# Designed Synthesis of Mononuclear Tris(heteroleptic) Ruthenium Complexes Containing Bidentate Polypyridyl Ligands

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A general synthetic methodology is reported for tris(bidentate)ruthenium(II) complexes containing three different polypyridyl ligands, based on the sequential addition of the ligands to the oligomer $[Ru(CO)_2Cl_2]_n$. The tris-(heteroleptic) complexes were characterized by FAB mass spectrometry and NMR spectroscopy. An X-ray crystal structure determination was made for the complex $[Ru(Me_2bpy)(phen)(bpa)](PF_6)_2 \cdot C_6H_{14}$ [$C_{40}H_{43}F_{12}N_7P_2Ru$, $M = 1062.8$; $Me_2bpy = 4,4'$-dimethyl-2,2'-bipyridine, phen = 1,10-phenanthroline, bpa = bis(2-pyridyl)amine]: triclinic, space group $P\bar{1}$, $a = 14.57(3)$ Å, $b = 13.50(3)$ Å, $c = 12.73(3)$ Å, $\alpha = 68.6(2)°$, $\beta = 63.5(1)°$, $\gamma = 79.8(2)°$, $V = 2082$ Å$^3$, $Z = 2$. Aspects of the electrochemistry, spectroscopy, and photophysics of the tris-(heteroleptic) species are discussed.

## Introduction

Coordination compounds of ruthenium(II) containing polypyridyl ligands have been the subject of a wide variety of photochemical studies directed toward their use as "photosensitizers" in photochemical molecular devices (PMDs).[1,2] The complex tris(2,2'-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, is the archetype of such species and demonstrates the combined attributes of significant absorption in the visible spectral region, the relative longevity of the metal-to-ligand charge transfer (MLCT) excited states formed on light absorption, the relative inertness of the metal center in a variety of oxidation states, and the rapidity of the redox reactions involving the excited states (quenching).

The excited state properties of complexes of this genre are controlled by the pattern of low-lying electronic levels which are ligand-dependent,[3,4] as is the redox behavior.[1,3−5] Indeed there are clear correlations between aspects of these two characteristics, as they share a dependence on the $\pi^*$ energies of the ligands and the $d\pi$ levels at the metal.[5] Accordingly, through a judicious choice of ligands, it is possible to "fine tune" the redox and photophysical properties of the ground and excited states of polypyridylruthenium(II) complexes. As alluded to previously,[1] with 200 bidentate ligands (pp), there are 200 homoleptic possibilities $[Ru(pp)_3]^{2+}$, ~4 × 10⁴ bis(hetereoleptic)

$[Ru(pp)_2(pp')]^{2+}$ species, and ~1.3 × 10⁶ tris(heteroleptic) complexes $[Ru(pp)(pp')(pp'')]^{2+}$!

The lack of a generalized synthetic methodology for tris-(bidentate) complexes of ruthenium(II) in which the three ligands are different {tris(heteroleptic) species} has limited the exploitation of this concept of rational control of their physical characteristics. Existing procedures are most effective for incorporation of at most two different ligands into the coordination sphere, and examples of tris(heteroleptic) complexes are very limited.[6−9] The synthetic technique described here and in preceding papers[10−16] provides a general route for the preparation of tris(heteroleptic) species of ruthenium(II). It presents new strategies for the design of visible-light sensitizers of the tris(bidentate)ruthenium(II) genre and for polymetallic molecular assemblies based on such centers.

## Experimental Section

**Physical Measurements.** UV/visible spectra were recorded on a Hewlett-Packard 8452A diode array, CARY 219, or CARY 14 spectrophotometer (the last being interfaced to an IBM PC by On-Line Systems, Inc.). NMR spectra were recorded on a BRUKER AM300 or AC200 spectrometer. Infrared spectra were recorded on

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either a Perkin Elmer Series 1600 FTIR or a Nicolet 20DX FTIR spectrometer. Electrochemical measurements were made in a drybox (Ar) using a Bioanalytical Systems (BAS) 100A electrochemical analyzer, an EG&G PAR Model 175 potentiostat and Model 175 waveform generator, or an EG&G Model 273 potentiostat. Unless otherwise indicated, cyclic voltammetry was carried out by using platinum working electrodes, and all potentials were measured relative to an Ag/AgNO$_3$ (0.01 M in acetonitrile) reference electrode: however, potentials are quoted relative to a saturated sodium chloride calomel electrode (SSCE) unless otherwise specified. Positive-ion fast atom bombardment mass spectra were recorded on a JEOL-DX300 probe (Ar$^+$ source) with samples mulled in 3-nitrobenzyl alcohol.

Prior to photophysical analysis, all metal complexes were purified by cation-exchange HPLC chromatography on a Brownlee CX-100 Prep10 column utilizing linear gradient elution with 0–400 mM KBr in 2:3 (v/v) CH$_3$CN/aqueous phosphate buffer (0.6 mM; pH = 7.2), controlled by a Perkin Elmer Series 4 pump control unit and monitored at a Perkin Elmer LC-95 variable UV–vis spectrophotometer detector fitted with a 4.5 μL path length flow cell.
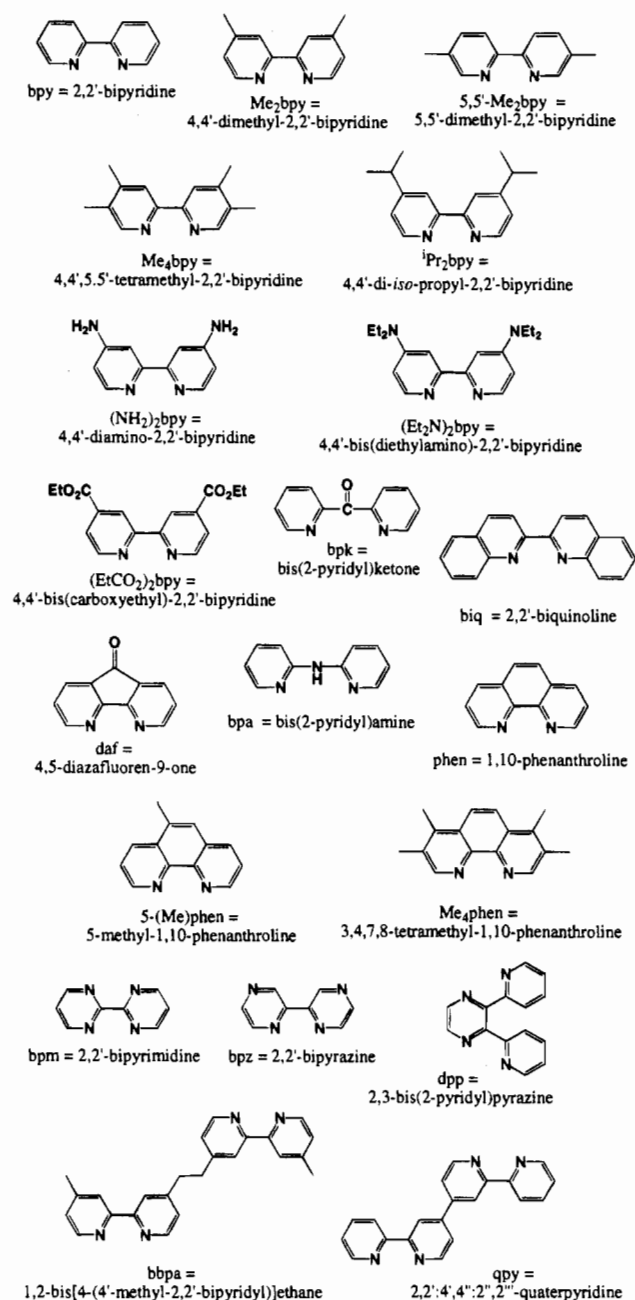
Photophysical measurements (emission spectra and time-resolved emission studies) were carried out as described previously,[17] as were the emission quantum yields ($\Phi_{em}$) using [Ru(bpy)$_3$](PF$_6$)$_2$ in CH$_3$CN ($\Phi_{em}$ = 0.062) or [Os(bpy)$_3$](PF$_6$)$_2$ in CH$_3$CN ($\Phi_{em}$ = 0.0046) as standards.[18] Due to limited detector response at low energies, approximately 30% of the emission band of [Ru(Me$_2$bpy){(EtCO$_2$)$_2$bpy}-{(Et$_2$N)$_2$bpy}](PF$_6$)$_2$ (**Vi**) could not be reliably measured. The full spectrum, as well as the spectrum for the [Os(bpy)$_3$](PF$_6$)$_2$ standard, was reconstructed using spectral fitting techniques described previously.[19] This method was found to reproduce the emission quantum yield for [Ru(bpy)$_3$](PF$_6$)$_2$ to within experimental error. Quantum yields for decomposition ($\Phi_{dec}$) were measured relative to [Ru(bpy)$_3$](PF$_6$)$_2$ ($\Phi_{dec} \sim 0.029$ [20]) at $\sim 2 \times 10^{-5}$ M in a freeze–pump–thaw degassed (4×) stirred 0.2 M [N(n-C$_4$H$_9$)$_4$]Cl/[CH$_3$CN solution at 295 K by measuring the decrease in emission intensity as a function of time (12 h). A collimated 75 W lamp was used as the source, with the intensity of irradiation measured using Reinicke's salt as a chemical actinometer.[20]

**Materials.** Hydrated RuCl$_3$·3H$_2$O (Strem), formic acid (BDH; AnalaR, 90%), and 1,2-dimethoxyethane (FLUKA; puriss) were used as supplied. Trifluoromethanesulfonic acid (3 M) was distilled under vacuum before use. Trimethylamine N-oxide (TMNO) was obtained by vacuum sublimation of the hydrate (FLUKA; purum) at 120 °C. The ligands (pp) were acquired as commercial reagents when available or obtained from reported synthetic routes. Reagent solvents were used without further purification. Spectral grade acetonitrile (Burdick and Jackson), methanol (Burdick and Jackson), and ethanol (freshly distilled over Mg/I$_2$) were used for all spectroscopic and electrochemical measurements.

**Syntheses.** Chemical analyses were performed by either Chemical & Micro Analytical Services Pty. Ltd. (Melbourne, Australia) or Oneida Research Services, Inc. (Whitesboro, NY). The microanalytical data for the compounds listed are available in the supplementary material (supplementary Table S1).

The ligands 5,5'-Me$_2$bpy and $^i$Pr$_2$bpy (see Chart 1) were synthesized by W. H. F. Sasse (Division of Applied Organic Chemistry, CSIRO),[21,22] (Et$_2$N)$_2$bpy[23] (see Chart 1) was kindly donated by P. Belser (Université de Fribourg Suisse), and the ligands Me$_4$bpy, (EtCO$_2$)$_2$bpy, (NH$_2$)$_2$bpy,[24] bbpa,[25] qpy,[26] and daf[27] (see Chart 1), were obtained by standard

**Chart 1**



bpy = 2,2'-bipyridine

Me$_2$bpy = 4,4'-dimethyl-2,2'-bipyridine

5,5'-Me$_2$bpy = 5,5'-dimethyl-2,2'-bipyridine

Me$_4$bpy = 4,4',5,5'-tetramethyl-2,2'-bipyridine

$^i$Pr$_2$bpy = 4,4'-di-*iso*-propyl-2,2'-bipyridine

(NH$_2$)$_2$bpy = 4,4'-diamino-2,2'-bipyridine

(Et$_2$N)$_2$bpy = 4,4'-bis(diethylamino)-2,2'-bipyridine

(EtCO$_2$)$_2$bpy = 4,4'-bis(carboxyethyl)-2,2'-bipyridine

bpk = bis(2-pyridyl)ketone

biq = 2,2'-biquinoline

daf = 4,5-diazafluoren-9-one

bpa = bis(2-pyridyl)amine

phen = 1,10-phenanthroline

5-(Me)phen = 5-methyl-1,10-phenanthroline

Me$_4$phen = 3,4,7,8-tetramethyl-1,10-phenanthroline

bpm = 2,2'-bipyrimidine

bpz = 2,2'-bipyrazine

dpp = 2,3-bis(2-pyridyl)pyrazine

bbpa = 1,2-bis[4-(4'-methyl-2,2'-bipyridyl)]ethane

qpy = 2,2':4',4":2",2"'-quaterpyridine

methods. Metathesis of Br$^-$ to the PF$_6^-$ salts were carried out by the addition of an aqueous solution of NH$_4$PF$_6$.

**[Ru(CO)$_2$Cl$_2$]$_n$ (I).** Paraformaldehyde (1 g) and RuCl$_3$·3H$_2$O (2.02 g, 9.74 mmol) were added to an Ar-sparged solution of 90% formic acid (50 mL), and the solution was then heated at reflux for 6 h. The solution changed in color from reddish-yellow to deep green over the course of 1 h. Further heating resulted in a change from green to yellow-orange in 4 h and a change to pale yellow in 6 h. The reaction vessel was cooled to room temperature and then stored at 4 °C overnight to allow complete conversion to the polymer. The solution was evaporated to dryness on a steam bath and the residue triturated with hexane and dried *in vacuo*; yield, 2.00 g (8.52 mmol, 90%). IR (Nujol): $\bar{\nu}_{CO}$ at 2074 and 2017 cm$^{-1}$ {$\bar{\nu}_{CO}$ at 2138 cm$^{-1}$ for the orange dimer [Ru(CO)$_3$Cl$_2$]$_2$, which may occur as an impurity}.

*trans(Cl)*-**[Ru(pp)(CO)$_2$Cl$_2$] (II).** In a typical experiment, bpy (1.03 g; 6.6 mmol) was mixed with sufficient AR methanol to dissolve at

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least two-thirds of the ligand (10 mL). Following deaeration (N$_2$) for 30 min, [Ru(CO)$_2$Cl$_2$]$_n$ (1.0 g; 4.4 mmol) was added and the mixture heated at reflux under the inert atmosphere for 30 min with vigorous stirring (3 h for **IId**). Extra methanol was added after 15 min of the reaction to facilitate stirring of the suspension as the product precipitated. After cooling to room temperature, the pale yellow precipitate was collected and recrystallized from boiling methanol to yield fine very pale yellow feathery crystals (orange for **IId**). The absence of ligand in the complex was confirmed by thin layer chromatography (TLC) (silica gel absorbent; acetonitrile eluent).

[Ru(bpy)(CO)$_2$Cl$_2$] (**IIa**); yield, 80%. IR (nujol): $\bar{\nu}_{CO}$ at 2057 and 1998 cm$^{-1}$. [Ru(Me$_2$bpy)(CO)$_2$Cl$_2$] (**IIb**); yield, 50% {recrystallized from CHCl$_3$}. IR (nujol): $\bar{\nu}_{CO}$ at 2060 and 1989 cm$^{-1}$. [Ru(Me$_4$bpy)-(CO)$_2$Cl$_2$] (**IIc**); yield, 81%. IR (nujol): $\bar{\nu}_{CO}$ at 2063 and 1996 cm$^{-1}$. NMR ($^1$H, CDCl$_3$): $\delta$ 2.42 (s), 2.48 (s), 7.90 (s), 8.84. [Ru{(EtCO$_2$)$_2$-bpy}(CO)$_2$Cl$_2$] (**IId**); yield, 78%. IR (nujol): $\bar{\nu}_{CO}$ at 2065 and 1992 cm$^{-1}$. NMR ($^1$H, CD$_2$Cl$_2$): $\delta$ 1.46 (t), 4.51 (q), 8.23 (d), 8.91 (s), 9.31 (d). [Ru(phen)(CO)$_2$Cl$_2$] (**IIe**); yield, 61%. IR (nujol): $\bar{\nu}_{CO}$ at 2060 and 2008 cm$^{-1}$.

*cis,cis*-[Ru(pp)(CO)$_2$(CF$_3$SO$_3$)$_2$] (**III**). **Method A.** In a typical experiment, [Ru(bpy)(CO)$_2$(Cl)$_2$] (0.290 g, 0.76 mmol) was added to an oven-dried Schlenck tube and the apparatus was purged with N$_2$ for 30 min. Freshly distilled trifluoromethanesulfonic acid (2.5 mL) was transferred into the apparatus (through a septum) resulting in a red-orange solution. The mixture was heated to 105–110 °C for 90 min with stirring under a continuous flow of dinitrogen bubbled through the solution. The reaction flask was cooled to 0 °C, and diethyl ether (10 mL) was injected through the septum with vigorous stirring, resulting in an off-white precipitate. The solid was collected under a constant flow of N$_2$ and washed with diethyl ether (5×), water (5×), and diethyl ether (5×). The white powdery product was collected, dried under vacuum, and stored under nitrogen. Recrystallization could be effected from dichloromethane/diethyl ether, although the product was generally used immediately without further purification.

[Ru(bpy)(CO)$_2$(CF$_3$SO$_3$)$_2$] (**IIIa**); yield, 55%. IR (nujol): $\bar{\nu}_{CO}$ at 2082 and 2020 cm$^{-1}$; $\bar{\nu}_{SO}$ at 1340, 1178, 1007 cm$^{-1}$; $\bar{\nu}_{CF}$ at 1235 cm$^{-1}$. [Ru(Me$_2$bpy)(CO)$_2$(CF$_3$SO$_3$)$_2$] (**IIIb**); yield, 39%. IR (nujol): $\bar{\nu}_{CO}$ at 2099 and 2027 cm$^{-1}$; $\bar{\nu}_{SO}$ at 1338, 1176, 1008 cm$^{-1}$; $\bar{\nu}_{CF}$ at 1238, 1205 cm$^{-1}$.

**Method B.** [Ru(Me$_2$bpy)(CO)$_2$Cl$_2$] (0.75 g, 1.82 mmol) in 1,2-dichlorobenzene (200 mL) was deaerated with dry nitrogen for 30 min, resulting in a cloudy yellow solution. CF$_3$SO$_3$H (0.5 mL) was added dropwise by syringe (platinum needle), and the solution heated to 110 °C for 1.5 h. The mixture was cooled to 0 °C and the product precipitated by the addition of diethyl ether (200 mL). The mixture was allowed to stir for 1 h, and the complex [Ru(Me$_2$bpy)(CO)$_2$(CF$_3$-SO$_3$)$_2$] (**IIIb**) collected by vacuum filtration under nitrogen and washed with diethyl ether (2 × 5 mL), cold distilled water (2 × 5 mL), and diethyl ether (2 × 5 mL); yield, 0.99 g, 85%.

[Ru(Me$_4$bpy)(CO)$_2$(CF$_3$SO$_3$)$_2$] (**IIIc**); yield, 60%. NMR ($^1$H, CD$_2$-Cl$_2$): $\delta$ 7.91 (s), 7.95 (s), 8.40 (s), 8.72 (s), 2.41 (s), 2.45 (s), 2.53 (s), 2.57 (s).

**Method C.** [Ru{(EtCO$_2$)$_2$bpy}(CO)$_2$(CF$_3$SO$_3$)$_2$] (**IIId**). Freshly distilled CH$_2$Cl$_2$ (750 mL) and [Ru{(EtCO$_2$)$_2$bpy}(CO)$_2$(Cl)$_2$] (0.320 g, 0.61 mmol) were added to an N$_2$-charged reaction vessel, and the mixture was allowed to stir at room temperature for 30 min, resulting in a yellow-orange solution. In the dark, Ag(CF$_3$SO$_3$) (0.32 g, 1.21 mmol) was added and the mixture refluxed for 3 h. The dark colored precipitate was filtered under N$_2$ through Celite (to remove AgCl), and the yellow filtrate, concentrated on a rotary evaporator. The concentrated solution (2–5 mL) was filtered dropwise into anhydrous diethyl ether (100 mL), resulting in a fine white precipitate which was collected on a medium porosity frit, washed with ether (5×), and dried under vacuum; yield, 0.10 g (1.58 mmol, 26%).

[**Ru(pp)(pp')(CO)$_2$](PF$_6$)$_2$ (IV).** In a typical experiment, [Ru(bpy)-(CO)$_2$(CF$_3$SO$_3$)$_2$] (0.15 g, 0.31 mmol) and Me$_2$bpy (0.113 g, 0.61 mmol) were dissolved in 95% ethanol (25 mL) under N$_2$. The solution was brought to reflux, resulting in a color change from colorless to yellow within 30 min. It was then allowed to continue to reflux for an additional 60 min before it was evaporated to dryness by rotary evaporation. The gray residue was dissolved in boiling water and

filtered to remove unreacted ligand (Me$_2$bpy) and a saturated aqueous solution of NH$_4$PF$_6$ (5 mL) added, resulting in an off-white precipitate which was collected and washed with cold water followed by copious amounts of ether. Recrystallization was achieved from hot ethanol/acetone (acetone aids in solubilization: the solution was warmed until it became cloudy as the acetone evaporated, and it was then cooled and placed in the freezer overnight).

Performing the synthesis by the alternative sequence of ligand addition for **IVa, c,** and **d** gave identical results.

[Ru(bpy)(Me$_2$bpy)(CO)$_2$](PF$_6$)$_2$ (**IVa**); yield, 55%. IR (CH$_2$Cl$_2$ solution): $\bar{\nu}_{CO}$ at 2098 and 2049 cm$^{-1}$. [Ru(bpy)(Me$_4$bpy)(CO)$_2$](PF$_6$)$_2$ (**IVb**); yield, 80%. IR (CH$_3$Cl solution): $\bar{\nu}_{CO}$ at 2096 and 2041 cm$^{-1}$. [Ru(bpy){(EtCO$_2$)$_2$bpy}(CO)$_2$](PF$_6$)$_2$ (**IVc**); yield, 40%. IR (CH$_2$Cl$_2$ solution): $\bar{\nu}_{CO}$ at 2102 and 2045 cm$^{-1}$. [Ru(Me$_2$bpy){(EtCO$_2$)$_2$bpy}-(CO)$_2$](PF$_6$)$_2$ (**IVd**); yield, 45%. IR (CH$_2$Cl$_2$ solution): $\bar{\nu}_{CO}$ at 2099 and 2042 cm$^{-1}$. [Ru(bpy){(NH$_2$)$_2$bpy}(CO)$_2$](PF$_6$)$_2$ (**IVe**); yield, 35%. IR (CH$_2$Cl$_2$ solution): $\bar{\nu}_{CO}$ at 2088 and 2038 cm$^{-1}$. [Ru(Me$_2$bpy)(Me$_4$-bpy)(CO)$_2$](PF$_6$)$_2$ (**IVf**); yield, 68%. IR (Nujol mull): $\bar{\nu}_{CO}$ at 2092 and 2036 cm$^{-1}$. NMR ($^1$H, acetone-$d_6$): $\delta$ 2.04 (s, 3H), 2.44 (s, 3H), 2.52 (s, 3H), 2.54 (s, 3H), 2.64 (s, 3H), 2.74 (s, 3H), 7.38 (s, 1H), 7.47 (d, 1H), 7.61 (d, 1H), 7.94 (d, 1H), 8.57 (s, 1H), 8.66 (s, 1H), 8.68 (s, 1H), 8.79 (s, 1H), 9.15 (s, 1H), 9.26 (d, 1H, $J = 5$ Hz). [Ru(Me$_4$-bpy){(EtCO$_2$)$_2$bpy}(CO)$_2$](PF$_6$)$_2$ (**IVg**); yield, 33%. IR (Nujol mull): $\bar{\nu}_{CO}$ at 2089 and 2040 cm$^{-1}$. NMR ($^1$H, acetone-$d_6$): $\delta$ 1.34 (t, $J = 7$ Hz), 1.46 (t, $J = 7$ Hz), 2.06 (s), 2.43 (s), 2.56 (s), 2.66 (s), 4.42 (q, $J = 7$ Hz), 4.56 (q, $J = 7$ Hz), 7.49 (s), 8.02 (d, $J = 5.8$ Hz), 8.08 (dd, $J = 5.8$ and 1.5 Hz), 8.50 (dd, $J = 5.8$ and 1.5 Hz), 8.59 (s), 8.70 (s), 9.17 (s), 9.29 (s), 9.42 (s), 9.72 (d, $J = 5.8$ Hz). [Ru(phen)(bpy)-(CO)$_2$](PF$_6$)$_2$ (**IVh**); yield, 53%. IR (Nujol mull): $\bar{\nu}_{CO}$ at 2090 and 2037 cm$^{-1}$). [Ru(phen)(Me$_4$bpy)(CO)$_2$](PF$_6$)$_2$ (**IVi**); yield, 71%. IR (KBr disk): $\bar{\nu}_{CO}$ at 2093 and 2048 cm$^{-1}$. [Ru{(EtCO$_2$)$_2$bpy}(bpz)-(CO)$_2$](PF$_6$)$_2$ (**IVj**); yield, 45%. IR (Nujol mull): $\bar{\nu}_{CO}$ at 2093 and 2038 cm$^{-1}$.

[**Ru(pp)(pp')(pp'')](PF$_6$)$_2$ (V).** Typically, 1 mol equiv [Ru(pp)(pp')-(CO)$_2$]$^{2+}$, 3 mol equiv of pp'', and dry 2-methoxyethanol (2.5 mL/10$^{-5}$ mole of complex) were combined in a round-bottom flask fitted with a condenser and Teflon needles to purge the solution with N$_2$. A 3-fold excess of freshly sublimed trimethylamine N-oxide was added to the yellow solution, which was heated at reflux for 3 h. The reaction took place with a color change from almost colorless to deep red with the concurrent production of trimethylamine—trapping of trimethylamine by bubbling through an HCl bubbler is strongly suggested. The reaction mixture was evaporated to dryness and redissolved in water (a minimum of acetone may be added to aid in dissolution of the product), and the product was purified by ion-exchange chromatography (SP-Sephadex C-25; eluent 0.2 M NaCl). Precipitation of the product as the PF$_6^-$ salt was achieved by addition of a saturated aqueous solution of NH$_4$PF$_6$ to the eluant containing the major band. The solid was collected on a medium porosity frit and then washed several times with cold water and copious quantities of diethyl ether. Reprecipitation from CH$_2$Cl$_2$/ether yielded a red powder. Yields were in the range of 50–85%.

[Ru(bpy)(Me$_2$bpy)(bpm)](PF$_6$)$_2$·3H$_2$O (**Va**). NMR ($^1$H, acetone-$d_6$): $\delta$ 2.55 (s), 2.56 (s), 7.40 (d), 7.57 (dd), 7.70 (t), 7.71 (t), 7.82 (d), 8.05 (d), 8.07 (d), 8.21 (dd), 8.24 (d), 8.44 (dd), 8.45 (dd), 8.69 (s), 8.80 (d), 9.17 (dd), 9.18 (dd). [Ru(bpy)(Me$_2$bpy)(5-(Me)phen)](PF$_6$)$_2$ (**Vb**). NMR ($^1$H, acetone-$d_6$): $\delta$ 2.49 (s), 2.60 (s), 2.90 (s), 7.21 (m), 7.35 (m), 7.44 (m), 7.63 (d), 7.85 (m), 7.93 (m), 8.16 (m), 8.31 (t), 8.40 (t), 8.65 (m), 8.82 (m). [Ru(bpy)(Me$_2$bpy)(dpp)](PF$_6$)$_2$·0.25HPF$_6$ (**Vc**), [Ru(bpy){(EtCO$_2$)$_2$bpy}(dpp)](PF$_6$)$_2$·0.25HPF$_6$ (**Vd**),[28] and [Ru(bpy)-(Me$_2$bpy){(EtCO$_2$)$_2$bpy}](PF$_6$)$_2$·H$_2$O (**Ve**). NMR ($^1$H, acetone-$d_6$): $\delta$ 1.37 (t, $J = 7$ Hz), 1.38 (t, $J = 7$ Hz), 2.55 (s), 2.57 (s), 4.44 (q, $J = 7$ Hz), 4.45 (q, $J = 7$ Hz), 7.36 (d, $J = 5$ Hz), 7.42 (d, $J = 5$ H), 7.52 (t, $J = 6$ Hz), 7.60 (t, $J = 6$ Hz), 7.83 (m), 7.97 (m), 8.04 (m), 8.35 (m), 8.60 (s), 8.81 (m), 9.27 (s). [Ru(Me$_2$bpy)(Me$_4$bpy)(4,7-Me$_2$phen)]-(PF$_6$)$_2$ (**Vf**) and [Ru(Me$_2$bpy)(Me$_4$bpy)(bpm)](PF$_6$)$_2$·2H$_2$O (**Vg**). NMR ($^1$H, acetone-$d_6$): $\delta$ 2.10 (s), 2.11 (s), 2.47 (s), 2.55 (s), 7.38 (d), 7.63 (s), 7.67 (t), 7.80 (d), 7.91 (s), 8.01 (d), 8.39 (dd), 8.40 (dd), 8.56 (s), 8.65 (s), 9.14 (d). [Ru(Me$_2$bpy){(EtCO$_2$)$_2$bpy}(dpp)](PF$_6$)$_2$·H$_2$O (**Vh**),[28]

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(28) Prepared as indicated above, but using 1,2-dimethoxyethane as the solvent.

**Table 1.** Crystallographic Data for
[Ru(Me$_2$bpy)(phen)(bpa)](PF$_6$)$_2$·C$_6$H$_{14}$ (**Vv**)

| | |
|---|---|
| formula | C$_{40}$H$_{43}$F$_{12}$N$_7$P$_2$Ru |
| MW | 1062.8. |
| $a$ (Å) | 14.57(3), |
| $b$ (Å) | 13.50(3) |
| $c$ (Å) | 12.73(3) |
| $\alpha$ (deg) | 68.6(2) |
| $\beta$ (deg) | 63.5(1) |
| $\gamma$ (deg) | 79.8(2) |
| $V$ (Å$^3$) | 2082 |
| Z | 2 |
| crystal system/space group | triclinic, $P\bar{1}$ ($C_i^1$, No. 2) |
| $T$ (K) | 295 |
| radiation; $\lambda$ (Å) | monochromatic Mo $K\alpha$; 0.710 69 |
| $d_{calc}$ (g cm$^{-3}$) | 1.70 |
| $\mu$ (Mo $K\alpha$) (cm$^{-1}$) | 4.7 |
| min/max transmn coeff | 0.86–0.91 |
| crystal dimens | 0.40 × 0.28 × 0.70 mm |
| no. of reflecns | 5408 |
| no. of reflecns ($I > 3\sigma(I)$) | 2892 |
| absorpn coeff (cm$^{-1}$) | 4.7 |
| $R(F_o)^a$ (%) | 6.4 |
| $R_w(F_o)^b$ (%) | 6.5 |

$^a$ $R = \Sigma(|\Delta|F||/\Sigma|F_o|$. $^b$ $R_w = (\Sigma\omega\Delta^2/\Sigma\omega F_o^2)^{1/2}$.

[Ru(Me$_2$bpy){(EtCO$_2$)$_2$bpy}{(Et$_2$N)$_2$bpy}](PF$_6$)$_2$·2H$_2$O (**Vi**),[28] [Ru(Me$_2$-bpy)(Me$_4$bpy)(dpp)](PF$_6$)$_2$·H$_2$O (**Vj**), [Ru(Me$_2$bpy)(Me$_4$bpy){(Et$_2$N)$_2$-bpy}](PF$_6$)$_2$·2H$_2$O (**Vk**), [Ru(Me$_2$bpy)(Me$_4$bpy)(bbpa)](PF$_6$)$_2$·0.5HPF$_6$ (**Vl**), [Ru(Me$_2$bpy){(EtCO$_2$)$_2$bpy}(bbpa)](PF$_6$)$_2$·0.5HPF$_6$ (**Vm**),[28] [Ru(Me$_2$-bpy){(EtCO$_2$)$_2$bpy}(bpm)](PF$_6$)$_2$·0.5H$_2$O (**Vn**),[27] [Ru(Me$_2$bpy)(Me$_4$-bpy)(qpy)](PF$_6$)$_2$·HPF$_6$ (**Vo**),[Ru(phen)(Me$_4$bpy)(bpm)](PF$_6$)$_2$·2H$_2$O (**Vp**), [Ru(bpy)(phen)(biq)](PF$_6$)$_2$ (**Vq**), [Ru(bpy)(phen)(bpa)](PF$_6$)$_2$ (**Vr**), [Ru-(bpy)(phen)(daf)](PF$_6$)$_2$ (**Vs**), [Ru(bpy)(phen)(bpk)](PF$_6$)$_2$ (**Vt**), [Ru(Me$_2$-bpy)(phen)(biq)](PF$_6$)$_2$ (**Vu**), [Ru(Me$_2$bpy)(phen)(bpa)](PF$_6$)$_2$ (**Vv**), [Ru(Me$_2$bpy)(phen)(5,5'-Me$_2$bpy)](PF$_6$)$_2$ (**Vw**), [Ru(Me$_2$bpy)(bpy)(5,5'-Me$_2$bpy)](PF$_6$)$_2$ (**Vx**), [Ru(Me$_2$bpy)(bpy)($^i$Pr$_2$bpy)](PF$_6$)$_2$ (**Vy**), [Ru(Me$_2$-bpy)(phen)(biq)](PF$_6$)$_2$ (**Vz**), [Ru(bpy){(NH$_2$)$_2$bpy}(bpz)](PF$_6$)$_2$ (**Vaa**), and [Ru(bpy){(EtCO$_2$)$_2$bpy}(bpz)](PF$_6$)$_2$ (**Vbb**).

**X-ray Structure Analysis.** Red-brown crystals of [Ru(Me$_2$bpy)-(phen)(bpa)](PF$_6$)$_2$·C$_6$H$_{14}$ were obtained by liquid diffusion of hexane into a solution of the complex in acetonitrile. The specimen available for structure determination was oversized and aggregated: a portion was mounted in a capillary to avoid loss of hexane. Tolerable alignment was achieved on the major component of the aggregate and a unique data set measured to $2\theta_{max} = 45°$ using a Syntex $P2_1$ four-circle diffractometer in a conventional $2\theta/\theta$ mode. A set of 5408 independent reflections was obtained, 2892 with $I > 3\sigma(I)$ being considered "observed" and used in the full matrix least squares refinement. Anisotropic thermal parameter refinement was achieved successfully for all atoms except C(1,5) of the hexane solvent; C(1) was modeled as equally disordered over two sites, while thermal motion of C(5) was exceedingly high, as in fact is true of the solvent generally. ($x$, $y$, $z$, $U_{iso}$)$_H$ were included, constrained at estimated values. Residuals on $|F|$ at convergence were $R$, $R' = 0.064$, 0.065, statistical reflection weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0001\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors[29] were employed; computation used the XTAL 2.2 program system[30] implemented by S. R. Hall. Material deposited comprises non-hydrogen atom thermal parameters, hydrogen atom parameters, ligand non-hydrogen geometries, anion and solvent non-hydrogen geometries, and structure factor amplitudes (supplementary material Tables S2–S6, respectively).

The crystal data are given in Table 1.

## Results and Discussion

**Synthesis.** The synthetic methodology we have used for the heteroleptic tris(bidentate)ruthenium(II) complexes is based on

(29) Ibers, J. A.; Hamilton, W. C. *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.
(30) Hall, S. R.; Stewart, J. M. *XTAL Users' Manual Version 2.2*; Universities of Western Australia and Maryland: Nedlands, Australia, and College Park, MD, 1987.

**Scheme 1.** Synthetic Strategy for Tris(heteroleptic) Complexes (pp = Bidentate Polypyridyl Ligands)
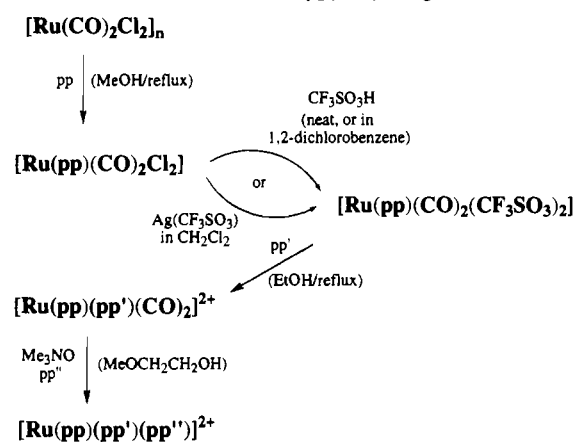


the sequential addition of the polypyridyl ligands to the oligomeric precursor [Ru(CO)$_2$Cl$_2$]$_n$, as summarized in Scheme 1.

Preliminary details of the scheme were reported earlier.[10–16]

The synthetic method described for [Ru(CO)$_2$Cl$_2$]$_n$ (**I**) is formally considered a RuCl$_3$-assisted decarbonylation of formic acid, and the reaction is promoted by formaldehyde as an initial reductant of Ru(III) to Ru(II).[31,32] Two products are formed—**I** and a chloro-bridged dimer, [Ru(CO)$_3$Cl$_2$]$_2$, generated as a side product—and variable relative yields are obtained depending on the purity of the starting materials (RuCl$_3$·3H$_2$O and formic acid). The presence of formaldehyde (via decomposition of paraformaldehyde at 192 °C and sublimation into the formic acid at 0 °C or direct addition of the paraformaldehyde to the reaction mixture) favors the formation of the polymer, **I**. The dimer arises from HCl formation during the course of the reaction, and certainly the addition of HCl to the reaction mixture substantially increases the proportion of the dimer byproduct.[31,32] Conversion of the dimer to the polymer by heating or treating with formaldehyde-saturated formic acid has been unsuccessful. Over the course of the synthesis, a characteristic color change from red to green to orange to pale yellow is observed. The reaction may be stopped following the formation of the orange intermediate, and conversion to the desired yellow polymeric material is achieved by maintaining the reaction mixture at 0 °C over several hours. Successive recrystallizations from acetone/diethyl ether yield pure polymer. Contamination by [Ru(CO)$_3$Cl$_2$]$_2$ in **I** may be identified by IR studies as the dimer exhibits a characteristic $\bar{\nu}_{CO}$ stretch at 2138 cm$^{-1}$ in the infrared spectrum.[31,32] Drying the polymer at elevated temperatures causes decomposition of the material.

The polymer reacts readily with bidentate ligands (pp) in refluxing methanol solution to yield [Ru(pp)(CO)$_2$Cl$_2$] (**II**). These complexes were recrystallized from hot methanol, producing feathery, yellow crystals. Purity (primarily absence of free ligand) was checked by TLC on silica gel, using acetonitrile as a solvent. The CO stretching frequencies ($\bar{\nu}_{CO}$) in this series are observed at *ca.* 2060(±5) and 1998(±10) cm$^{-1}$ and do not appear to show predictable dependence on the nature of the pp ligand. In general, the yields for the complexes of substituted bipyridyl ligands are lower (~50%) than for 2,2'-bipyridine itself (~80%), presumably due to solubility characteristics of the substituted-bipyridine species in methanol. Longer reaction times improved the reaction yields for prepara-

(31) Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Vol. 4, p 661.
(32) Cleare, M. J.; Griffith, W: P. *J. Chem. Soc. A* **1969**, 372.

tion of [Ru(pp)(CO)$_2$Cl$_2$] in which the ligand (pp) contains electron-withdrawing substituents.

In $^1$H NMR studies in this work, substantial use was made of the ligand 4,4′,5,5′-tetramethyl-2,2′-bipyridine (Me$_4$bpy) as the particular pattern of substitution results in each ring showing only two singlet aliphatic resonances (the methyl groups) and two singlet aromatic resonances (the protons in the ring 3- and 6-positions), simplifying the spectrum. The ligand (Et$_2$CO)$_2$bpy was also chosen as it is an example of an analogous derivative, but with electron-withdrawing substitutuents (rather than electron-donating for the methyl groups), and it gives rise to distinctive triplet and quartet resonances associated with the ethyl groups.

The NMR data are given for the two representative examples [Ru(Me$_4$bpy)(CO)$_2$Cl$_2$] and [Ru{(EtCO$_2$)$_2$bpy}(CO)$_2$Cl$_2$] (data are available for other complexes in supplementary material Table S7): they indicate the equivalence of the two sides of a symmetrical pp ligand in [Ru(pp)(CO)$_2$Cl$_2$], so that the complex may only possess either the *trans*-(Cl),*cis*-(CO) or *trans*-(CO),*cis*-(Cl) geometries. From group theory calculations, the existence of two $\bar{\nu}_{CO}$ absorptions in the IR spectrum is consistent with either geometry. However, the carbonyl ligands would be expected to adopt a *cis*-relationship due to competition for π-back-bonding from the metal d-orbitals. On this basis, the stereochemistry of [Ru(pp)(CO)$_2$Cl$_2$] would therefore be *trans*-(Cl),*cis*-(CO), in agreement with previous studies.[14,15,33] A recent structural determination on a sample of [Ru(bpy)(CO)$_2$Cl$_2$] having an $^1$H NMR spectrum identical to that of the sample obtained by our synthetic procedure confirms this assignment.[34] No evidence was obtained during the present chromatographic or spectroscopic studies for isomeric forms of these species.

The reaction of [Ru(pp)(CO)$_2$Cl$_2$] with a second bidentate ligand (pp′) was accomplished by initial conversion of [Ru(pp)(CO)$_2$Cl$_2$] to the corresponding bis(trifluoromethansulfonato) {"bis(triflato)"} species, [Ru(pp)(CO)$_2$(CF$_3$SO$_3$)$_2$], to utilize the enhanced lability of the CF$_3$SO$_3^-$ ligand.[35] This conversion may be achieved by any one of three methods. In two of these, the dichloro species is heated in the presence of trifluoromethansulfonic acid, with the HCl formed being removed to drive the reaction: i.e., heating **II** in neat trifluoromethansulfonic acid[14] or in 1,2-dichlorobenzene solution in the presence of the acid (in both cases at 110 °C).[36] The reaction yields were ~65 and ~85%, respectively. For some complexes such as [Ru{(EtCO$_2$)$_2$bpy}(CO)$_2$Cl$_2$], such reaction conditions result in decomposition of the ligand—in this case, acid hydrolysis of the ester group. This was circumvented by reaction of [Ru{(EtCO$_2$)$_2$bpy}(CO)$_2$Cl$_2$] with Ag(SO$_3$CF$_3$) at reflux in CH$_2$Cl$_2$, producing the desired bis(trifluoromethanesulfato) species, albeit in disappointingly low yields (~26%).

Decomposition of the triflato species was observed if temperatures above 110 °C were sustained in the reaction, presumably due to degradation of the complex and protonation of the polypyridyl ligands. The washing of the product with water is an important aspect in ensuring the removal of the protonated ligand impurity from the desired dicarbonyl species. The triflato species are stable for long periods of time if the residual trifluoromethanesulfonic acid is removed by washing thoroughly with water and drying *in vacuo*.

For [Ru(pp)(CO)$_2$(CF$_3$SO$_3$)$_2$] species (**III**), the $\bar{\nu}_{CO}$ stretching frequencies are observed at 2082 and 2020 cm$^{-1}$ for pp = bpy and 2099 and 2027 cm$^{-1}$ for pp = Me$_2$bpy. Characteristic infrared bands assignable in the infrared spectrum for the bound trifluoromethanesulfonate can be identified for the $\bar{\nu}_{SO}$ stretches at *ca.* 1340, 1180, and 1010 cm$^{-1}$ and the $\bar{\nu}_{CF}$ stretches at ~1240 and 1200 cm$^{-1}$.[14,15]

From the available IR data, we infer that the carbonyl groups remain in a *cis* disposition. Earlier reports have claimed that, in the [Ru(pp)(CO)$_2$(CF$_3$SO$_3$)$_2$] complexes prepared by reaction of the dichloro species with trifluoromethanesulfonic acid, the trifluoromethanesulfonato ligands also had a *cis* disposition—i.e., the stereochemistry was *cis*-(CO),*cis*-(CF$_3$SO$_3$)—based on the inequivalence of the two halves of a symmetrical pp ligands as seen in the $^1$H NMR spectrum.[14] We would concur with that analysis, on the basis of the $^1$H NMR spectrum of [Ru(Me$_4$bpy)(CO)$_2$(CF$_3$SO$_3$)$_2$], in which the ligand Me$_4$bpy exhibits four aromatic and four aliphatic singlet resonances (δ 7.91, 7.95, 8.40, 8.72, 2.41, 2.45, 2.53, 2.57), consistent with *cis*-(CO),*cis*-(CF$_3$SO$_3$), i.e., point group symmetry $C_2$. The *cis*-(CO),*trans*-(CF$_3$SO$_3$) isomer has been identified in related studies.[15]

Reaction of the bis(trifluoromethanesulfonato) species with pp′ gave the cation [Ru(pp)(pp′)(CO)$_2$]$^{2+}$, which was precipitated as the PF$_6^-$ salt, in *ca.* 60% yield. Purity was checked by TLC on alumina plates using H$_2$O (10% in NH$_4$Cl/DMF/MeOH (2:1:1) or H$_2$O (10% in NaCl)/acetone (1:1) as the eluents. Small-scale chromatographic separations were also achieved by PLC using the same adsorbent and solvents.

The IR spectra for [Ru(pp)(pp′)(CO)$_2$]$^{2+}$ are consistent with the retention of the *cis*-CO configuration. The $^1$H NMR characteristics of the complexes [Ru(Me$_4$bpy){(EtCO$_2$)$_2$bpy}(CO)$_2$]$^{2+}$ and [Ru(Me$_2$bpy)(Me$_4$bpy)(CO)$_2$]$^{2+}$ are provided in the Experimental Section (and data for the other complexes of this type are available in supplementary material Table S8). The $^1$H NMR data indicate the inequivalence in the complex of the two halves of each of the "symmetrical" bidentate ligands, pp and pp′. For example, in [Ru(Me$_4$bpy){(EtCO$_2$)$_2$bpy}(CO)$_2$]$^{2+}$, the inequivalent CH$_3$ protons of Me$_4$bpy are easily identified as four singlets occurring at δ 2.06, 2.43, 2.56, and 2.66 ppm. Magnetic inequivalency at H$_3$ and H$_{3'}$, and at H$_6$ and H$_{6'}$, in the Me$_4$bpy ligand is also clearly illustrated by well-resolved singlets at δ 8.59, 9.17, 9.29, and 9.42 ppm. The same rationalization can be made for the resonances of the (Et$_2$CO)$_2$bpy ligand and for the resonances of the two polypyridyl ligands in [Ru(Me$_2$bpy)(Me$_4$bpy)(CO)$_2$]$^{2+}$. Accordingly, the NMR and IR data are consistent with a *cis* disposition of the two CO ligands.

No evidence was obtained in any of the complexes investigated for formation of *trans*-CO species.

The tris(bidentate) complexes of ruthenium(II), [Ru(pp)(pp′)(pp″)]$^{2+}$, are generated by decarbonylation of [Ru(pp)(pp′)(CO)$_2$]$^{2+}$ using trimethylamine *N*-oxide (TMNO), in the presence of the third bidentate ligand pp″.[11,37,38] This reaction was normally performed in 2-methoxyethanol as solvent, although the reaction can also be undertaken in acetone.

In cases involving the ligand (EtCO$_2$)$_2$bpy it was observed that the decarbonylation reaction took place with transesterification (presumably base catalyzed by trimethylamine formed during the decarbonylation process), resulting in replacement of R = —Et by —CH$_2$CH$_2$OMe as determined by NMR studies of the product. In these cases, the solvent 1,2-dimethoxyethane was successfully used as an alternative to 2-methoxyethanol.

(33) Kelly, J. M.; O'Connell, C. M.; Vos, J. G. *Inorg. Chim. Acta* **1982**, *64*, L75.

(34) Haukka, M.; Kiviaho, J.; Ahlgrén, M.; Pakkanen, T. A. *Organometallics* **1995**, *14*, 825.

(35) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

(36) Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241.

(37) Black, D. S.; Deacon, G. B.; Thomas, N. C. *Inorg. Chim. Acta* **1981**, *54*, L143.

(38) Luh, T.-Y. *Coord. Chem. Rev.* **1984**, *60*, 255.

In general, where such a complication was not involved, 2-methoxyethanol was found to be a superior solvent for the reaction.

The rate of the decarbonylation reaction of $[Ru(pp)(pp')(CO)_2]^{2+}$ was observed to depend significantly on the nature of the two ligands pp and pp': *viz.*, in cases where these ligands had electron-withdrawing substituents, the rate of the reaction was more rapid. TMNO-assisted decarbonylations are generally thought to occur via oxygen atom transfer to the carbonyl carbon atom,[39] and the present observations support that assertion. The substantial partial negative charge on the oxygen atom of TMNO suggests the mechanism may involve nucleophilic attack on the carbon atom,[40,41] and its susceptibility to such attack (i.e. electrophilicity) would be enhanced by the lowering of the electron density of the metal center—such would be the case where electron-withdrawing substituents were present on the "innocent" pp-type ligands. A corollary of this rationale is that such substituents should reduce the $\pi$-back-bonding from the metal to the carbonyl ligands, thereby increasing the bond order of the C≡O bond and weakening the Ru—C bond, and indeed the propensity of carbonyl groups to such decarbonylation reactions has previously been shown to be greater when the $\bar{\nu}_{CO}$ stretching frequencies are high.[42,43]

The complexes were examined and characterized by a number of physical methods. The following discussion briefly describes the outcomes of those studies, in each area using a limited number of examples which best illustrate the point at hand, in preference to an exhaustive coverage. Further details may be obtained from the authors on written request.

**Microanalyses.** Satisfactory elemental analyses ($\pm 0.4\%$ for C, H, and N) were obtained for all the tris(heteroleptic) complexes reported. For complexes containing additional nonligating N atoms in the heterocyclic rings (e.g., in the potential bridging ligands bpm, dpp, bbpa, and qpy) it was found that there was often either water (**Vh, Vi, Vj, Vk, Vn, Vp**) or HPF$_6$ (**Vd, Vl, Vm, Vo**) contained in the lattice. In separate measurements made in our laboratories of the p$K_a$ values of the species of this type, it is clear that only one protonation occurs and that the proton interacts (e.g., by hydrogen bonding) to both N atoms.[44]

Microanalytical data for the tris(heteroleptic) complexes, and the precursor species, are available in Supporting Information Table S1.

**Fast Atom Bombardment Mass Spectrometry.** Fast atom bombardment (FAB) has been proposed as a probe for the differentiation of mixed-ligand complexes with those that are mixtures of complexes, since no scrambling is detected in the mass specra of species such as $[Ru(Me_2bpy)_2(phen)](PF_6)_2$.[45] Such techniques have been used previously in the identification and characterization of tris(bidentate) polypyridyl complexes of ruthenium(II).[45-47] In the present case, three tris(heteroleptic) species were studied in particular—*viz.*, [Ru(bpy)(Me$_2$bpy)(5-

(Me)phen)](PF$_6$)$_2$, [Ru(bpy)(Me$_2$bpy)(bpm)](PF$_6$)$_2$, and [Ru(bpy)(Me$_2$bpy){(EtCO$_2$)$_2$bpy}](PF$_6$)$_2$—using a 3-nitrobenzyl alcohol matrix. In all cases, the ion pair {[Ru(pp)(pp')(pp'')]·(PF$_6$)}$^+$ was observed, together with the reduced species [Ru(pp)(pp')(pp'')]$^+$, and peaks due to the sequential loss of the remaining polypyridyl ligands. No peaks of the type "[Ru-(pp)$_2$]$^+$" were observed, attesting to the tris(heteroleptic) assignment. Only in the case of [Ru(bpy)(Me$_2$bpy)(bpm)](PF$_6$)$_2$ is another significant peak observed, at $m/z = 460$, corresponding to the ion-pair {[Ru(bpy)(Me$_2$bpy)]·F}$^+$: the presence of fluoride ion in such ion pairs, arising from reductive elimination of HF, has been observed previously in FAB spectra of hexafluorophosphate salts.[47]

**NMR Studies.** The NMR spectral behavior of homoleptic (point group symmetry $D_3$) and bis(heteroleptic) complexes ($C_2$) of symmetrical bidentate ligands have been discussed previously.[48-52] In the case of tris(heteroleptic) ligands, there is a further complication that the symmetry is lowered to $C_1$ so that the two halves of each ligand are necessarily in magnetically inequivalent environments.[52] As an example, for the complex $[Ru(Me_2bpy)(Me_4bpy)(bpm)]^{2+}$, the assignments of individual resonances in the ligands were made using the COSYRCT (relayed coherence transfer) technique, which shows the chain of coupling around each heterocyclic ring. The chemical shifts associated with the resonances at the various protons are indicated below (acetone-$d_6$ solution):
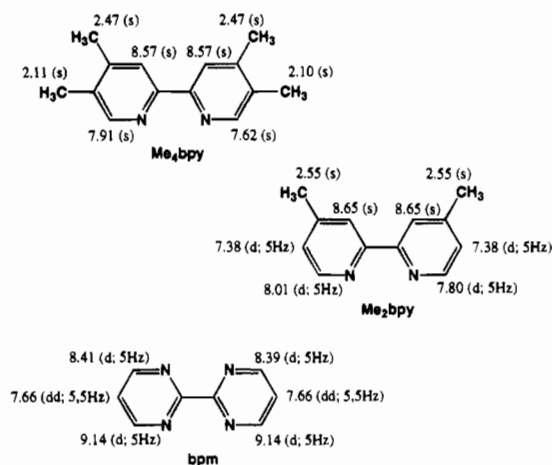


In the spectrum, the methyl groups in the 5- and 5'-positions in Me$_4$bpy are seen to be in different environments, and the protons in the 6- and 6'-positions in both Me$_4$bpy and Me$_2$bpy are differentiated in that one proton in each case lies over a ring of the bpm ligand and the other over a ring of the Me$_4$bpy ligand. In bpm, the 3- and 3'-protons are differentiated for similar reasons.

In cases where the three ligands in a tris(heteroleptic) species are different derivatives of the same bidentate ligand, the aromatic regions are relatively simplified as there is some overlap of resonances. For example, the spectrum of [Ru(phen)-(Me$_2$bpy)(5,5'-Me$_2$bpy)]$^{2+}$ contains four methyl resonances (two singlets separated by 0.11 ppm assigned to the Me$_2$bpy and two singlets separated by 0.23 ppm assigned to 5,5'-Me$_2$bpy).

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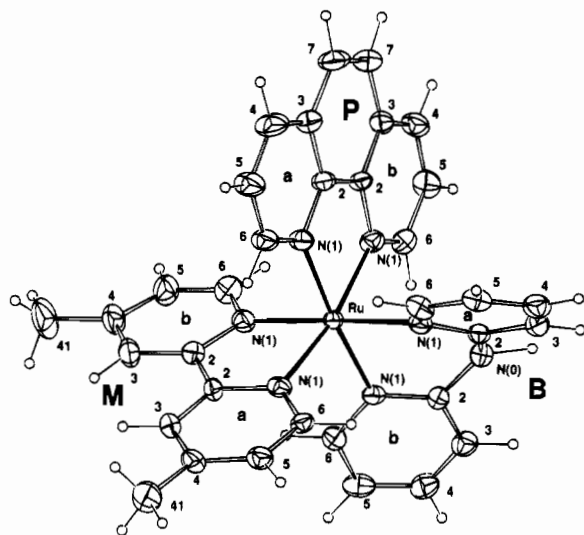(52) Rutherford, T. J.; Reitsma, D. A.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1994**, 3659.

**Figure 1.** Projection of cation [Ru(Me$_2$bpy)(phen)(bpa)]$^{2+}$ {[Ru mpd]$^{2+}$} showing non-hydrogen atoms with 20% probability thermal elloipsoids and labeling. Hydrogen atoms have an arbitrary radius of 0.1 Å.

However, the spectrum of [Ru(bpy)(Me$_2$bpy)(5,5'-Me$_2$bpy)]$^{2+}$ contains only two methyl singlets. Presumably, since all the ligands contain similar 2,2'-bipyridine ring systems, the 5- and 5'-methyl groups in 5,5'-Me$_2$bpy experience similar magnetic environments, as do the 4- and 4'-methyl groups in Me$_2$bpy. The related complex [Ru(bpy)(Me$_2$bpy)($^i$Pr$_2$bpy)]$^{2+}$ also exhibits only one singlet for the methyl groups in the Me$_2$bpy ligand, and the isopropyl groups are also magnetically equivalent (one doublet at $\delta$ 1.31 and one quartet at $\delta$ 3.16).

It is noted that the precursor dicarbonyl complexes, [Ru(pp)-(pp')(CO)$_2$]$^{2+}$, also possess $C_1$ point group symmetry so that the two halves of each bidentate ligand are inequivalent. By comparison with the tris(heteroleptic) complexes, the chemical shift differences observed between identical substitutents in the 4- and 4'-positions of a 2,2'-bipyridine parent ligand are greater for the dicarbonyl species. In earlier discussions, the coordination-induced shifts in the resonances of the 4- and 4'-protons of 2,2'-bipyridine were attributed to the $\sigma$-donor and $\pi$-acceptor characteristics of the ligand, as these positions were considered sufficiently isolated to preclude anisotropic interactions.[48] In the present case, it is tempting to evoke a similar rationalization for the observed shifts of substituents in these positions for the dicarbonyl and tris(heteroleptic) complexes, in view of the differences in $\pi$-acceptor characteristics of the CO and pp ligands. However, our recent NMR studies involving geometric isomers in bis(bidentate)dicarbonyl and tris(bidentate) species containing the unsymmetrical ligand 4-methyl-4'-*neo*-pentyl-2,2'-bipyridine (pmb) are inconsistent with a unilateral rationalization of substituent shifts based on bonding effects alone, and they indicate that anisotropic effects are also important;[52] i.e., there is an interaction of the magnetic fields of rings of adjacent ligands. The same situation is likely to pertain in the present series of complexes.

**X-ray Structural Study.** The crystal structure of [Ru(Me$_2$-bpy)(phen)(bpa)](PF$_6$)$_2$ (for which tolerable single crystals were obtained) was carried out to establish the coordination of three different bidentate heterocyclic nitrogen ligands attached to ruthenium—no similar X-ray structure has been carried out on a tris(heteroleptic)ruthenium(II) species. The results of the structure determination confirm the cation formulation: however, a relatively low precision was obtained for the structure as a consequence of a high degree of thermal motion in the PF$_6^-$ anions (which were modeled as ordered) and a solvent

(hexane) residue. Nevertheless, a number of features may be noted about the cation. The structure of the cation is displayed in Figure 1, atom coordinates are listed in Table 2, and bond distances and angles relating to the ruthenium environment are given in Table 3.

Ruthenium has approximately octahedral stereochemistry from chelation of the three different bidentate ligands. The Me$_2$-bpy ligand is almost flat with a dihedral angle of 6.3(4)° between the two pyridine rings, with Ru lying 0.29(2) and 0.15(2) Å out of the planes of rings A and B, respectively. On the other hand, the dihedral angle between the 2-pyridyl rings of bpa is 35.5(4)° with Ru lying 0.34(2) and 0.18(2) Å out of the planes of rings A and B, respectively. The 1,10-phenanthroline ligand is very close to planar, with Ru being only 0.090(8) Å out of the C$_{12}$N$_2$ plane in the chelate ring formed with that ligand.

There is some suggestion of an increase in the Ru–N distance for binding the three ligands in the series Me$_2$bpy (2.056 Å), phen (2.083 Å), and bpa (2.100 Å), with the difference between the two Ru–N distances in any one ligand significant only for 4,4'-dimethyl-2,2'-bipyridine (2.040(8), 2.072(9) Å). The Ru–N(Me$_2$bpy) distances are similar to Ru–N in [Ru(bpy)$_3$]X$_2$ complexes, e.g., X = ClO$_4$ (2.056(3)–2.060(3) Å)[53] or PF$_6$ (2.056(2) Å at 298[54] and 143 K;[55] 2.053(2) Å at 105 K[54]), and in [Ru(bpy)$_2$L]$^{2+}$, e.g., L = 2,3-bis(2-pyridyl)quinoxaline (Ru–N, 2.06 Å),[56] [Ru(bpy)$_2$L]$^+$ (LH = 3-methyl-5-(pyridin-2'-yl)-1,2,4-triazole,[57] 2.042(5)–2.060(4) Å; LH = 2-(2-hydroxyphenyl)-pyridine,[58] 2.022(4)–2.049(5) Å), and [Ru(bpy)$_2$(NH=CMe$_2$)$_2$]$^{2+}$ (2.035(9), 2.081(9) Å).[59] For the 1,10-phenanthroline ligand, the Ru–N bond length is at the higher end of values for reported Ru$^{II}$–phen complexes, e.g., [RuL$_3$]$^{2+}$ (L = 4,7,-diphenyl-1,10-phenanthroline) (Ru–N, 2.06 Å, with a range 2.029(2)–2.079-(2) Å),[60] [RuL$_2$L']$^{2+}$ (L = phen, Ru–N, 2.06, 2.07 Å; L' = 2,9-dimethyl-1,10-phenanthroline, Ru–N, 2.09 Å),[61] and *trans*-[Ru(phen)$_2$(py)$_2$]$^{2+}$ (2.096(5), 2.100(5) Å).[62] In the last example, the bonds are lengthened by steric repulsion between the *trans*-phen ligands and this factor also causes significant nonplanarity of these ligands as well as their inclination to the N$_4$(phen)Ru plane. For both the Me$_2$bpy and phen ligands, the bite angles are unexceptional and consistent with reported values.[53–55,57,58,60,62]

No structural charaterization of Ru$^{II}$–bpa complexes has previously been reported. However, the Ru–N(bpa) distances are very similar to those for Ru–N(py) bonds of *trans*-[Ru-(phen)$_2$(py)$_2$]$^{2+}$ (2.097(5) Å)[62] and [Ru(tpy)(bpy)(py)]$^{2+}$ (tpy = 2,2':6',2''-terpyridine) (2.114(6) Å),[63] as might be expected for the separated 2-pyridyl units. These distances are somewhat larger than Ru–N for bis{tris(2-pyridyl)amine}ruthenium(II) (2.064(3), 2.066(3), 2.069(3) Å).[64] In contrast to the bite angles

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**Table 2.** Non-hydrogen Atom Coordinates Data for $[Ru(Me_2bpy)(phen)(dpa)](PF_6)_2 \cdot C_6H_{14}$ (Vv)

| atom | A | | | B | | |
|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| cation | | | | | | |
| Ru | 0.18103(6) | 0.25502(6) | 0.07402(8) | | | |
| bpy ligand | | | | | | |
| N(n1) | 0.2617(6) | 0.3949(6) | −0.0058(6) | 0.3247(6) | 0.2078(6) | −0.0269(7) |
| C(n2) | 0.3653(8) | 0.3832(8) | −0.0626(8) | 0.4014(8) | 0.2774(9) | −0.0763(9) |
| C(n3) | 0.4296(7) | 0.4665(9) | −0.1055(9) | 0.5024(8) | 0.2520(9) | −0.1379(11) |
| C(n4) | 0.3906(9) | 0.5655(9) | −0.0929(9) | 0.5208(9) | 0.1515(11) | −0.1526(11) |
| C(n41) | 0.4582(9) | 0.6558(9) | −0.1294(12) | 0.6413(9) | 0.1238(11) | −0.2166(14) |
| C(n5) | 0.2854(9) | 0.5748(8) | −0.0367(9) | 0.4528(10) | 0.0843(9) | −0.1082(12) |
| C(n6) | 0.2235(7) | 0.4915(8) | 0.0029(8) | 0.3535(9) | 0.1102(9) | −0.0451(11) |
| phen ligand | | | | | | |
| N(n1) | 0.2143(6) | 0.2055(6) | 0.2286(7) | 0.1214(6) | 0.1018(6) | 0.1637(7) |
| C(n2) | 0.1775(7) | 0.1078(8) | 0.3084(9) | 0.1286(7) | 0.0513(7) | 0.2741(9) |
| C(n3) | 0.1892(8) | 0.0612(9) | 0.4188(10) | 0.0943(7) | −0.0522(8) | 0.3469(10) |
| C(n4) | 0.2381(10) | 0.1212(10) | 0.4480(10) | 0.0504(8) | −0.1057(8) | 0.3065(11) |
| C(n5) | 0.2742(9) | 0.2205(10) | 0.3684(11) | 0.0429(8) | −0.0573(9) | 0.1970(12) |
| C(n6) | 0.2617(8) | 0.2581(8) | 0.2599(9) | 0.0801(8) | 0.0460(8) | 0.1259(9) |
| C(n7) | 0.1488(9) | −0.0439(10) | 0.4960(10) | 0.1060(9) | −0.0985(9) | 0.4600(11) |
| dpa ligand | | | | | | |
| N(0) | −0.0389(6) | 0.2671(6) | 0.0736(8) | | | |
| N(n1) | 0.0393(6) | 0.3159(6) | 0.1747(7) | 0.1346(6) | 0.2953(6) | −0.0715(7) |
| C(n2) | −0.0467(8) | 0.3041(7) | 0.1671(9) | 0.0359(8) | 0.2905(7) | −0.0472(9) |
| C(n3) | −0.1415(8) | 0.3259(9) | 0.2475(10) | 0.0056(8) | 0.3071(8) | −0.1430(11) |
| C(n4) | −0.1518(9) | 0.3660(9) | 0.3378(10) | 0.0765(10) | 0.3296(9) | −0.2608(11) |
| C(n5) | −0.0641(10) | 0.3859(8) | 0.3404(9) | 0.1762(10) | 0.3397(9) | −0.2870(9) |
| C(n6) | 0.0291(8) | 0.3600(8) | 0.2611(9) | 0.2032(7) | 0.3202(8) | −0.1900(10) |
| anion | | | | | | |
| P | 0.7815(3) | 0.4393(3) | −0.3173(3) | −0.2490(3) | 0.0639(3) | 0.1789(4) |
| F(1) | 0.8282(7) | 0.5281(6) | −0.4392(7) | −0.2999(11) | 0.0839(8) | 0.0931(14) |
| F(2) | 0.7310(8) | 0.3483(8) | −0.1932(7) | −0.1935(8) | 0.0465(8) | 0.2609(8) |
| F(3) | 0.8383(6) | 0.4766(7) | −0.2607(7) | −0.2544(8) | 0.1811(6) | 0.1630(12) |
| F(4) | 0.7261(7) | 0.4006(8) | −0.3734(8) | −0.2309(9) | −0.0512(8) | 0.1746(12) |
| F(5) | 0.8739(8) | 0.3687(8) | −0.3669(9) | −0.1425(9) | 0.0885(12) | 0.0713(9) |
| F(6) | 0.6914(7) | 0.5100(8) | −0.2644(9) | −0.3464(9) | 0.0367(13) | 0.2827(13) |
| solvent | | | | | | |
| C(n1)[a] | 0.571(4) | 0.068(4) | 0.576(5) | 0.569(2) | 0.497(2) | 0.405(2) |
| C(n2) | 0.507(6) | 0.165(4) | 0.503(5) | 0.501(6) | 0.381(5) | 0.474(7) |
| C(n3) | 0.442(2) | 0.264(4) | 0.513(4) | 0.543(8) | 0.290(6) | 0.491(8) |

[a] C(A1) is disordered; the second component (CA1′) (both fragments populated at 0.5) is at (0.610(2), 0.169(2), 0.520(3)).

**Table 3.** Ruthenium Environment in Structure of $[Ru(Me_2bpy)(phen)(dpa)](PF_6)_2 \cdot C_6H_{14}$ (Vv)[a]

| atom | $r$ | N(mB1) | N(pA1) | N(pB1) | N(bA1) | N(bB1) |
|---|---|---|---|---|---|---|
| N(mA1) | 2.072(9) | 78.4(4) | 93.3(4) | 169.7(4) | 96.7(4) | 91.9(4) |
| N(mB1) | 2.040(8) | | 89.6(4) | 94.9(4) | 175.0(4) | 93.6(4) |
| N(pA1) | 2.078(10) | | | 78.7(4) | 89.7(4) | 174.3(3) |
| N(pB1) | 2.088(8) | | | | 89.9(3) | 96.3(4) |
| N(bA1) | 2.095(8) | | | | | 87.5(4) |
| N(bB1) | 2.105(11) | | | | | |

[a] $r$ is the Ru−N distance (Å); other entries in the matrix are the angles subtended at the ruthenium by the relevant atoms at the head of the row and column. The abbreviations m, p, and b are 4,4′-dimethyl-2,2′-bipyridine, 1,10-phenanthroline, and bis(2-pyridyl)amine, respectively.

of $Me_2bpy$ and phen $(78.4(4), 78.7(4)°)$, the bite angle of bpa is much larger $(87.5(4)$ Å$)$, in keeping with the increased size of the metallocycle ring, with a concomitant effect on the ruthenium environment; e.g., the *trans* angles associated with the bpa ligand $(175.0(4), 174.3(3)$ Å$)$ differ considerably from that between the two other ligands $(169.7(4)°)$. In another of the few X-ray characterized examples of a bpa ligand chelated in a six-coordinate metal atom environment, *viz.*, *trans*-[Cd-$(bpa)_2(ONO)_2$],[65] M−N is increased $(2.310(4), 2.316(3)$ Å$)$ with a concomitant decrease in the bite angle to $79.0(1)°$. In both

of these complexes it is of interest to find the ligand "folded", so that the dihedral angles between the two $C_5N$ planes are very similar $(35.5(4)°$ (Ru); $33.6(2)°$ (Cd)$)$. These data contrast with the many examples of bpa complexes in a four-coordinated environment about copper(I) (e.g., refs 66 and 67). In the less crowded array, the ligands are more nearly planar. The interplanar dihedral angles in the ten ligands quoted in these references have a distribution of $17.2(9)$ (maximum), $15.7(2)$, $11(1)$, and the remainder $8°$ or less. Bite angles range between $92.5(2)$ and $94.6(3)°$ and Cu−N is $1.96-2.05$ Å. The origin of the nonplanarity in the six-coordinate species presumably originates in the requirement for a smaller bite angle coupled with the greater steric hindrance between ligands in opposition in the *trans* disposition or because of steric interactions between *ortho*-hydrogen atoms in the tris(bidentate) array. The noncoplanarity of the two pyridine rings is reflected in the angle at the bridging nitrogen atom, C−N−C, being $128(1)$ and $128.8-(3)°$ in the present ruthenium complex and the cadmium complex,[65] while in all of the copper compounds quoted (except $[bpaCuBr_2]^-$ where the precision is poor[67]) it rises above $130°$.

**Scrambling.** One of the critical issues in the utilization of this synthetic methodology is the elimination of scrambling of the three ligands within the steps of the scheme. Clearly, by the observations given above for the FAB experiments, and the

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conclusions of the NMR studies, the occurrence of bis-(heteroleptic) or homoleptic species is minimal. A detailed study of this issue revealed that minor scrambling does occur, specifically during the final decarbonylation reaction. In addition, decomposition was sometimes observed in the step involving conversion of the dichloro → bis(triflato) species and was greatest in complexes containing the ligands with the highest basicity, as discussed above. Extremely pure bis(triflato) complexes could be obtained, but in reduced yield, by recrystallization from hot $CH_2Cl_2/Et_2O$.

A series of reactions was undertaken in which the complex $[Ru(bpy)(Me_4bpy)(CO)_2]^{2+}$ was produced by both possible alternatives of the sequential addition and the products closely examined by ${}^1H$ NMR techniques for $[Ru(Me_4bpy)_2(CO)_2]^{2+}$, which would be quite apparent if present in even small quantities. No such product was detected. Indeed, in the present studies there was only one circumstance, involving the addition of a very basic ligand pp′ to $[Ru(pp)(CO)_2(CF_3SO_3)_2]$, where a small amount (<3%) of the product $[Ru(pp')_2(CO)_2]^{2+}$ was detected as a product in this step of the scheme. The subsequent addition of the third bidentate ligand bpm to $[Ru(bpy)(Me_4bpy)(CO)_2]^{2+}$ under decarbonylation conditions in refluxing 2-methoxyethanol indicated $[Ru(Me_4bpy)_2(bpm)]^{2+}$ as a minor impurity (<5%). In this particular experiment (which is consistent with all other observations during this work), the scrambling clearly occurs in the decarbonylation step. Recrystallization of the tris(bidentate) species almost invariably allowed removal of the impurity, or purification was achieved by cation-exchange chromatographically (*vide supra*). However, detailed studies on the decarbonylation process revealed that it could be undertaken at lower temperatures (<25 °C) for longer periods, under which conditions no scrambling was detected, although yields tended to be lower. This observation is in complete agreement with associated stereochemical studies involving the decarbonylation reactions of complexes of the type $[Ru(pp)(pp')(CO)_2]^{2+}$.[52,68]

In order to probe the mechanism of the decarbonylation process, we have followed this step of the synthetic scheme by IR and NMR spectroscopic methods. In a typical case, a dicarbonyl compound was mixed with 2 equiv of TMNO and 2 equiv of *tert*-butylpyridine (('Bu)py) in $CD_2Cl_2$. At room temperature, the two $\bar{v}_{CO}$ stretching frequencies at 2100 and 2050 cm$^{-1}$ (solution cell) gave way to two extremely closely spaced peaks (<2 cm$^{-1}$ difference) centered around 1990 cm$^{-1}$. If the reaction was stopped at this point, $[Ru(pp)(pp')(('Bu)py)(CO)]^{2+}$ could be isolated and characterized by ${}^1H$ NMR spectroscopy. The two possible geometric isomers were always found in a 1:1 ratio, indicating that TMNO had no preference for the two CO sites. When this species was resubmitted to a $CH_2Cl_2$ solution of pyridine (py) and TMNO, and the mixture heated to 35 °C, the complex $[Ru(pp)(pp')(('Bu)py)(py)]^{2+}$ was produced (characterized by NMR and IR). Since the reaction could be separated into two steps—a facile one at room temperature or below and a subsequent step that required heating—the removal of the second carbonyl is apparently more difficult, an observation which has also been made for related halogenated compounds.[11,37] This observation appears entirely reasonable given our earlier analysis of the effect of electron-withdrawing groups: the replacement of one CO by a less back-bonding pyridine derivative would be expected to retard the second decarbonylation. However, while this second step may be facilitated in the case where the ligand involved is a bidentate, the opportunity for ligand scrambling clearly occurs at elevated temperatures. The precise mechanism of such a process is uncertain, and its elucidation would require further detailed studies, but this path is depressed when the entire reaction is conducted at lower temperatures.

**Chromatography.** The separation of mixtures of tris-(bidentate)ruthenium(II) complexes of the type involved in this study was necessary for proof that the methodology realized tris(heteroleptic) species and ultimately for their purification. In earlier studies, we reported the use of cation-exchange chromatography in the separation of diastereoisomeric ligand-bridged dinuclear complexes of the type $[(pp)_2Ru(BL)Ru-(pp')_2]^{4+}$ and $[(pp)_2Ru(BL)Os(pp')_2]^{4+}$ (where pp and pp′ may or may not be the same).[69] The technique involved the use of an aromatic anion (such as 4-toluenesulfonate) as the counterion in the electrolyte of the eluent: such anions appear to have different associations with the stereoisomers, allowing their chromatographic separation. In the present study, it was observed, in all cases where the chromatography of the tris-(heteroleptic) complex $[Ru(pp)(pp')(pp'')]^{2+}$ was undertaken in the presence of any of the possible bis(heteroleptic) ($[Ru(pp)_2-(pp')]^{2+}$) or homoleptic species ($[Ru(pp)_3]^{2+}$), that their separation was achieved under the same conditions. In other work, we have also shown that optical isomers of tris(bidentate) complexes,[70] and the geometric isomers of complexes of this genre containing unsymmetical ligands,[52] may be separated by this technique. A detailed study of the interaction of such anions with these complexes, and the consequences in the chromatographic process, is in progress and will be published subsequently.[71]

**Electrochemical Studies.** The electrochemical behavior of polypyridyl complexes of ruthenium(II) has been rationalized in terms of a metal-based oxidation and a series of reductions which are ligand-based and occur in a stepwise manner to each ligand $\pi^*$-system, with the order of the reduction correlating with the ease of reduction of the uncoordinated ligands.[7,8,72−74] The extensive variation of the ligand environment available through this general synthetic procedure for tris(heteroleptic) compounds allows a wider assessment of these proposals and in particular of the mutual interdependence of the ligands. The redox properties of the tris(heteroleptic) complexes were determined by cyclic voltammetry and differential pulse voltammetry, and Table 4 shows the potentials for a selection of the tris(heteroleptic) complexes synthesized in the study.

Lever and co-workers have recently proposed a scheme for the parametrization of the oxidation[75,76] and reduction potentials[77] of metal complexes, by using a ligand electrochemical series based on their Ru(III)/Ru(II) redox couples. The fundamental electrochemical parameter is $E_L(L)$, defined as one-sixth the potential for the Ru(III)/Ru(II) couple for $RuL_6$ in acetonitrile solution. The metal-based Ru(III)/Ru(II) couple of any complex may be calculated using the formulation

$$E_{calc}\{Ru(III)/Ru(II)\} = S_M\sum E_L(L) + I_M \qquad (1)$$

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**Table 4.** Electrochemical Characteristics of Selected Tris(heteroleptic) Complexes

| complex[a] | $E_{1/2}$ values (vs SSCE)[b] | | |
|---|---|---|---|
| | oxidation | reduction | $\Delta E_{1/2}$[c] |
| $[Ru(bpy)_3]^{2+}$ | +1.29 | −1.33 | 2.62 |
| | | −1.52 | |
| | | −1.78 | |
| $[Ru(bpy)(Me_2bpy)(5\text{-}(Me)phen)]^{2+}$ | +1.24 | −1.37 | 2.61 |
| | | −1.56 | |
| | | −1.81 | |
| $[Ru(bpy)(Me_2bpy)(bpm)]^{2+}$ | +1.37 | −1.03 | 2.40 |
| | | −1.49 | |
| | | −1.74 | |
| $[Ru(bpy)(Me_2bpy)\{(EtCO_2)_2bpy\}]^{2+}$ | +1.35 | −1.01 | 2.36 |
| | | −1.48 | |
| | | −1.69 | |
| $[Ru(Me_2bpy)(Me_4bpy)(dpp)]^{2+}$ | +1.26 | −1.09 | 2.35 |
| | | −1.61 | |
| | | −1.98 | |
| $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(dpp)]^{2+}$ | +1.45 | −0.96 | 2.41 |
| | | −1.19 | |
| | | −1.66 | |
| $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}\{(Et_2N)_2bpy\}]^{2+}$ | +0.97 | −1.09 | 2.06 |
| | | −1.61 | |
| | | −1.88[d] | |
| $[Ru(Me_2bpy)(Me_4bpy)\{(Et_2N)_2bpy\}]^{2+}$ | +0.79 | −1.55 | 2.34 |
| | | −1.86 | |
| | | −2.13 | |

[a] As $PF_6^-$ salts. [b] Acetonitrile/0.1 M $[N(n\text{-}C_4H_9)_4]PF_6$ solution; Pt button working electrode; 298 K; scan rate 100 mV/s; measured vs Ag/Ag⁺ reference electrode and quoted vs saturated sodium chloride calomel (SSCE). [c] $\Delta E_{1/2} = E_{1/2}(Ru(III)/Ru(II)) − E_{1/2}(\text{first ligand reduction})$. [d] Estimated from shoulder on solvent decomposition.

where $S_M$ and $I_M$ are constants for a particular metal. For the first ligand-based reduction process, there is a similar relationship

$$E_{red} = S_L \sum E_L(L) + I_L \qquad (2)$$

An implication of the use of the paramter $E_L(L)$ in these contexts is that all ligands behave in the same way to many redox metal couples and also to the same metal center in circumstances where the other ligands may be widely varied in terms of their σ-donor and π-donor/-acceptor characteristics. Because of the paucity of tris(heteroleptic) species available, previous assessment of this hypothesis in terms of ligand variation has been rather limited,[75,77] and the present synthetic methodology allows a wider analysis. The conclusions are rather compelling.

For the metal-based Ru(III)/Ru(II) couples, the values of $S_M$ and $I_M$ (eq 1) were assumed in the first approximation to be equal to unity and zero, respectively, since the $E_L(L)$ values were themselves derived from the redox couples of ruthenium species.[75] For complexes as widely disparate as $[Ru(phen)(CO)_2Cl_2]$ (**IIe**; calculated, 1.75 V vs SSCE; observed, 1.73 V), $[Ru(Me_2bpy)(phen)(bpa)]^{2+}$ (**Vv**; 1.07 V *cf.* 1.06 V), $[Ru(Me_2bpy)(Me_4bpy)(dpp)]^{2+}$ [78] (**Vj**; 1.28 V *cf.* 1.26 V), $[Ru(Me_2bpy)(Me_4bpy)\{(Et_2N)_2bpy\}]^{2+}$ (**Vk**; 0.83 V *cf.* 0.79 V),[78] $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(dpp)]^{2+}$ (**Vh**; 1.43 V *cf.* 1.45 V),[78] and $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}\{(Et_2N)_2bpy\}]^{2+}$ (**Vi**; 0.99 V *cf.* 0.97 V),[78] there is clearly a close correspondence between the calculated and observed values. Accordingly, the contributions

of the ligands to the overall potential appears to be additive, with no significant synergism between the individual contributions.

For the ligand-based reduction processes, the values of $S_L$ and $I_L$ (eq 2) of Ru(pp) may be deduced from electrochemical data on the assumption of the assignment of the most reducible ligand. In previous studies, the values for Ru(bpy) ($S_L = 0.25$; $I_L = −1.40$)[80] and Ru(bpm) ($S_L = 0.31$; $I_L = −1.08$)[80] are provided,[77] and using similar procedures values can be calculated from previous electrochemical studies[1] as well as the present study to show for Ru{$(EtCO_2)_2$bpy} ($S_L = 0.36$, $I_L = −1.10$, $R = 0.98$)[80] and Ru(dpp) ($S_L = 0.38$, $I_L = −1.20$, $R = 0.99$).[80] Again the results of application of eq 2 are impressive. The potential of the first reduction of $[Ru(bpy)(Me_2bpy)(bpm)]^{2+}$, which is isolated at the bpm ligand, is then predicted to be −1.04 V (observed −1.03 V vs SSCE), and the values obtained for the complexes $[Ru(bpy)(Me_2bpy)\{(EtCO_2)_2bpy\}]^{2+}$ (calculated, −0.98 V; observed, −1.01 V), $[Ru(Me_2bpy)(Me_4bpy)(dpp)]^{2+}$ (−1.10 V *cf.* −1.09 V), and $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}\{(Et_2N)_2bpy\}]^{2+}$ (−1.10 V *cf.* −1.09 V) are all closely comparable. For the complex $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(dpp)]^{2+}$, the first reduction couple is calculated to be −1.04 or −0.94 V, based on the assumption of dpp or $(EtCO_2)_2$bpy, respectively, as the ligand with the lowest π* energy; the observed value of −0.96 V would lead to the assignment of the ligand $(EtCO_2)_2$bpy having the lower π*-value, which is consistent with the reductions of the respective $[Ru(pp)_3]^{2+}$ complexes.[1]

Since the π*-orbital involved in the first reduction process is the same as that involved in the lowest MLCT absorption and emission processes, linear correlations have been established between the energy difference between the dπ (HOMO) and π* (LUMO) orbitals—established electrochemically by $\Delta E_{1/2} = [E_{1/2}(Ru(III)/Ru(II)) − E_{1/2}(Ru(II)/Ru(I))]$—and the absorption or emission maxima.[7,8,72–74] For the complexes of this study, such linear correlations were also observed, in an analogous manner to those established in an earlier study of a smaller series of tris(heteroleptic) complexes by Juris *et al.*[8]

**Electronic Spectra.** Visible light absorptivity in polypyridyl complexes of ruthenium(II) arises primarily from charge transfer transitions from filled dπ(Ru^II) levels to multiple, low-lying π*-(ligand) levels.[81] For the archetype tris(bidentate) species $[Ru(bpy)_3]^{2+}$; this can be represented as

$$Ru^{II}(bpy)_3^{2+} \xrightarrow{h\nu} Ru^{III}(bpy^{\bullet-})(bpy)_2^{2+}*$$

In this example, the dπ → $\pi_1$* transition results in an absorption at 450 nm and the dπ → $\pi_2$* transition at 243 nm in acetonitrile solution.[1] Ligand-based π → π* transitions dominate the near-UV region.[82] The MLCT transitions produce excited states that are largely singlet, e.g., $^1(d\pi^6) → {}^1(d\pi^5\pi^{*1})$, but possess significant triplet character due to spin–orbit coupling.[81] In mixed-chelate complexes, separate transitions may occur to each of the ligands, but rapid intramolecular charge transfer leads ultimately to a triplet MLCT state in which the excited electron is localized on the ligand having the lowest π*-acceptor orbital:[83–89] the implications in terms of the

(78) $E_L(L)$ values for $Me_4bpy$ and $(EtCO_2)_2bpy$ are derived from data in ref 1; the $E_L(L)$ value for $(Et_2N)_2bpy$ is derived from data in ref 79.

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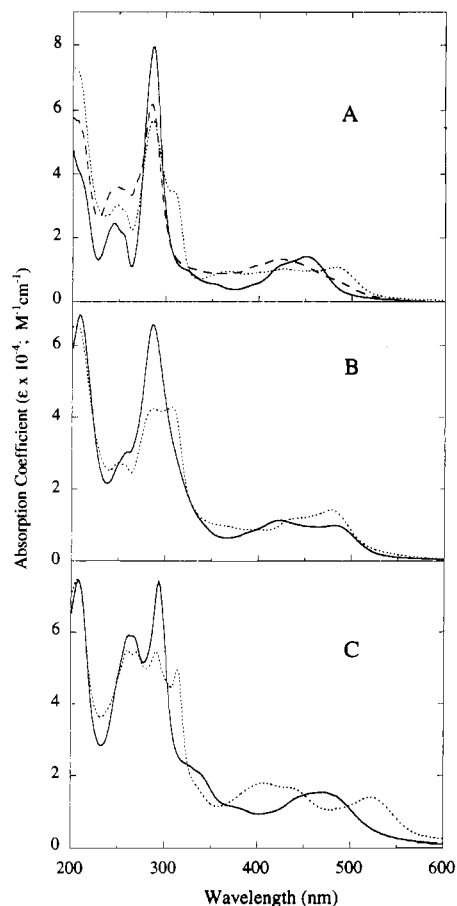(86) Ford, W. E.; Calvin, M. *Chem. Phys. Lett.* **1980**, *76*, 105.

**Figure 2.** Electronic spectra (acetonitrile solution) of (A) [Ru(bpy)₃]²⁺ (—), [Ru(bpy)(Me₂bpy){(EtCO₂)₂bpy}]²⁺ {**Ve**} (- -), and [Ru(bpy)(Me₂-bpy)(bpm)]²⁺ {**Vb**} (— —); (B) [Ru(Me₂bpy)(Me₄bpy)(dpp)]²⁺ {**Vj**} (—) and [Ru(Me₂bpy){(EtCO₂)₂bpy}(dpp)]²⁺ {**Vh**} (- -); and (C) [Ru-(Me₂bpy)(Me₄bpy){(Et₂N)₂bpy}]²⁺ {**Vk**} (—) and [Ru(Me₂bpy)-{(EtCO₂)₂bpy}{(Et₂N)₂bpy}]²⁺ {**Vi**} (- -).

photophysical properties of these tris(heteroleptic) complexes is considered below.

Figure 2A shows the electronic spectra of [Ru(bpy)(Me₂bpy)-(pp)]²⁺ {pp = 5-(Me)phen, bpm, and (EtCO₂)₂bpy}. The spectra of the series [Ru(Me₂bpy)(Me₄bpy)(pp′)]²⁺ and [Ru-(Me₂bpy){(EtCO₂)₂bpy}(pp′)]²⁺ are shown for pp′ = dpp (Figure 2B) and pp′ = (Et₂N)₂bpy in Figure 2C.

It is apparent from these data that the MLCT transitions to the lowest π*-levels of the individual ligands are broadly conserved within the various combinations of the bidentate ligands.[8,90] Rational design of the ligand environment therefore enables the production of "black absorbers" by systematically shifting the dπ → π* bands to the red region of the spectrum—either by using ligands with lower π*-levels (e.g., bpm, (EtCO₂)₂bpy, or dpp) or by stabilization of the "hole" at Ruᴵᴵᴵ in the MLCT state by the introduction of electron-donating ligands. This theme has been developed elsewhere.[90]

An interesting feature in Figure 2C is the enhancement of the absorption in the region λ ≈ 400—440 nm for [Ru(Me₂-bpy){(EtCO₂)₂bpy}{(Et₂N)₂bpy}]²⁺. Solvent-dependent spectral studies allow assignment of this broad absorption to MLCT transitions from the dπ → π* levels of the Me₂bpy and (Et₂N)₂-

bpy ligands, with the absorption at λ ≈ 522 nm attributed to the dπ → π*{(EtCO₂)₂bpy} transition. On replacement of (EtCO₂)₂bpy by Me₄bpy in the coordination sphere, there is a reduced dπ → π* energy gap for the Me₂bpy and (Et₂N)₂bpy ligands, and a broad MLCT absorption is observed at λ ≈ 470 nm for the complex [Ru(Me₂bpy)(Me₄bpy){(Et₂N)₂bpy}]²⁺. This reflects the relative effects induced on the dπ level in these two species by the electron-withdrawing (EtCO₂)₂bpy and the electron-donating Me₄bpy ligands.

**Photophysical Studies.** The luminescence properties of a number of the tris(heteroleptic) complexes in CH₃CN (1 × 10⁻⁵M) at 298 K are given in Table 5. Emission occurs from the lowest MLCT state in the tris(heteroleptic) complexes, where there are separate dπ → π*(pp), dπ → π*(pp′), and dπ → π*-(pp″) transitions: the emitting state is based on the ligand having the most positive reduction potential. Band shapes are typical of MLCT emitters—broad and structureless at room temperature and exhibiting vibronic structure at 77 K.[91] The independence of emission band shape and quantum yields on excitation wavelength from 350 to 600 nm, and excitation and absorption profiles, which are identical within experimental error, indicate that excitation into any of the three MLCT excitations leads to rapid population of the lowest ³MLCT transition.

Excited state resonance Raman and transient absorbance studies[16,92–94] show that on the nanosecond time scale (<10 ns) photophysical excitation is localized on the lowest lying π*-acceptor orbital. In the present series of complexes, by comparison of the excited state resonance Raman spectra of the tris(heteroleptic) complexes with those of each of the homoleptic complexes derived from the three ligands, the spectrum of the excited state for the tris(heteroleptic) complexes was consistent with rapid population of the lowest MLCT state, without evidence of significant population of the higher lying π*-orbitals of the other two ancillary ligands.[16,92] For example, for [Ru(bpy)(Me₂bpy)(bpm)]²⁺, where bpm has the lowest lying π*-acceptor level, intense excited state resonance Raman bands characteristic of Me₂bpy in [Ru(Me₂bpy)₃]²⁺* at 1202, 1321, 1445, and 1624 cm⁻¹ and of bpy in [Ru(bpy)₃] ²⁺* at 1211, 1321, and 1624 cm⁻¹ were not observed, while bands from bpm in [Ru(bpm)₃]²⁺* at 766, 1012, 1034, 1174, 1249, 1421, 1490, and 1560 cm⁻¹ were observed. In a similar manner, the excited state in [Ru(bpy)(Me₂bpy){(EtCO₂)₂bpy}]²⁺* could be identified as being localized on the (EtCO₂)₂bpy ligand.[92]

The quantum yields (Φₑₘ) and excited state decay lifetimes are similar to those for the homoleptic analogues, although excited state lifetimes (τ) can be longer for the tris(heteroleptic) species than might be expected on the basis of the energy gap law. This is best illustrated by two examples. For [Ru(Me₂-bpy)(bpy)(5-(Me)phen)]²⁺ and [Ru(bpy)₃]²⁺, absorption and emission maxima are nearly identical (λₐᵦₛ = 453 nm, λₑₘ = 627 nm and λₐᵦₛ = 451 nm, λₑₘ = 626 nm, respectively) and the excited state is bpy-localized in either case. The excited state lifetime and quantum yield for the former are noticeably larger (τ = 1115 ns cf. 920 ns; Φₑₘ = 0.069 cf. 0.062[18]). Calculation of the radiative (kᵣ) and nonradiative (kₙᵣ) decay rate constants using τ and φₑₘ reveal that kₙᵣ is less for the tris-(heteroleptic) complexes than for [Ru(bpy)₃]²⁺. Similarly, [Ru-(bpy)(Me₂bpy){(EtCO₂)₂bpy}]²⁺ has a small energy gap (emitting ~1750 cm⁻¹ lower in energy than [Ru(bpy)₃]²⁺), but it

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**Table 5.** Spectral and Photophysical Data for Selected Tris(heteroleptic) Complexes ($CH_3CN$ Solution)

| complex | UV/vis spectrum $\lambda_{max}$ ($\pm 2$) (nm) ($\epsilon \times 10^{-3}$ ($M^{-1}$ $cm^{-1}$)) | photophysical data[a] | | | |
|---|---|---|---|---|---|
| | | $\lambda_{em}$ ($\pm 3$)[b] (nm) | $\Phi_{em}$ ($\pm 5\%$)[b] | $\tau$ ($\pm 5\%$)[b] (ns) | $\Phi_{dec}$ ($\pm 10\%$) |
| $[Ru(bpy)_3]^{2+}$ | 244 (24.4) | 626 | 0.062 | 920 | 0.029 |
| | 254 (sh) (21.4) | | | | |
| | 288 (79.5) | | | | |
| | 451 (14.0) | | | | |
| $[Ru(bpy)(Me_2bpy)(5\text{-}(Me)phen)]^{2+}$ | 268 (68.8) | 627 | 0.069 | 1115 | 0.011 |
| | 286 (68.5) | | | | |
| | 385 (sh) (8.96) | | | | |
| | 429 (20.1) | | | | |
| | 453 (17.2) | | | | |
| $[Ru(bpy)(Me_2bpy)(bpm)]^{2+}$ | 269 (50.7) | 665 | 0.007 | 67 | <0.001 |
| | 286 (62.9) | | | | |
| | 395 (sh) (9.59) | | | | |
| | 429 (13.2) | | | | |
| | 448 (13.1) | | | | |
| $[Ru(bpy)(Me_2bpy)\{(EtCO_2)_2bpy\}]^{2+}$ | 286 (56.7) | 702 | 0.055 | 772 | <0.001 |
| | 309 (34.4) | | | | |
| | 366 (9.63) | | | | |
| | 399 (sh) (9.19) | | | | |
| | 426 (10.3) | | | | |
| | 483 (10.7) | | | | |
| $[Ru(Me_2bpy)(Me_4bpy)(dpp)]^{2+}$ | 260 (30.3) | 717 | 0.029 | 232 | <0.001 |
| | 286 (65.7) | | | | |
| | 422 (11.2) | | | | |
| | 482 (9.77) | | | | |
| $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(dpp)]^{2+}$ | 250 (27.3) | 678 | 0.037 | 788 | <0.001 |
| | 256 (sh) (26.7) | | | | |
| | 288 (42.2) | | | | |
| | 308 (42.7) | | | | |
| | 441 (11.7) | | | | |
| | 479 (14.1) | | | | |
| $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}\{(Et_2N)_2bpy\}]^{2+}$ | 206 (74.4) | 810 | 0.0002 | 60 | |
| | 260 (55.0) | | | | |
| | 270 (54.4) | | | | |
| | 292 (54.4) | | | | |
| | 314 (49.5) | | | | |
| | 408 (17.8) | | | | |
| | 432 (16.6) | | | | |
| | 522 (13.8) | | | | |
| $[Ru(Me_2bpy)(Me_4bpy)\{(Et_2N)_2bpy\}]^{2+}$ | 208 (74.3) | 700 | 0.0050 | 154 | <0.001 |
| | 262 (59.1) | | | | |
| | 294 (74.1) | | | | |
| | 320 (sh) (23.8) | | | | |
| | 470 (15.2) | | | | |

[a] Measured at 295 K. [b] $\lambda_{ex}$ = 460 nm.

has a lifetime and quantum yield comparable with the latter. In this case, $k_{nr}$ is less than would be predicted from the energy gap law. These differences can arise from changes in the acceptor characteristics of the ligand and in the extent of nonradiative decay by thermal activation and decay from the upper states.[95]

Upper limits for the quantum yield for ligand loss ($\Phi_{dec}$) for the same series were measured in $[N(n\text{-}C_4H_9)_4]Cl$ (2 mM)/acetonitrile solutions. Compared with $[Ru(bpy)_3]^{2+}$ the tris(heteroleptic) complexes are much less prone to photochemically-induced ligand loss. The comparison between $[Ru(Me_2bpy)(bpy)(5\text{-}(Me)phen)]^{2+}$ and $[Ru(bpy)_3]^{2+}$ demonstrates this point. While the ground state electrochemical properties, absorption characteristics, and excited state energies of the two species are very similar, the tris(heteroleptic) species is more photoinert by a factor of ~3. Ligand-loss photochemistry in these complexes is usually associated with thermal activation to and reactivity from low-lying dd states. Temperature dependent lifetime measurements in 4:1 (v/v) ethanol−methanol

between 160 and 298 K on the series of compounds $[Ru(bpy)(Me_2bpy)(pp)]^{2+}$, where pp = $\{(EtCO_2)_2bpy\}$, bpm, and 5-(Me)-phen, show only a slight temperature dependence above the glass to fluid transition. This behavior and the photolysis data are consistent with a decrease in thermally activated ligand-loss photochemistry. Similar observations have been made in $[Ru(bpy)_2(bpy\text{-}OH)]^{2+}$ and $[Ru(Me_2bpy)_2(vbpy)]^{2+}$ (vbpy = 4-methyl-4'-vinyl-2,2'-bipyridine).[96]

In the photolysis experiments there is no evidence for photochemically-induced scrambling in the tris(heteroleptic) species, and no detectable decomposition was noted either. In addition, during the time-resolved resonance Raman studies—in which the solutions were subjected to long-term intense radiation at 355 nm—there was no indication in any complex of any emission except that corresponding to the excited state involving the ligand of lowest $\pi^*$-energy: this observation also argues strongly against photochemically-induced scrambling.

The decrease in photolability and the apparent increase in the energy of the low-lying dd states may arise from the lowered

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electronic symmetry. More electron-donating ancillary ligands have the effect of destabilizing the $d\sigma^*$-orbitals, resulting in a larger $d\pi-d\sigma^*$ energy gap: an interesting case in point is the complex $[Ru(Me_2bpy)(Me_4bpy)\{(Et_2N)_2bpy\}]^{2+}$ (for which all the ligands are "electron-donating") which is extremely photoinert (Table 5). On the other hand, electron-withdrawing substituents on the polypyridyl ligands lower $\pi^*$-acceptor levels. The combination of the two affects the energy of dd states $(d\pi^5 d\sigma^*)$ relative to MLCT $(d\pi^5 d\pi^*)$[97] and would be responsible for the photoinertness observed in a number of other tris(heteroleptic) species.

## Significance

Application of the synthetic methodology presented here has three important consequences for future studies.

Firstly, it allows systematic control of the spectral and electrochemical characteristics of the complexes because of the ability to "tune" the $\pi^*$-levels by appropriate variation of the ligands. This may be useful in designing potential photosensitizers with broad band absorption ("black absorbers"), complexes with desired redox characteristics,[90] and complexes with controllable photophysical properties, particularly with regard to lifetimes and photoinertness.

Secondly, the scheme may be extended to the synthesis of assemblies of higher nuclearity,[69] utilizing the "complexes as ligands" approach,[98-101] in particular as described for [Ru-(pp)$_2$Cl$_2$][100] and $[Ru(pp)_2(py)_2]^{2+}$[101] species (py = pyridine). The general principle is shown in Scheme 2—the advantage of using the present dicarbonyl complexes as precursors is the added variation that mixed-ligand $[Ru(pp)(pp')]^{2+}$ moieties can be incorporated into the polynuclear compounds.

Preliminary synthetic studies have also shown that the general synthetic Scheme 1 can be used to prepare mononuclear

**Scheme 2.** Synthetic Strategy for Dinuclear Species (pp = Bidentate Polypyridyl Ligands)
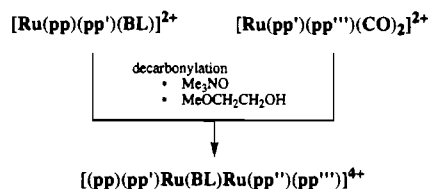


complexes of the type $[Ru(pp)(pp')XY]^{n+}$, where X and Y are monodentate ligands containing N, O, P, or S donor atoms.[102]

Thirdly, separate studies in our laboratory have demonstrated that decarbonylation will occur under controlled conditions with retention of the stereochemical relationship of the pp and pp' ligands in the $[Ru(pp)(pp')(CO)_2]^{2+}$ precursor.[52,68] Accordingly, the procedure provides the possibility of the predetermining the stereochemistry of ligand-bridged polynuclear assemblies.

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