For most cases, microanalysis, which indicated the composition $[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]X$ ($X = PF_6^-$ or ClO_4^-), and electrospray mass spectra (ES-MS), which were consistent with a single ionic weight parent ion even when the ^{1}H NMR spectra were indicating the presence of two species, supported the proposal that major and minor isomers had the same composition. Exceptions were $[Ru(dpk)(4,7\text{-}Me_2phen)(CO)Cl](PF_6)$ and $[Ru(dpk)(bpy)(CO)Cl](PF_6)$, for which pure samples could not be obtained, because the 2-methoxyethanol solvent reacted with the coordinated dpk (Scheme 2). Peaks attributable to methoxyethanol adducts were evident in the ES-MS of the bulk product obtained from the reaction of $[Ru(dpk)(CO)Cl_2]_2$ with 4,7-Me_2phen (597 *m/z*, $M^+ + (CH_3OCH_2CH_2O) - Cl$).

Scheme 2. Reaction of 2-Methoxyethanol with Coordinated Dipyridyl Ketone (dpk)



The assignments of the NMR spectra given in the Experimental Section are based on (i) the asymmetry of all bidentate ligands owing to mutual shielding by adjacent pyridyl rings leading to pronounced shifts in the chemical shifts of the shielded rings to lower frequency (as elucidated for $[Ru(bpy)_2(CO)_2]^{25}$ and $[Ru(bpy)_2Cl_2]^{26}$); (ii) detailed consideration of coupling constants illuminated by the fact that ^3J(H,H) values for protons ortho to N are low (4.5−6 Hz); (iii) consistency in chemical shifts and their differences for H_n and H_n' for a particular ligand in a particular stereochemistry. The major isomer isolated from each synthesis (except those from $[Ru(dpk)(CO)Cl]_2$) was that expected from cleavage of the $RuCl_2Ru$ bridge of the reactant. That is, for an initial complex with a particular diimine ligand having N *trans* to Cl, the isomer with N *trans* to Cl (and N″ from the incoming ligand *trans* to CO) is obtained as the major product. This was shown by X-ray studies on representative compounds.

Analysis of the ^{1}H NMR spectra of products initially isolated from these cleavage reactions indicates the achievement of some degree of specificity (in some cases, >20:1) for one *cis*-isomer over the other. This is highlighted by a comparison of the ^{1}H NMR spectrum of the products obtained by cleavage of $[Ru(bpy)(CO)Cl_2]_2$ with phen (designated $[Ru(bpy)(phen)(CO)Cl]^+$) and the complementary cleavage of $[Ru(phen)(CO)Cl_2]_2$ with bpy ($[Ru(phen)(bpy)(CO)Cl]^+$), two reactions that yield products with the same stoichiometry. For $[Ru(bpy)(phen)(CO)Cl]^+$, resonances attributable to the most deshielded protons of phen and bpy of the major isomer can be found at δ 9.87 and δ 9.76 ppm, respectively, while for the minor isomer these signals are observed at δ 9.61 (bpy) and δ 9.91 (phen) ppm. For the complementary cleavage yielding [Ru(phen)(bpy)-

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(CO)Cl]$^+$, the intensities of the ^{1}H NMR resonances attributable to the two *cis*-isomers of [Ru(phen)(bpy)(CO)Cl]$^+$ are inverted, and the identity of [Ru(phen)(bpy)(CO)Cl]$^+$ was confirmed by X-ray crystallography. Hence, in both cases the major product is the isomer having the first coordinated diimine trans to the chloride ligand (as is produced by the replacement of the dichloride bridge) (Scheme 1 (**A**)).

Cleavage of the dpk complex [Ru(dpk)(CO)Cl$_2$]$_2$, however, should give rise to a different isomer since the chlorides in the starting material have a *trans* rather than a *cis* orientation and one imine nitrogen of dpk is *trans* to CO.[23a] In this case, the major product would be expected to have the second ligand coplanar with the remaining chloride, rather than in the same plane as the carbonyl as found in the previously discussed examples. The ^{1}H NMR spectra of the products obtained by reaction of [Ru(dpk)(CO)Cl$_2$]$_2$ with bpy and [Ru(bpy)(CO)Cl$_2$]$_2$ with dpk displayed a complex array of similar intensity resonances in identical positions that could not be assigned unambiguously. Nevertheless, the spectra clearly indicate that the cleavage of [Ru(dpk)(CO)Cl$_2$]$_2$ with $\mathbf{L^1}$ ($\mathbf{L^1}$ = diimine ligand ≠ dpk) and the cleavage of [Ru($\mathbf{L^1}$)(CO)Cl$_2$]$_2$ with dpk yield the same major product **B**, as expected given the difference in the stereochemistries of their dimeric precursors (see Scheme 1).

Although the order of addition of the ligands confers some degree of geometric specificity, significant enhancement of this discrimination could not be achieved by variation of reaction conditions, viz., solvent, temperature, and reaction time.

Structures of Bis(bidentate)carbonylchlororuthenium(II) Complexes. Single crystal X-ray studies of [Ru(phen)(bpy)(CO)Cl](PF$_6$), [Ru(bpy)(dpk)(CO)Cl](PF$_6$), [Ru(dpk)(4,7-Me$_2$phen)(CO)Cl](ClO$_4$), [Ru(bpy)(dpa)(CO)Cl](ClO$_4$), [Ru(4,4′-Me$_2$bpy)(4,7-Me$_2$phen)(CO)Cl](ClO$_4$), [Ru(5,5′-Me$_2$bpy)(dpa)(CO)Cl](ClO$_4$), and two polymorphs of [Ru(4,4′-Me$_2$bpy)(5,6-Me$_2$phen)(CO)Cl](PF$_6$) have been carried out. Molecular projections of the structures can be found in Figure 3a−f, and parameters pertinent to the geometry of the Ru(II) center in Table 1. In comparing the structural geometries of these complexes it should be noted that the structure of [Ru(dpk)(4,7-Me$_2$phen)(CO)Cl](ClO$_4$) was determined from data obtained at 173 K, while the others were determined from data measured at room temperature.

In every complex studied, one [Ru($\mathbf{L^1}$)($\mathbf{L^2}$)(CO)Cl]$^+$X$^-$(.S) unit devoid of crystallographic symmetry comprises the asymmetric unit in a crystallographically centrosymmetric structure, the role of any solvent fragments present simply being that of space-filling. The anions in all cases are the quasi-spherical perchlorate or hexafluorophosphate, both notoriously prone to disorder in the crystal as is found in about half of the present examples, with consequent impact on the precision of the determinations. In the cations, the carbonyl and chloride ligands are universally *cis* in the six-coordinate environments of the ruthenium atoms. The diimine ligands are either substantially planar or contain substantial planar moieties, prone to the familiar charge-transfer stacking which is widespread throughout the series. The effects of this may be manifest in distortions imposed on the coordination environments of the ruthenium atoms, perhaps most immediately evident in the sometimes very large deviations of the ruthenium atoms from associated ligand planes, or in inconsistencies in putatively equal geometrical parameters. Although the prime function of the crystallographic work here is to define the particular isomers produced as precursors for further synthesis, we comment in particular on the following features:

(a) The geometries of all [Ru($\mathbf{L^1}$)($\mathbf{L^2}$)(CO)Cl]$^+$ complexes are consistent with those observed in closely related complexes such as [Ru(bpy)$_2$(CO)Cl](ClO$_4$)[22] [Ru−Cl 2.396(7) Å, Ru−C 1.86(3) Å, Ru−C−O 175(3)°] and *cis*-carbonylchlorobis[1-methyl-3-(pyridin-2-yl)-1,2,4-triazole-*N*^{4},*N*′]-ruthenium hexafluorophosphate[27] [Ru−Cl 2.382(2) Å, Ru−C 1.839(7) Å, Ru−C−O 174.9(6)°, Cl−Ru−C 87.6(2)°]. No anomalous distortions of the diimine ligands were noted in any of the present structures, and the geometries of the ligands and metal centers are consistent throughout the array.

(b) Aromatic ligand substituents are, in general, well removed from the ruthenium atom, with their presence or absence not correlating directly with changes in the ruthenium geometry.

(c) Ligand "bites" as measured by N−Ru−N differ considerably among the complexes. For the bpy and phen ligands these are in the range 77.5(5)−79.3(2)° and 78.0(1)−80.9(3)°, respectively. Similarly, the bite angles for the dpa and dpk ligands are comparable, viz., 85.4(5)°, 86.4(1)° for the former and 86.6(2)°, 87.4(7)° for the latter, in keeping with the presence of additional atoms in their chelate rings. Associated Ru−N distances are concomitantly longer for these complexes, despite the larger bites of the ligands. Interplanar (C_5N/C_5N) dihedral angles are greater for the dpk than for the dpa ligands.

The structure of the complex cation in each structurally characterized bis-diimine complex conforms to the stereochemistry expected if direct substitution had occurred at the dichloride bridge of the binuclear precursor. Therefore, cleavage of dimers incorporating ligands other than dpk results in the formation of a product which predominantly consists of the isomer depicted in Figure 1 **(I)**. In every case, the molecular structure, determined by X-ray crystallography, was that with one nitrogen from the incoming diimine *trans* to CO (and hence the predominant isomer shown by ^{1}H NMR spectroscopy). This was so even for [Ru(4,4′-Me$_2$bpy)(5,6-Me$_2$phen)(CO)Cl](PF$_6$), for which crystals with two habits were separated, yellow polyhedra (more common) and orange prismatic. Both habits crystallize in the same $P2_1/n$ space group ($Z = 4$), and in each case the 4,4′-Me$_2$bpy ligand is coplanar with the Ru−Cl bond, the isomer predicted assuming direct cleavage of the dichloride bridge. A comparison of the ruthenium geometries in the two structures can beseen in Table 1 (Figure 3c i and ii**)**. Bond distances are in agreement to within 0.02 Å, while angles are concordant to

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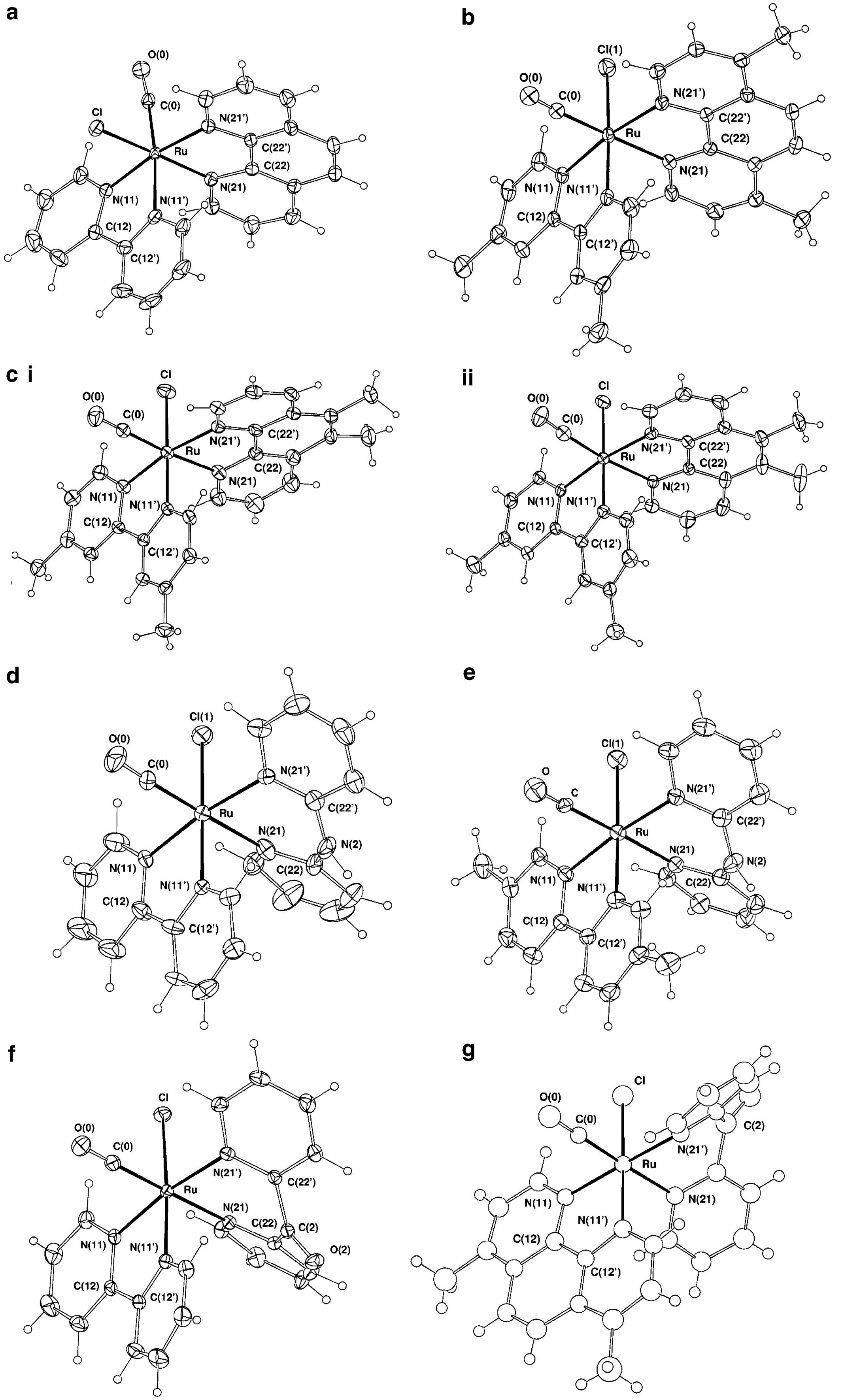
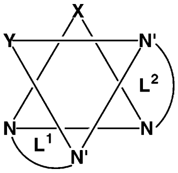


Figure 3. Projections of the X-ray structures of the cations: (**a**) $[Ru(bpy)(phen)(CO)Cl]^+$; (**b**) $[Ru(4,4'\text{-}Me_2bpy)(4,7\text{-}Me_2phen)(CO)Cl]^+$ (major component); (**c**) $[Ru(4,4'\text{-}Me_2bpy)(5,6\text{-}Me_2phen)(CO)Cl]^+$, (i) orange, (ii) yellow; (**d**) $[Ru(bpy)(dpa)(CO)Cl]^+$; (**e**) $[Ru(5,5'\text{-}Me_2bpy)(dpa)(CO)Cl]^+$; (**f**) $[Ru(bpy)(dpk)(CO)Cl]^+$; (**g**) $[Ru(dpk)(4,7\text{-}Me_2phen)(CO)Cl]^+$.

Table 1. Selected Bond Angles and Distances for $[Ru(\mathbf{L^1})(\mathbf{L^2})(CO)Cl]^+$ Complexes[a]



X, Y:	C(0), Cl	Cl, C(0) (or)	Cl, C(0) (y)	Cl, C(0)	Cl, C(0)	Cl, C(0)	Cl, C(0)	Cl, C(0)
$\mathbf{L^1}$:	bpy	4,4′-Me$_2$bpy	4,4′-Me$_2$bpy	4,4′-Me$_2$bpy[b]	bpy	5,5′-Me$_2$bpy	bpy	4,7′-Me$_2$phen
$\mathbf{L^2}$:	phen	5,6-Me$_2$phen	5,6-Me$_2$phen	4,7-Me$_2$phen	dpa	dpa	dpk	dpk
Distances (Å)								
Ru−X	1.857(4)	2.401(2)	2.391(2)	2.335(5)	2.398(4)	2.392(1)	2.405(2)	2.389(3)
Ru−Y	2.386(2)	1.867(5)	1.880(7)	1.95(2)	1.88(2)	1.917(4)	1.880(5)	1.82(1)
Ru−N(11)	2.067(4)	2.074(4)	2.079(5)	2.080(7)	2.058(9)	2.083(4)	2.070(4)	2.090(9)
Ru−N(11′)	2.114(3)	2.062(4)	2.058(5)	2.079(8)	2.15(1)	2.083(3)	2.062(4)	2.092(9
Ru−N(21)	2.072(4)	2.127(4)	2.131(5)	2.107(5)	2.15(1)	2.146(3)	2.157(4)	2.131(8)
Ru−N(21′)	2.076(4)	2.077(4)	2.079(5)	2.075(7)	2.086(9)	2.105(4)	2.090(4)	2.105(8)
H(16)···Cl[c]	*c*	2.8$_0$	2.7$_3$	(2.7$_6$)	2.7$_7$	2.7$_7$	2.7$_3$	2.8$_0$
Angles (deg)								
Cl−Ru−C(0)	90.6(2)	89.8(2)	89.0(2)	91.1(8)	90.0(5)	90.8(1)	90.3(2)	89.2(4)
X−Ru−N(11)	95.1(2)	96.6(1)	94.7(1)	97.2(1)	96.8(3)	96.6(1)	95.3(1)	94.5(2)
X−Ru−N(11′)	172.8(2)	173.8(1)	171.8(2)	176.1(2)	172.7(3)	174.6(1)	174.1(1)	173.2(2)
X−Ru−N(21)	96.3(2)	85.7(1)	88.6(1)	93.1(2)	89.3(3)	89.8(1)	88.7(1)	88.3(2)
X−Ru−N(21′)	93.2(2)	88.3(1)	89.6(1)	87.1(2)	88.1(3)	86.4(1)	88.7(1)	88.4(3)
Y−Ru−N(11)	88.6(1)	89.3(2)	91.3(2)	91.6(9)	92.0(6)	89.7(2)	93.6(2)	86.0(4)
Y−Ru−N(11′)	87.7(1)	93.9(2)	96.7(2)	89.7(8)	94.8(6)	91.4(2)	90.6(2)	95.4(4)
Y−Ru−N(21)	171.0(1)	175.0(2)	173.5(2)	172(1)	179.0(6)	178.3(2)	179.0(2)	177.5(4)
Y−Ru−N(21′)	94.6(1)	99.7(2)	95.8(3)	95.7(9)	93.8(6)	95.2(2)	93.2(2)	92.8(4)
N(11)−Ru−N(11′)	77.8(2)	78.5(1)	79.3(2)	79.1(3)	77.5(5)	78.6(2)	78.8(2)	80.9(3)
N(11)−Ru−N(21)	96.6(2)	93.5(2)	94.9(2)	94.1(2)	88.9(5)	88.6(1)	86.7(2)	93.9(3)
N(11)−Ru−N(21′)	171.1(1)	169.9(2)	171.8(2)	171.5(2)	172.4(4)	174.2(1)	172.1(2)	176.9(4)
N(11′)−Ru−N(21)	86.2(1)	90.7(2)	86.3(2)	86.5(2)	85.9(4)	87.9(1)	90.4(2)	87.0(3)
N(11′)−Ru−N(21′)	93.9(1)	96.0(2)	95.7(2)	96.5(3)	97.0(5)	98.2(2)	97.0(2)	96.4(3)
N(21)−Ru−N(21′)	79.2(2)	78.0(1)	78.2(2)	78.3(2)	85.4(5)	86.4(1)	86.6(2)	87.4(3)
Plane Parameters[b,d]								
$\theta(L_1)$	22.5(1)	4.5(2)	9.4(2)	3.7(3)	1.9(5)	6.7(2)	12.2(2)	
$\delta(L_1)$	0.241(8), 0.063(7)	0.037(7), 0.075(6)	0.053(8), 0.348(9)	0.07(1), 0.06(1)	0.29(2), 0.22(2)	0.262(7), 0.033(7)	0.089(8), 0.010(8)	0.171(7)
$\theta(L_2)$		9.6(2)	3.2(2)		31.8(7)	38.5(2)	46.9(2)	42.5(4)
$\delta(L_2)$	0.136(4)	0.262(8), 0.025(7)	0.019(9), 0.057(9)	0.051(5)	0.32(2), 0.30(2)	0.278(7), 0.052(7)	0.368(8), 0.019(8)	0.06(1), 0.46(2)

[a] To aid comparison, a common numbering scheme is adopted, based on the composition of each ligand as a pair of primed and unprimed pyridine rings (linked through NH or CO for dpa and dpk, respectively). $\mathbf{L^1}$ and $\mathbf{L^2}$ are disposed as shown relative to ligands X and Y (usually Cl and CO) in a common Δ chirality. [b] Geometry here pertains to the major carbonyl and chlorine components of the disorder, and these, in particular, should be treated with circumspection, e.g. the Ru−X,Y distances are clearly aberrant in this case. [c] Distances are from the H(16) of ligand 1 to the in-plane chlorine; for the first column, Cl/CO are interchanged. Here H(16)···Cl is 2.8$_0$ Å. [d] For bpy derived ligands, θ° is angle between the two C_5N planes, and δ Å are the distances of the metal atom from that plane (in the case of phen moieties, the distances from the $C_{12}N_2$ array is given). In the dpk complexes, the dihedral angles of the peripheral C_5N rings to the central C.CO.C planes are 34.4(2)°, 41.6(2)° (bpy complex) and 38.2(4)°, 30.1(4)° (Me$_2$phen complex).

within 1°. As in the case of $[Ru(tpy)(CO)_2Br_2]$,[28] which crystallizes in red and yellow forms with the same isomer, differences in packing or intermolecular effects may be presumed responsible for this behavior.

The results of the X-ray structure determinations of [Ru(5,5′-Me$_2$bpy)(dpa)(CO)Cl](ClO_4) and [Ru(bpy)(dpa)(CO)Cl](ClO_4) indicate the formation of the predicted major isomer with the 5,5′-Me$_2$bpy and bpy *trans* to the chloride, respectively. Apart from differences in intermolecular ordering resulting from packing considerations, the two structures are very similar. Intramolecular geometries in the two complexes are, as expected, closely related.

The [Ru(4,4′-Me$_2$bpy)(4,7-Me$_2$phen)(CO)Cl](ClO_4) complex differs from the others in that the two *cis*-isomers appear to have cocrystallized. Disorder was observed for the carbonyl and chloride ligands and modeled by refinement with partial occupancies with the carbonyl ligand constrained to an ideal geometry. This resulted in the determination of a population distribution of 0.70(1) (expected major isomer) where the chloride is *trans* to the 4,4′-Me$_2$bpy, and 0.30(1) where the chloride is *trans* to the 5,6-Me$_2$phen. The ^{1}H NMR spectrum of the bulk material contained a similar distribution of the two isomers (3:2).

Recrystallization of the product mixture isolated from the reaction of $[Ru(bpy)(CO)Cl_2]_2$ with dpk and $[Ru(dpk)(CO)Cl_2]_2$ with bpy gave crystals with similar habits and unit cells. The structure of [Ru(bpy)(dpk)(CO)Cl](PF_6) again confirmed that the bpy ligand assumes a position coplanar with (and hence *trans* to) the chloride ligand. This is consistent with Scheme 1, which shows that, due to the different structure of $[Ru(bpy)(CO)Cl_2]_2$ and $[Ru(dpk)(CO)Cl_2]_2$, their reaction with dpk and bpy respectively should give the same product.

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Likewise, the X-ray study of the crystals isolated from the addition of 4,7-Me_2phen to $[Ru(dpk)(CO)Cl_2]_2$ showed the 4,7-Me_2phen to be *trans* to the coordinated chloride.

Bis(bidentate)carbonylnitratoruthenium(II). Substitution of chloride in $[Ru(bpy)_2(CO)Cl]^+$ has been demonstrated previously through the syntheses of various derivatives,[29] including $[Ru(bpy)_2(CO)(H)](PF_6)$, $[Ru(bpy)_2(CO)(NCS)](PF_6)$, $[Ru(bpy)_2(CO)(pyridine)](ClO_4)$, $[Ru(bpy)_2(CO)(CH_3CN)](ClO_4)_2$, and $[Ru(bpy)_2(CO)(4\text{-vinylpyridine})](PF_6)_2$. In an extension of the synthetic utility of carbonylchlorobis(diimine)ruthenium(II) complexes, a nitrato complex, *cis*-$[Ru(4,4'\text{-}Me_2bpy)(5,6\text{-}Me_2phen)(CO)(NO_3)]^+$, was prepared by heating a chloro complex (obtained by the cleavage of $[Ru(4,4'\text{-}Me_2bpy)(CO)Cl_2]_2$ with 5,6-Me_2phen) with an excess of silver nitrate in methanol, the product being isolated as a hexafluorophosphate salt.

Confirmation of composition was obtained by microanalysis and by the observation of a single group of peaks in the ES-MS matching the expected isotopic distribution pattern with the most intense peak at 584 *m*/*z*. In the IR spectrum, a peak at 1271 cm^{-1}, clear of aromatic absorptions, indicates the presence of coordinated nitrate,[30] while a single ν(CO) at 1986 cm^{-1} confirms the persistence of the carbonyl ligand. Although the ^{1}H NMR spectra of $[Ru(4,4'\text{-}Me_2bpy)(5,6\text{-}Me_2phen)(CO)Cl]^+$ and $[Ru(4,4'\text{-}Me_2bpy)(5,6\text{-}Me_2phen)(CO)(NO_3)]^+$ are similar (14 of 16 resonances correspond closely), there is a significant effect of substitution on the chemical shift of the 4,4′-Me_2bpy proton resonating at the highest frequency. Assuming the nitrate to be *trans* to one of the 4,4′-Me_2bpy rings and adjacent to the other, as expected from the X-ray study of the starting $[Ru(4,4'\text{-}Me_2bpy)(5,6\text{-}Me_2phen)(CO)Cl]^+$ complex, the proton *ortho* to the pyridyl nitrogen on this adjacent ring is likely to experience the greatest deshielding from the neighboring chloride or nitrate substituent. Thus, the resonance due to the proton *ortho* to the nitrogen in 4,4′-Me_2bpy is shifted from δ 9.54 to δ 8.89 ppm in the nitrate product. There is a smaller shift in the H2(phen) resonance in the opposite direction.

Experimental Section

Physical Measurements. Infrared spectra were recorded using a Perkin-Elmer 1640 (1600 series) FTIR spectrophotometer at a resolution of 4.0 cm^{-1} as Nujol mulls between sodium chloride plates. Far IR spectra of samples in petroleum jelly mulls between polystyrene plates were recorded on a Bruker IFS 120HS spectrometer to a resolution of 8.0 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker AM300 spectrometer at 300 MHz or on a Bruker DRX400 spectrometer at an operating frequency of 400 MHz. Shifts are reported in parts per million referenced relative to an internal standard of tetramethylsilane (TMS). NMR spectra are not reported for cases where these were poorly resolved. t* indicates an apparent triplet. Electrospray mass spectra were recorded on either a Micromass platform quadrupole mass spectrometer fitted with an electrospray source or a Bruker BioApex 47e Fourier transform mass spectrometer with a 4.7 T superconducting magnet and an Analytica electrospray source. The most intense peak of each cluster is listed. Isotope patterns were in agreement with calculated values. Assignments to ions are correspondingly based upon the mass of highest relative abundance as calculated from the isotope pattern of constituent elements. Elemental microanalyses were performed either by Chemical and Micro Analytical Services (CMAS), Melbourne, Australia, or by the Campbell Microanalytical Services, Dunedin, New Zealand.

Materials. Reagent grade chemicals and solvents, obtained from commercial suppliers, were used as received. 5,5′-Dimethyl-2,2′-bipyridine was prepared by a published method.[31] $[Ru(bpy)(CO)Cl_2]_2$, $[Ru(phen)(CO)Cl_2]_2$, $[Ru(4,7\text{-}Me_2phen)(CO)Cl_2]_2$, $[Ru(4,4'\text{-}Me_2bpy)(CO)Cl_2]_2$, and $[Ru(5,5'\text{-}Me_2bpy)(CO)Cl_2]_2$ were prepared by a literature method.[23a]

Syntheses. ***CAUTION:*** *Although no problems were encountered in this work, metal perchlorate complexes are potentially explosive. They should be prepared in small quantities and handled with care.*

***cis*-Carbonylchloro(2,2′-bipyridine)(1,10-phenanthroline)-ruthenium(II) Hexafluorophosphate.** $[Ru(bpy)(CO)Cl_2]_2$ (0.14 g, 0.39 mmol) was suspended in 2-methoxyethanol (20 cm^3), which had been deoxygenated (by passing a stream of nitrogen through the ebullient solvent) immediately prior to use. 1,10-Phenanthroline (0.10 g, 0.57 mmol) was added to the orange suspension under a constant flow of nitrogen. The resultant mixture was then heated at reflux and stirred for a period of 2 h. The slow cleavage of the suspended complex is manifested by the formation of a dark yellow/pale orange solution. The light orange residue obtained from the evaporation of this solution was suspended in distilled water (25 cm^3) and sonicated for 4 min and the pale yellow suspension cooled to 2 °C before filtration through diatomaceous earth. Treatment of the filtered solution with an excess of an aqueous solution of potassium hexafluorophosphate (8 cm^3, 1.0 M) rapidly precipitated a canary yellow solid. This product was collected by filtration and washed thoroughly with three aliquots of water and once with a 50:50 mixture of water and 95% ethanol. The product was then dried at 70 °C. Yield: 0.24 g (96%). Alternately, the semidry product was dissolved in an acetone/ethanol mixture and re-precipitated by the addition of diethyl ether. ES-MS (acetone): *m*/*z* 501 (100%, $[Ru(bpy)(phen)(CO)Cl]^+$). Anal. Calcd for $[C_{23}H_{16}N_4ClF_6OPRu]$: C 42.8, H 2.5, N 8.7. Found: C 42.9, H 2.5, N 8.6. IR (Nujol) cm^{-1}: 2066w, 1966s ν(CO); 1632w, 16106w, 1518w, 1430m, 1312w, 1165w, 878m(sh), 842s $\nu(PF_6)$; 771m. Far IR (cm^{-1}): 332s ν(Ru−Cl). ^{1}H NMR spectrum (300 MHz, d_6-acetone, major isomer): 9.88 (1H, dd, H2(phen)); 9.75 (1H, dd, H6(bpy)); 8.97 (1H, dd, H4(phen)); 8.87 (2H, dd, H7(phen) + H(bpy)); 8.70 (1H, d, H3′(bpy)); 8.56 (1H, t*d, H4(bpy)); 8.40, 8.36 (AB doublet, 2H, H5,6(phen)); 8.26 (1H, dd, H3(phen)); 8.16−8.06 (complex m, 3H, H9(phen) + H5,4′(bpy)); 7.95 (1H, dd, H6′(bpy)); overlapping 7.92 (1H, dd, H8(phen)); 7.32 (1H, ddd, H5′(bpy)). Isomer ratio (by integration of ^{1}H NMR): >20:1. UV−visible spectrum in CH_2Cl_2 (λ_{max}, nm (ϵ, $M^{-1}cm^{-1}$)): 354 (4500), 312sh (10000), 282 (26000), 264 (40000).

***cis*-Carbonylchloro(1,10-phenanthroline)(2,2′-bipyridyl)-ruthenium(II) Hexafluorophosphate.** A mixture of $[Ru(phen)(CO)(Cl)_2]_2$ (0.189 g, 0.25 mmol) and 2,2′-bipyridyl (0.154 g, 0.98 mmol) was heated under reflux in 2-methoxyethanol (25 cm^3) for ca. $1^1/_2$ h. The solvent was evaporated to dryness, and the remaining solid was then dissolved in hot water (15 cm^3). The hot solution

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(30) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1963; p 161.

(31) (a) Badger, G. M.; Sasse, W. H. F. *Adv. Heterocycl. Chem.* **1963**, *2*, 179. (b) Rosevear, P. E.; Sasse, W. H. F. *Heterocycl. Chem.* **1971**, *8*, 483.

was filtered and added to an excess of potassium hexafluorophosphate (KPF_6). The precipitated product was collected by filtration and recrystallized from acetone/ether. Yield: 0.08 g (45%). Infrared absorptions: 1984vs (ν(CO)), 1601m, 1580w, 1310w, 1145m, 920m, 838vs (ν(PF_6 + phen)), 762s, 720s, 558s. Far IR (cm^{-1}): 327m [ν(Ru−Cl)]. ^1H NMR spectrum [$(CD_3)_2CO$, major isomer]: 9.91 (dd, 1H, H2(phen)); 9.61 (dd, 1H, H6(bpy)); 9.11 (dd, 1H H4(phen)); 8.82 (dd, 1H, H3(bpy)); 8.79 (dd, 1H, H3′ (bpy)); 8.73 (dd, 1H, H7(phen)); 8.32−8.49 (m, 5H, H4(bpy), H3,5,6,9(phen)); 8.19 (td, 1H, H4′ (bpy)); 7.93 (ddd, 1H, H5(bpy)); 7.82 (dd, 1H, H8(phen)); 7.56 (dd, 1H H6′ (bpy)); 7.39 (ddd, 1H, H5′ (bpy)). Isomer ratio: 9:1 (integrating H6(bpy) of the isomers). UV−visible spectrum in CH_2Cl_2 (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 421sh (2100), 360sh (3000).

***cis*-Carbonylchloro(2,2′-bipyridine)(4,4′-dimethyl-2,2′-bipyridine)ruthenium(II) Hexafluorophosphate.** [Ru(bpy)(4,4′-Me_2bpy)(CO)Cl](PF_6) was synthesized from [Ru(bpy)(CO)Cl_2]$_2$ (0.16 g, 0.23 mmol) and 4,4′-dimethyl-2,2′-bipyridine (0.13 g, 0.69 mmol) by the method used to form [Ru(bpy)(phen)(CO)Cl](PF_6). The complex was obtained as a bright yellow powder. Yield: 0.27 g (92%). ES-MS (acetone): *m*/*z* 505 (100%, [Ru(bpy)(4,4′-Me_2bpy)(CO)Cl]$^+$). Anal. Calcd for [$C_{23}H_{20}N_4ClF_6OPRu$]: C 40.6, H 3.0, N 8.2. Found: C 40.5, H 2.8, N 8.2. IR (Nujol) cm^{-1}: 2063w, 1970s ν(CO); 1620m, 1560w, 1450m, 1313w, 1243w, 1162w, 1032w, 846s ν(PF_6); 770m. ^1H NMR spectrum (300 MHz, d_6-acetone, major isomer): 9.66 (1H, dt*, H6(bpy)); 9.28 (1H, d, H6(Me_2bpy)); 8.82 (1H, dt*, H3(bpy)); 8.69 (1H, d, H3′(bpy)); 8.65 (1H, s, H3(Me_2bpy)); 8.60 (1H, s, H3′(Me_2bpy)); 8.50 (1H, t*d, H4(bpy)); 8.19 (1H, t*d, H4′(bpy)); 8.00−8.05 (2H, m, H5(bpy, Me_2bpy)); 7.73 (1H, dt*, H6′(bpy)); 7.54 (1H, d, H6′(Me_2bpy)); 7.49 (1H, ddd, H5′(bpy)); 7.38 (1H, dm, H5′(Me_2bpy)); 2.70 (3H, s, −C**H**$_3$); 2.53 (3H, s, −C**H**$_3$′). Isomer ratio (by integration of ^1H NMR): 7:1.

***cis*-Carbonylchloro(2,2′-bipyridine)(5,6-dimethyl-1,10-phenanthroline)ruthenium(II) Hexafluorophosphate.** [Ru(bpy)(5,6-Me_2bpy)(CO)Cl](PF_6) was obtained as a bright yellow powder by a procedure similar to that used to form [Ru(bpy)(phen)(CO)Cl](PF_6), but using [Ru(bpy)(CO)Cl_2]$_2$ (0.46 g, 0.64 mmol) and 5,6-dimethyl-1,10-phenanthroline (0.37 g, 1.6 mmol). Yield: 0.77 g (89%). ES-MS (acetone): *m*/*z* 529 (100%, [Ru(bpy)(5,6-Me_2bpy)(CO)Cl]$^+$). IR (Nujol) cm^{-1}: 2059w, 1969s ν(CO); 1597w, 1313w, 1245w, 1165w, 1073w, 843s ν(PF_6); 770m. Far IR (cm^{-1}): 329s ν(Ru−Cl). ^1H NMR spectrum (300 MHz, d_6-acetone, major isomer): 9.81 (1H, dd, H2(phen)); 9.76 (1H, dt*, H6(bpy)); 9.08 (1H, dd, H4(phen); 8.98 (1H, dd, H7(phen)); 8.87 (1H, dd, H3(bpy)); 8.70 (1H, d, H3′(bpy)); 8.55 (1H, t*d, H4(bpy)); 8.23 (1H, dd, H3(phen)); 8.13 (1H, t*d, H4′(bpy)); 8.04−8.09 (2H, m, H5(bpy), H9(phen)); 7.92 (1H, dd, H6′(bpy)); 7.90 (1H, dd, H8(phen)); 7.32 (1H, ddd, H5′(bpy)); 2.94 (3H, s, −C**H**$_3$, 5); 2.88 (3H, s, −C**H**$_3$, 6). Isomer ratio (by integration of ^1H NMR): 3:1.

***cis*-Carbonylchloro(2,2′-bipyridine)(4,7-dimethyl-1,10-phenanthroline)ruthenium(II) Hexafluorophosphate.** The bright yellow [Ru(bpy)(4,7-Me_2phen)(CO)Cl](PF_6) was synthesized from [Ru(bpy)(CO)Cl_2]$_2$ (0.16 g, 0.22 mmol) and substitution of 4,7-dimethyl-1,10-phenanthroline (0.15 g, 0.68 mmol) for 1,10-phenanthroline in the preparation of [Ru(bpy)(phen)(CO)Cl](PF_6). Yield: 0.30 g (98%). ES-MS (acetone): *m*/*z* 529 (100%, [Ru(bpy)(4,7-Me_2phen)(CO)Cl]$^+$). Anal. Calcd for [$C_{25}H_{20}N_4ClF_6OPRu$]: C 44.6, H 3.0, N 8.3. Found: C 44.5, H 3.1, N 8.1. IR (Nujol) cm^{-1}: 1966s ν(CO); 1626w, 1605w, 1579w, 1525w, 1425m, 1314w, 1229w, 1176w, 1032w, 853s(sh), 839s ν(PF_6); 772m. Far IR (cm^{-1}): 302s ν(Ru−Cl). ^1H NMR spectrum (300 MHz, d_6-acetone, major isomer): 9.75 (1H, dd, H6(bpy); 9.68 (1H, d, H2(phen)); 8.85 (1H, d, H3(bpy)); 8.68 (1H, d, H3′(bpy)); 8.54 (1H, t*d, H4(bpy)); 8.50 (1H, s, H5(phen)); 8.48 (1H, s, H6(phen)); 8.04−8.17 (3H, m, H4′(bpy), H5(bpy), H3(phen)); 7.96 (1H, d, H9(phen)); 7.91 (1H, dm, H8(phen)); 7.73 (1H, dd, H6′(bpy); 7.31 (1H, ddd, H5′(bpy); 3.10 (3H, s, −C**H**$_3$, 4); 2.94 (3H, s, −C**H**$_3$, 7). Isomer ratio (by integration of ^1H NMR): 19:1.

***cis*-Carbonylchloro(2,2′-bipyridine)(di(2-pyridyl)amine)ruthenium(II) Hexafluorophosphate.** The bright yellow [Ru(bpy)(dpa)(CO)Cl](PF_6) was synthesized by means analogous to the synthesis of [Ru(bpy)(phen)(CO)Cl](PF_6) using [Ru(bpy)(CO)Cl_2]$_2$ (0.12 g, 0.17 mmol) and di(2-pyridyl)amine (0.11 g, 0.64 mmol). The crude product was dissolved in acetone and reprecipitated by the addition of diethyl ether. Yield: 0.20 g (86%). ES-MS (acetone): *m*/*z* 492 (100%, [Ru(bpy)(dpa)(CO)Cl]$^+$). Anal. Calcd for [$C_{21}H_{17}N_5ClF_6OPRu$]: C 39.6, H 2.7, N 11.0. Found: C 39.6, H 2.5, N 11.0. IR (Nujol) cm^{-1}: 3386m ν(NH); 1967s ν(CO); 1630m, 1604w, 1587m, 1528w, 1316w, 1272w, 1233w, 1167w, 1124w, 1072w, 1023w, 842s ν(PF_6); 766s. ^1H NMR spectrum (300 MHz, d_6-acetone, major isomer): 9.75 (1H, dt*, H6(bpy)); 8.87 (1H, dd, H6(dpa)); 8.59 (1H, d, H3(bpy)); 8.52 (1H, d, H3′(bpy)); 8.46 (1H, dt*, H6′(bpy); 8.40 (1H, t*d, H4(bpy)); 8.20 (1H, t*d, H4′(bpy)); 7.99−8.10 (2H, m, H6′(dpa) + H4(dpa)); 7.75−7.83 (2H, m, H5(bpy) + H4′(dpa)); 7.63 (1H, ddd, H5(dpa)); 7.53 (1H, d, H3(dpa)); 7.36 (1H, ddd, H5′(dpa)); 7.20 (1H, d, H3(dpa)); 6.96 (1H, ddd, H5′(dpa)); (δ(N-**H**) > 10.0 ppm). Isomer ratio (by integration of ^1H NMR): major isomer >20:1

***cis*-Carbonylchloro(4,4′-dimethyl-2,2′-bipyridine)(5,6-dimethyl-1,10-phenanthroline)ruthenium(II) Hexafluorophosphate.** [Ru(4,4′-Me_2bpy)(5,6-Me_2phen)(CO)Cl](PF_6) was made by the method used to prepare [Ru(bpy)(phen)(CO)Cl](PF_6) but using [Ru(4,4′-Me_2bpy)(CO)Cl_2]$_2$ (0.13 g, 0.17 mmol) and 5,6-dimethyl-1,10-phenanthroline (0.12 g, 0.59 mmol). The bright yellow product was purified by dissolution in acetone and reprecipitation with diethyl ether to yield crystals with two habits, yellow polyhedra (more common) and orange prismatic (see X-ray structure determinations). Yield: 0.17 g (72%). ES-MS (acetone): *m*/*z* 557 (100%, [Ru(4,4′-Me_2bpy)(5,6-Me_2phen)(CO)Cl]$^+$), 529 (10%, [Ru(4,4′-Me_2bpy)(5,6-Me_2phen)Cl]$^+$). Anal. Calcd for [$C_{27}H_{24}N_4ClF_6OPRu$]: C 46.2, H 3.4, N 8.0. Found: C 46.2, H 3.3, N 7.9. IR (Nujol) cm^{-1}: 1978s ν(CO); 1619m, 1599w, 1307w, 1241w, 1224w, 1169w, 1081w, 1034w, 845s ν(PF_6); 740w. Far IR (cm^{-1}): 306m ν(Ru−Cl). ^1H NMR spectrum (300 MHz, d_6-acetone, major isomer): 9.78 (1H, dd, H2(phen)); 9.54 (1H, d, H6(bpy)); 9.06 (1H, dd, H4(phen)); 8.97 (1H, dd, H7(phen)); 8.72 (1H, s, H3(bpy)); 8.56 (1H, s, H3(bpy)); 8.21 (1H, dd, H3(phen)); 8.05 (1H, dd, H9(phen)); 7.87−7.91 (2H, m, H5(bpy) + H8(phen)); 7.70 (1H, d, H6′(bpy)); 7.14 (1H, dd, H5′(bpy)); 2.94 (3H, s, phen 5-C**H**$_3$); 2.88 (3H, s, phen 6-C**H**$_3$); 2.77 (3H, s, bpy 4-C**H**$_3$); 2.44 (3H, s, bpy 4′-C**H**$_3$). Isomer ratio (by integration of ^1H NMR): major isomer >20:1.

***cis*-Carbonyl(4,4′-dimethyl-2,2′-bipyridine)(5,6-dimethyl-1,10-phenanthroline)nitratoruthenium(II) Hexafluorophosphate.** [Ru(4,4′-Me_2bpy)(5,6-Me_2phen)(CO)Cl](PF_6) (0.17 g, 0.25 mmol) and silver nitrate (0.11 g, 0.63 mmol) were suspended in methanol (40 cm^3). The mixture was heated at reflux for 18 h. To the resultant mixture was added ammonium hexafluorophosphate (0.32 g, 2.0 mmol), and the suspension was sonicated for 5 min. The yellow/gray suspension was evaporated to dryness under reduced pressure. Acetone (20 cm^3) was used to extract the mustard-colored residue. Following filtration through diatomaceous earth, the yellow filtrate was reduced in volume to 5 cm^3. Addition of aqueous potassium hexafluorophosphate (5 cm^3, 1.0 M) precipitated a yellow solid. The product was collected by filtration, washed thoroughly with water, and dried in air. Yield: 0.17 g (96%). ES-MS (acetone):

m/z 584 (100%, [Ru(4,4-Me$_2$bpy)(5,6-Me$_2$phen)(CO)NO$_3$]$^+$). Anal. Calcd for [C$_{27}$H$_{24}$N$_5$F$_6$O$_4$PRu]: C 44.5, H 3.3, N 9.6. Found: C 43.5, H 3.5, N 8.9. IR (Nujol) cm^{-1}: 3414w(br) (H$_2$O); 1986s ν(CO); 1620m, 1271s ν(NO$_3$); 1244w, 1224w, 1155w, 1037w, 994w, 847s ν(PF$_6$). ^{1}H NMR spectrum (300 MHz, d_6-acetone, major isomer): 9.96 (1H, dd, H2(phen)); 9.10 (1H, dd, H4(phen)); 9.04 (1H, dd, H7(phen)); 8.89 (1H, d, H6(bpy)); 8.77 (1H, s, H3(bpy)); 8.57 (1H, s, H3′(bpy)); 8.25 (1H, dd, H3(phen)); 8.08 (1H, dd, H9-(phen)); 7.99 (1H, dm, H5(bpy)); 7.94 (1H, dd, H8(phen)); 7.67 (1H, d, H6′(phen)); 7.15 (1H, dm, H5′(bpy)); 2.94 (3H, s, phen-C**H**$_3$); 2.88 (3H, s, phen-C**H**$_3$); 2.79 (3H, s, bpy-C**H**$_3$); 2.45 (3H, s, bpy-C**H**$_3$′). Isomer ratio (by integration of ^{1}H NMR); major isomer >20:1.

***cis*-Carbonylchloro(4,4′-dimethyl-2,2′-bipyridine)(5,5′-dimethyl-2,2′-bipyridine)ruthenium(II) Perchlorate Hydrate.** Reaction of [Ru(4,4′-Me$_2$bpy)(CO)Cl$_2$]$_2$ (0.41 g, 0.53 mmol) with 5,5′-Me$_2$bpy (0.28 g, 1.5 mmol) under the conditions used to prepare [Ru(bpy)-(phen)(CO)Cl](PF$_6$) forms the complex, which precipitated as a yellow solid, [Ru(4,4′-Me$_2$bpy)(5,5′-Me$_2$bpy)(CO)Cl](ClO$_4$) on addition of an excess of NaClO$_4$ (aq). Yield: 0.46 g (68%). ES-MS (acetone): m/z 533 (100%, [Ru(4,4′-Me$_2$bpy)(5,5′-Me$_2$bpy)-(CO)Cl]$^{+\prime\prime}$), 505 (10%, [Ru(4,4′-Me$_2$bpy)(5,5′-Me$_2$bpy)Cl]$^+$). Anal. Calcd for [C$_{25}$H$_{26}$N$_4$Cl$_2$O$_6$Ru]: C 46.2, H 4.0, N 8.6. Found: C 46.4, H 3.8, N 8.6. IR (Nujol) cm^{-1}: 3500w(br) ν(H$_2$O); 1975s ν(CO); 1617m, 1582w, 1315w, 1245w, 1098s(br) ν(ClO$_4$), 928w, 898w, 838m. Far IR (cm^{-1}): 322m ν(Ru−Cl). ^{1}H NMR spectrum (300 MHz, d_6-acetone, major isomer): 9.44 (1H, d, H6(4Me$_2$bpy)); 9.27 (1H, d, H6(5Me$_2$bpy)); 8.67 (1H, s, H3(4Me$_2$bpy)); 8.60 (1H, d, H3(5Me$_2$bpy)); 8.57 (1H, d, H3′(5Me$_2$bpy)); 8.13 (1H, dt* H4(5Me$_2$bpy)); 8.05 (1H, dt* H4′(5Me$_2$bpy)); 8.02 (1H, s, H3(4Me$_2$bpy)); 7.85 (1H, d, H5(4Me$_2$bpy)); 7.81 (1H, dd, H6′(4Me$_2$bpy)); 7.47 (1H, m, H6′(5Me$_2$bpy)); 7.29 (1H, d, H5′(4Me$_2$bpy)); 2.74 (3H, s, 4Me$_2$bpy-C**H**$_3$); 2.62 (3H, s, 5Me$_2$bpy-C**H**$_3$); 2.50 (3H, s, 4Me$_2$bpy-C**H**$_3$′); 2.20 (3H, s, 5Me$_2$bpy-C**H**$_3$′). Isomer ratio (by integration of ^{1}H NMR): 3:1.

***cis*-Carbonylchloro(5,5′-dimethyl-2,2′-bipyridine)(di(2-pyridyl)amine)ruthenium(II) Hexafluorophosphate.** [Ru(5,5′-Me$_2$bpy)-(dpa)(CO)Cl](PF$_6$) was prepared by the procedure used to synthesize [Ru(bpy)(phen)(CO)Cl](PF$_6$). [Ru(5,5′-Me$_2$bpy)(CO)Cl$_2$]$_2$ (0.15 g, 0.19 mmol) was reacted with di(2-pyridyl)amine (0.11 g, 0.63 mmol) to give the desired product. Yield: 0.25 g (97%). ES-MS (acetone): m/z 520 (100%, [Ru(5,5-Me$_2$bpy)(dpa)(CO)Cl]$^+$). Anal. Calcd for [C$_{23}$H$_{21}$N$_5$ClF$_6$OPRu]: C 41.5, H 3.2, N 10.5. Found: C 42.4, H 3.2, N 10.9. IR (Nujol) cm^{-1}: 3381m ν(NH); 1972s ν(CO); 1630m, 1585m, 1520w, 1314w, 1244w, 1164w, 1056w, 1023w, 846s ν(PF$_6$); 774m. Far IR (cm^{-1}): 309m ν(Ru−Cl). ^{1}H NMR spectrum (300 MHz, d_6-acetone, major isomer): 9.90 (1H, s (broad), −N**H**−); 9.53 (1H, d, H6(Me$_2$bpy)); 8.87 (1H, dt*, H6(dpa)); 8.40 (1H, d, H3(Me$_2$bpy)); 8.33 (1H, d, H3′(Me$_2$bpy)); 8.28 (1H, d, H6′(Me$_2$bpy)); 8.18 (1H, ddd, H3(dpa)); 8.07 (1H, dt*, H6′(dpa)); 8.01 (1H, ddd, H4(dpa)); 7.76−7.83 (2H, m, H4(Me$_2$bpy) + H4′(dpa)); 7.48 (1H, dd, H4′(Me$_2$bpy)); 7.35 (1H, ddd, H5(dpa)); 7.16 (1H, dm, H3′(dpa)); 6.93 (1H, dt*$_{\text{(unsymmetrical)}}$, H5′(dpa)); 2.65 (3H, s, 5-C**H**$_3$); 2.36 (3H, s, 5′-C**H**$_3$). Isomer ratio (by integration of ^{1}H NMR): 3:1.

***cis*-Carbonylchloro(4,4′-dimethyl-2,2′-bipyridine)(4,7-dimethyl-1,10-phenanthroline)ruthenium(II) Hexafluorophosphate.** [Ru(4,4′-Me$_2$bpy)(4,7-Me$_2$phen)(CO)Cl](PF$_6$) was obtained as a bright yellow powder by minor modification of the procedure outlined for the synthesis of [Ru(bpy)(phen)(CO)Cl](PF$_6$) using [Ru(4,4′-Me$_2$bpy)(CO)Cl$_2$]$_2$ (0.16 g, 0.22 mmol) and 4,7-dimethyl-1,10-phenanthroline (0.11 g, 0.50 mmol). Yield: 0.28 g (93%). ES-MS (acetone): m/z 557 (100%, [Ru(4,4′-Me$_2$bpy)(4,7-Me$_2$phen)(CO)-Cl]$^+$). Anal. Calcd for [C$_{27}$H$_{24}$N$_4$ClF$_6$OPRu]: C 46.2, H 3.4, N 8.0. Found: C 46.4, H 3.3, N 8.0. IR (Nujol) cm^{-1}: 1967s ν(CO); 1620m, 1579w, 1522w, 1424m, 1306w, 1244w, 1170w, 1034w, 844s ν(PF$_6$). Far IR (cm-^{1}): 304s ν(Ru−Cl). Isomer ratio (by integration of ^{1}H NMR): 3:2.

***cis*-Carbonylchloro(4,7-dimethyl-1,10-phenanthroline)(2,2′-bipyridine)ruthenium(II) Hexafluorophosphate.** Reaction of [Ru(4,7-Me$_2$phen)(CO)Cl$_2$] (0.14 g, 0.17 mmol) and 2,2′-bipyridine (0.11 g, 0.70 mmol), according to the method used to prepare [Ru(bpy)-(phen)(CO)Cl](PF$_6$), yielded [Ru(4,7-Me$_2$phen)(bpy)(CO)Cl](PF$_6$) as a fine yellow powder. Yield: 0.23 g (98%). ES-MS (acetone): m/z 529 (100%, [Ru(4,7-Me$_2$phen)(bpy)(CO)Cl]$^+$). Anal. Calcd for [C$_{25}$H$_{20}$N$_4$ClF$_6$OPRu]: C 44.6, H 3.0, N 8.3. Found: C 44.6, H 2.8, N 8.1. IR (Nujol) cm^{-1}: 1974s ν(CO); 1625w, 1605m, 1576w, 1520w, 1424m(sh), 1315w, 1230w, 1171w, 1070w, 1032w, 838s ν(PF$_6$); 773s. Far IR (cm^{-1}): 305w ν(Ru−Cl). Isomer ratio (by integration of ^{1}H NMR): 3:2.

***cis*-Carbonylchloro(2,2′-bipyridine)(di(2-pyridyl)ketone)-ruthenium(II) Hexafluorophosphate.** Reaction of [Ru(bpy)(CO)-Cl$_2$]$_2$ with di(2-pyridyl)ketone gave a mixture of products containing predominantly [Ru(bpy)(dpk)(CO)Cl](PF$_6$), contaminated by ketal adducts. A small amount of the complex was obtained by manual separation of isolated single crystals. Fractional recrystallization of the crude product from ethanol also afforded small amounts of the complex. ES-MS (acetone, recrystallized material): m/z 505 (100%, [Ru(bpy)(dpk)(CO)Cl]$^+$). IR (Nujol, bulk) cm^{-1}: 1970s ν(CO); 1684m, 1600m, 1310m, 1281m, 1250m, 1161w, 1106w, 1071w, 1030w, 977w, 942w; 856s, 837s ν(PF$_6$), 762s. Isomer ratio (by integration of ^{1}H NMR): 4:1.

***cis*-Carbonylchloro(di(2-pyridyl)ketone)(2,2′-bipyridine)-ruthenium(II) Hexafluorophosphate.** As in the case of [Ru(bpy)-(dpk)(CO)Cl](PF)$_6$, the desired complex, prepared from [Ru(dpk)-COCl$_2$]$_2$ with bpy, could be obtained pure only by manual extraction of isolated single crystals from the bulk product, or fractional recrystallization in minute quantities. ES-MS (acetone): m/z 505 (100%, [Ru(dpk)(bpy)(CO)Cl]$^+$). IR (Nujol) cm^{-1}: 1976ν(CO); 1686m, 1597m, 1310m, 1281m, 1250w, 1161w, 1104w, 1072w, 1029w, 977w, 941w; 857s, 838s ν(PF$_6$), 762s. Isomer ratio (by integration of ^{1}H NMR): 3:1.

***cis*-Carbonylchloro(di(2-pyridyl)ketone)(4,7-dimethyl-1,10-phenanthroline)ruthenium(II) Hexafluorophosphate.** The procedure was that followed for [Ru(dpk)(bpy)(CO)Cl](PF)$_6$. ES-MS (acetone): m/z 557 (100%, [Ru(dpk)(4,7-Me$_2$phen(CO)Cl]$^+$), 581 (50%), 597 (60%, [Ru(dpk)(4,7-Me$_2$phen(CO)] + (CH$_3$OCH$_3$-CH$_2$O)). IR (Nujol) cm^{-1}: 1976ν(CO); 1681m, 1626w, 1598w, 1580w, 1521w, 1311w, 1284w, 1157w, 1080w, 1030w, 968w, 943w, 842s ν(PF$_6$); 760m.

Structure Determinations. Except as noted, unique room-temperature "four-circle"/single-counter diffractometer data sets were measured ($2\theta/\theta$ scan mode, $2\theta_{\max} = 50°$; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T ca. 295 K) yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full matrix least squares refinements after Gaussian or analytical absorption correction. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, $(x,y,z,U_{\text{iso}})_{\text{H}}$ being constrained at estimated values. Conventional R, R_w on $|F|$ are quoted at convergence (statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$). Neutral atom complex scattering factors were used in the context of the Xtal 3.2 program system.[32] In the

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(32) *The Xtal 3.4 User's Manual*; Hall, S. R., King, G. S. D., Stewart, J. M., Eds.; University of Western Australia: Lamb, Perth, 1995. *The Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; University of Western Australia: Lamb, Perth, 1992.

figures, 20% displacement envelopes are shown for the nonhydrogen atoms (50% for the low-temperature study), hydrogen atoms being shown with arbitrary radii of 0.1 Å. Pertinent data are given below and in the figures and tables. Variations in procedure, individual idiosyncrasies, etc. are noted below and as “variata”.

Crystal/Refinement Details (in the Formulas, Me Denotes Methyl). [Ru(phen)(bpy)(CO)Cl](PF$_6$)·(CH$_3$)$_2$CO ≡ $C_{26}H_{22}ClF_6N_4O_2PRu$. $M = 704.0$. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $a = 8.173(3)$ Å, $b = 21.675(7)$ Å, $c = 16.414(7)$ Å, $\beta = 107.68(3)°$, $V = 2770$ Å^3. D_c ($Z = 4$) $= 1.69_2$ g cm^{-3}. $\mu_{Mo} = 7.3$ cm^{-1}; specimen: 0.28 × 0.12 × 0.12 mm; $A^*_{min,max} = 1.14, 1.18$ (analytical correction). $N = 4794$, $N_o = 3488$; $R = 0.039$, $R_w = 0.040$. $|\Delta\rho_{max}| = 0.58$ e Å^{-3}.

[Ru(4,4′-Me$_2$bpy)(4,7-Me$_2$phen)(CO)Cl](ClO$_4$) ≡ $C_{27}H_{24}Cl_2N_4O_5Ru$. $M = 656.5$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 15.97(1)$ Å, $b = 11.172(6)$ Å, $c = 8.192(4)$ Å, $\alpha = 68.26(4)°$, $\beta = 81.69(4)°$, $\gamma = 81.05(5)°$, $V = 1335$ Å^3. D_c ($Z = 2$) $= 1.63_3$ g cm^{-3}. $\mu_{Mo} = 8.3$ cm^{-1}; specimen: 0.45 × 0.22 × 0.06 mm; $A^*_{min,max} = 1.05, 1.13$. $N = 9183$ (full sphere), $N = 4697$ ($R_{int} = 0.046$), $N_o = 3470$; $R = 0.061$, $R_w = 0.079$. $|\Delta\rho_{max}| = 1.3$ e Å^{-3}.

Variata. Perchlorate oxygens O(2−4) were modeled as disordered over two sets of sites, occupancies refining to 0.70(2) and complement, seemingly concerted with corresponding disorder, modeled and refined similarly, between the CO and Cl groups. CO geometries were modeled constrained to estimated values.

[Ru(4,4′-Me$_2$bpy)(5,6-Me$_2$phen)(CO)Cl](PF$_6$) ≡ $C_{27}H_{24}ClF_6N_4OPRu$. $M = 702.0$. Monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14, variant), $Z = 4$.

(i) Orange form: $a = 18.799(7)$ Å, $b = 8.545(3)$ Å, $c = 19.402(8)$ Å, $\beta = 115.51(3)°$, $V = 2813$ Å^3. $D_c = 1.65_8$ g cm^{-3}. $\mu_{Mo} = 7.8$ cm^{-1}; specimen: 0.45 × 0.20 × 0.40 mm; $A^*_{min,max} = 1.13, 1.24$. $N = 4940$, $N_o = 3657$; $R = 0.047$, $R_w = 0.057$. $|\Delta\rho_{max}| = 0.94$ e Å^{-3}.

Variata. The “observed” criterion was $I > 2\sigma(I)$. An additional quadrant of data was measured to $2\theta_{max} = 40°$, and merged ($R_{int} = 0.038$).

(ii) Yellow form: $a = 14.092(5)$ Å, $b = 14.203(4)$ Å, $c = 14.701(5)$ Å, $\beta = 106.99(3)°$, $V = 2814$ Å^3. $D_c = 1.65_7$ g cm^{-3}. $\mu_{Mo} = 7.8$ cm^{-1}; specimen: 0.08 × 0.20 × 1.20 mm; $A^*_{min,max} = 1.06, 1.09$. $N = 4530$, $N_o = 3227$; $R = 0.049$, $R_w = 0.063$. $|\Delta\rho_{max}| = 1.16$ e Å^{-3}.

Variata. The fluorine atoms of the anion were modeled as disordered over two sets of sites, set at equal occupancy after trial refinement.

[Ru(bpy)(dpa)(CO)Cl](ClO$_4$) ≡ $C_{21}H_{17}Cl_2N_5O_5Ru$. $M = 591.4$. Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 17.082(5)$ Å, $b = 13.275(2)$ Å, $c = 10.479(2)$ Å, $V = 2376$ Å^3. D_c ($Z = 4$) $= 1.65_3$ g cm^{-3}. $\mu_{Mo} = 9.3$ cm^{-1}; specimen: 0.26 × 0.32 × 0.17 mm; $A^*_{min,max} = 1.16, 1.22$. $N = 2384$, N_o ($I > 2\sigma(I)$) $= 1619$. $R = 0.052$, $R_w = 0.060$. $|\Delta\rho_{max}| = 1.09$ e Å^{-3}.

Variata. A hemisphere of data (8547 reflections) was measured. After refinement of x_{abs} had produced no definitive assignment of chirality, these “Friedel” data were merged ($R_{int} = 0.12$).

[Ru(5,5′-Me$_2$bpy)(dpa)(CO)Cl](ClO$_4$) ≡ $C_{23}H_{21}Cl_2N_5O_5Ru$. $M = 619.4$. Monoclinic, space group $P2_1/c$, $a = 13.828(4)$ Å, $b = 12.515(2)$ Å, $c = 15.501(4)$ Å, $\beta = 109.26(2)°$, $V = 2532$ Å^3. D_c ($Z = 4$) $= 1.62_4$ g cm^{-3}. $\mu_{Mo} = 8.7$ cm^{-1}; specimen: 0.75 × 0.44 × 0.25 mm; $A^*_{min,max} = 1.36, 1.49$. $N = 4433$, N_o ($I > 2\sigma(I)$) $= 3773$; $R = 0.053$, $R_w = 0.061$. $|\Delta\rho_{max}| = 0.84$ e Å^{-3}.

Variata. The perchlorate group was modeled as disordered rotationally about Cl−O(1), O(2−4) being disposed over two sets of sites, occupancies refining to 0.72(1) and complement.

[Ru(bpy)(dpk)(CO)Cl](PF$_6$)·H$_2$O ≡ $C_{22}H_{18}ClF_6N_4O_3PRu$. $M = 667.9$. Monoclinic, space group $P2_1/n$, $a = 8.612(5)$ Å, $b = 13.314(8)$ Å, $c = 22.73(1)$ Å, $\beta = 94.48(4)°$, $V = 2598$ Å^3. D_c ($Z = 4$) $= 1.70_7$ g cm^{-3}. $\mu_{Mo} = 8.4$ cm^{-1}; specimen: 0.46 × 0.43 × 0.43 mm; $A^*_{min,max} = 1.33, 1.43$. $N = 7886$, N_o ($I > 2\sigma(I)$) $= 4743$; $R = 0.057$, $R_w = 0.042$. $|\Delta\rho_{max}| = 0.89$ e Å^{-3}.

Variata. Difference map residues were modeled in terms of a water molecule (oxygen only) disordered over a pair of sites, occupancies refining to 0.6 and complement. Data were measured by the ω-scan technique to $2\theta_{max} = 60°$.

[Ru(dpk)(4,7-Me$_2$phen)(CO)Cl](ClO$_4$) ≡ $C_{26}H_{20}Cl_2O_6Ru$. $M = 656.4$. Monoclinic, space group $P2_1/c$, $a = 13.801(9)$ Å, $b = 11.907(9)$ Å, $c = 16.050(10)$ Å, $\beta = 102.30(6)°$, $V = 2577$ Å^3. D_c ($Z = 4$) $= 1.69_2$ g cm^{-3}. $\mu_{Mo} = 8.7$ cm^{-1}; specimen: 0.26 × 0.22 × 0.06 mm; $A^*_{min,max}$ (analytical correction) $= 1.08, 1.21$. $N = 3538$, N_o ($I > 2.5\sigma(I)$) $= 2157$; $R = 0.064$, $R_w = 0.055$. $|\Delta\rho_{max}| = 1.3$ e Å^{-3}.

Variata. Limited data, measured by the ω-scan technique at ca. 173 K to $2\theta_{max} = 45°$, would support meaningful refinement of anisotropic displacement parameter forms for Ru, Cl, ClO$_4$ only.

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Supporting Information Available: X-ray crystallographic files in CIF format and representative examples of the ^{1}H NMR spectra of [Ru(**L^1**)(**L^2**)(CO)Cl]$^+$ complexes, viz., [Ru(bpy)(phen)(CO)Cl]$^+$ and [Ru(phen)(bpy)(CO)Cl]$^+$ prepared from [Ru(bpy)(CO)Cl$_2$]$_2$ and [Ru(phen)(CO)Cl$_2$]$_2$, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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