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Convenient Synthesis of Tris-Heteroleptic Ruthenium(II) Polypyridyl Complexes

Daniel A. Freedman,[*,†,‡] **Jon K. Evju,**[‡]
Marie K. Pomije,[‡] **and Kent R. Mann**[*,‡]

Department of Chemistry, University of Minnesota,
Minneapolis, Minnesota 55455, and
Department of Chemistry, State University of
New York at New Paltz, New Paltz, New York 12561

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Introduction

We have been interested for some time in the synthetic applications of the photochemical displacement of benzene from M(II) complexes (M = Fe, Ru, Os).[1−4] For instance, photolysis of $[\mathrm{CpRu(Bz)}]^+$ (Cp = η^5-C_5H_5, Bz = η^6-C_6H_6) in acetonitrile solution gives $[\mathrm{CpRu(CH_3CN)_3}]^+$ (reaction 1).

$$[\mathrm{CpRu(Bz)}]^+ \xrightarrow[\mathrm{CH_3CN}]{h\nu} [\mathrm{CpRu(CH_3CN)_3}]^+ + \mathrm{C_6H_6} \qquad (1)$$

$[\mathrm{CpRu(CH_3CN)_3}]^+$ is a particularly useful synthetic intermediate because the acetonitrile ligands are readily replaced under mild conditions to give a variety of CpRu(II)L_3 complexes. Previous work suggested that the photochemical arene ring displacement from BzRu(II)L_3 complexes containing an ancillary polypyridyl ligand would be a useful synthetic strategy for heteroleptic $[\mathrm{Ru(pp)(pp')(pp'')}]^{2+}$ complexes (where pp, pp′, and pp″ represent different polypyridyl ligands).

Considerable efforts to synthesize Ru−polypyridyl complexes with unique photochemical, photophysical, and electrochemical properties based on the $[\mathrm{Ru(bpy)_3}]^{2+}$ (bpy = 2,2′-bipyridine) prototype have been expended.[5−8] Most previous studies have been conducted with homoleptic dipyridyl complexes or complexes of the type $[\mathrm{Ru(pp)_2(pp')}]^{2+}$ because of their synthetic availability. These studies suggest that complete control of the properties in these systems can only be attained by varying all three polypyridyl ligands, i.e., by preparing $[\mathrm{Ru(pp)(pp')(pp'')}]^{2+}$ complexes.

Although there are several synthetic routes for the preparation of $[\mathrm{Ru(pp)(pp')(pp'')}]^{2+}$ complexes,[9−14] only the two most recent ones are at all general. Even so, both methods are somewhat inconvenient. Specifically, one procedure[13] requires freshly distilled CF_3SO_3H and freshly sublimed Me_3NO, and the final polypyridyl ligand is introduced by a reaction with $[\mathrm{Ru(pp)(pp')(CO)_2}]^{2+}$. A second procedure relies on $\mathrm{Ru(pp)(pp')Cl_2}$ as a synthetic intermediate for tris-$[\mathrm{Ru(pp)(pp')(pp'')}]^{2+}$ complexes, but only an inconvenient synthesis of mixed ligand $\mathrm{Ru(pp)(pp')Cl_2}$ complexes is available.[14] The forcing conditions (refluxing DMF) in this procedure may cause decomposition of polypyridyl ligands containing unusual substituents, and the high-boiling DMF must be evaporated to isolate the product. Our work addresses both of these problems. We report the high-yield synthesis and thorough characterization of two $[\mathrm{Ru(pp)(pp')(pp'')}]^{2+}$ complexes via a convenient synthesis of $\mathrm{Ru(pp)(pp')Cl_2}$ complexes under mild conditions that require no special reagents.

Experimental Section

General Considerations. All synthetic procedures were carried out under an inert Ar or N_2 atmosphere unless otherwise noted. Acetonitrile was HPLC grade and was distilled from P_2O_5 under N_2 prior to use unless otherwise noted. Acetone was distilled under nitrogen from B_2O_3. Polypridyl ligands were purchased from Aldrich. Tetrabutylammonium hexafluorophosphate ($\mathrm{TBA^+PF_6^-}$) was purchased from Southwestern Analytical Chemicals and stored in a vacuum prior to use. The η^6-benzeneruthenium-μ-dichloro dimer, $[\mathrm{BzRuCl_2}]_2$, was prepared according to a literature procedure.[15,16] Synthetic scale photolyses (~1 g scale) were carried out with a quartz immersion well photolysis apparatus that utilized a 450 W Hg vapor lamp. Selective wavelength photolysis experiments were performed with a 200 W, high-pressure Hg vapor lamp. The wavelength of interest was isolated with the appropriate interference filter. Elemental analyses were performed by MHW Laboratories. ^{1}H NMR spectra were recorded on Varian 300 and 500 spectrometers. ^{1}H NMR chemical shifts are relative to $(CH_3)_4Si$. Low-resolution fast atom bombardment mass spectra (FABMS) of the complexes in a *m*-nitrobenzoic acid matrix were obtained with a VG 7070E-HF mass spectrometer. The theoretical isotopic abundance patterns of the $[\mathrm{Ru(pp)(pp')(pp'')}]\mathrm{PF_6}^+$ and $[\mathrm{Ru(pp)(pp')(pp'')}]^{2+}$ ions were calculated and compared to those observed to verify the identity of the peaks. UV−vis spectra were recorded on a Cary 1 spectrometer. Emission spectra were recorded at room temperature with a Princeton Instruments ST138 UV−vis/NIR-sensitive LN/CCD spectrometer. The Winspec v1.6.1.3 software package was used for acquiring the emission spectra. The emission spectra (front face detection from optically dense solutions in acetonitrile) were collected from samples irradiated at 435.8 nm with the interference-filtered output of a medium-pressure 175 W Hg/Na lamp. The emission spectra were corrected for grating efficiency and detector response.[17] Electrochemical experiments were performed with a BAS 100B electrochemical analyzer as described previously.[3] In all experiments, the electrolyte solution (0.1 M $\mathrm{TBA^+PF_6^-}$ in acetonitrile) was passed down a column of activated alumina prior to the electrochemical experiments. The working compartment of the cell was bubbled with solvent-saturated argon to deaerate the solution. The working solutions were prepared by recording the background cyclic voltammograms of the electrolyte solution prior to the addition of the solid sample. Potentials are reported vs aqueous Ag/AgCl and are not

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[*] To whom correspondence should be addressed.
[†] State University of New York at New Paltz.
[‡] University of Minnesota.

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corrected for the junction potential. The $E^{\circ\prime}$ value ($E^{\circ\prime} = +0.51$ V) for the ferrocenium/ferrocene couple in 0.1 M $TBA^+PF_6^-$ was determined to allow correlations to past and future studies.

[BzRu(bpy)Cl]Cl. The procedure below is an improvement over the one originally published by Stephenson et al.[18] $[BzRuCl_2]_2$ (1.00 g, 2.00 mmol) and 2,2′-bipyridine (0.656 g, 4.20 mmol) were added to 50 mL of acetonitrile (HPLC grade, used without further purification). The resulting slurry was purged with nitrogen for 20 min and then refluxed for 4 h. During this period, the precipitate changed color from the rust color of $[BzRuCl_2]_2$ to bright orange. The flask was cooled in an ice bath, and the product was filtered and washed with acetonitrile. The product was then dissolved in methanol, filtered, and precipitated by the addition of diethyl ether yielding 1.45 g (89% yield) of bright orange microcrystals.

[BzRu(Me$_2$bpy)Cl]Cl. $[BzRuCl_2]_2$ (0.500 g, 1.00 mmol) and 4,4′-dimethyl-2,2′-bipyridine (0.406 g, 2.20 mmol) were treated the same as above to give 0.704 g (81% yield) of bright orange microcrystals.

Ru(bpy)(CH$_3$CN)$_x$Cl$_2$. [BzRu(bpy)Cl]Cl (1.00 g, 2.46 mmol) was added to 300 mL of HPLC grade CH_3CN (used without further purification) in a quartz immersion well photolysis apparatus. The resulting slurry was purged with argon for 1 h and then photolyzed for 15 h with a 450 W Hg vapor lamp. The volume of the resulting clear, dark red solution was reduced to ca. 50 mL. This solution was filtered through a short column of diatomaceous earth to remove unreacted solid [BzRu(bpy)Cl]Cl. Addition of Et_2O precipitated the product, which was filtered and washed with Et_2O yielding 0.85 g (77% yield) of dark red powder. $Ru(bpy)(CH_3CN)_xCl_2$ was found to be a mixture of $[Ru(bpy)(CH_3CN)_3Cl]Cl$ and $Ru(bpy)(CH_3CN)_2Cl_2$ (vide infra).

Ru(Me$_2$bpy)(CH$_3$CN)$_x$Cl$_2$. [BzRu(Me$_2$bpy)Cl]Cl (0.600 g, 1.25 mmol) was treated in the same manner as [BzRu(bpy)Cl]Cl yielding 0.500 g (83% yield) of dark red powder. $Ru(Me_2bpy)(CH_3CN)_xCl_2$ was found to be a mixture of $[Ru(Me_2bpy)(CH_3CN)_3Cl]Cl$ and $Ru(Me_2bpy)(CH_3CN)_2Cl_2$ (vide infra).

Ru(bpy)(Me$_2$bpy)Cl$_2$. Under an argon purge, freshly distilled acetone (25 mL) was added to a 50 mL three-necked flask containing $Ru(bpy)(CH_3CN)_xCl_2$ (0.125 g, 0.280 mmol) and Me$_2$bpy (0.051 g, 0.277 mmol). The solution was purged with argon for 20 min and then refluxed for 14 h. The solution was cooled, and the product was filtered off as a dark purple powder, which was washed with CH_3CN and Et_2O (0.124 g, 87.4% yield). Anal. Calcd for $C_{22}H_{20}Cl_2N_4Ru{\cdot}H_2O$: C, 49.81; H, 4.19; N, 10.56. Found: C, 49.99; H, 4.24; N, 10.64. ^1H NMR (300 MHz, CD_2Cl_2): bpy signals (H^3−H^6 are *cis* to chloride, $H^{3'}$−$H^{6'}$ are *trans* to chloride) 10.18 (H^6, d, $J_{H^5-H^6} = 4.8$ Hz), 8.19 ($H^{3/3'}$, d, $J_{H^{3/3'}-H^{4/4'}} = 7.8$ Hz), 8.04 ($H^{3/3'}$, obscured), 7.89 ($H^{4,4'}$, obscured), 7.60 (H^5, d of d of d, $J_{H^5-H^4} = 7.5$ Hz, $J_{H^5-H^6} = 5.7$ Hz, $J_{H^5-H^3} = 1.5$ Hz), 7.50 ($H^{4,4'}$, obscured), 7.46 ($H^{6'}$, d of d, $J_{H^{6'}-H^{5'}} = 5.7$ Hz, $J_{H^{4'}-H^{6'}} = 1.5$ Hz), 6.92 ($H^{5'}$, d of d of d, $J_{H^{4'}-H^{5'}} = 7.4$ Hz, $J_{H^{5'}-H^{6'}} = 5.7$ Hz, $J_{H^{3'}-H^{5'}} = 1.5$ Hz); Me$_2$bpy signals 9.96 (H^6, d, 5.7 Hz), 8.03 ($H^{3/3'}$, s), 7.88 ($H^{3/3'}$, s), 7.68 (H^5, d, $J_{H^5-H^6} = 5.4$ Hz), 7.42 ($H^{6'}$, d, $J_{H^{5'}-H^{6'}} = 5.7$ Hz), 6.77 ($H^{5'}$, d, $J_{H^{5'}-H^{6'}} = 5.6$ Hz), 2.64 (CH_3, s), 2.39 (CH_3, s).

Ru(Me$_2$bpy)(phen)Cl$_2$. $Ru(Me_2bpy)(CH_3CN)_xCl_2$ (0.250 g, 0.527 mmol) and 1,10-phenanthroline monohydrate (0.103 g, 0.520 mmol) were treated the same as above yielding 0.228 g (81.7% yield) of dark powder. Anal. Calcd for $C_{24}H_{20}Cl_2N_4Ru{\cdot}H_2O$: C, 51.98; H, 4.01; N, 10.11. Found: C, 51.53; H, 4.20; N, 10.39. ^1H NMR (500 MHz, CD_2Cl_2): Me$_2$bpy signals (H^3−H^6 are *cis* to chloride, $H^{3'}$−$H^{6'}$ are *trans* to chloride) 10.41 (H^6, d, $J_{H^5-H^6} = 5.8$ Hz), 8.08 ($H^{3/3'}$, s), 7.89 ($H^{3/3'}$, s), 7.53 (H^5, d of d, $J_{H^5-H^6} = 5.8$ Hz, $J_{H^3-H^5} = 0.6$ Hz), 7.28 (d, $H^{6'}$, $J_{H^{5'}-H^{6'}} = 5.7$ Hz), 6.65 (d of d, $H^{5'}$, $J_{H^{5'}-H^{6'}} = 6.0$ Hz, $J_{H^{3'}-H^{5'}} = 0.6$ Hz), 2.72 (CH_3, s), 2.38 (CH_3, s); phen signals (H^2−H^4 are *cis* to chloride, H^7−H^9 are *trans* to chloride) 10.41 (H^2, d of d, $J_{H^2-H^3} = 5.3$ Hz, $J_{H^2-H^4} = 1.3$ Hz), 8.09 (H^4, d of d, $J_{H^3-H^4} = 8.2$ Hz, $J_{H^2-H^4} = 1.3$ Hz), 8.04 (d, $H^{5/6}$, $J_{H^5-H^6} = 8.9$ Hz), 8.03−7.97 (m, H^3, H^7, H^8), 7.92 (d, $H^{5/6}$, $J_{H^5-H^6} = 8.9$ Hz), 7.30 (H^9, d of d, $J_{H^8-H^9} = 5.4$ Hz, $J_{H^7-H^9} = 1.8$ Hz).

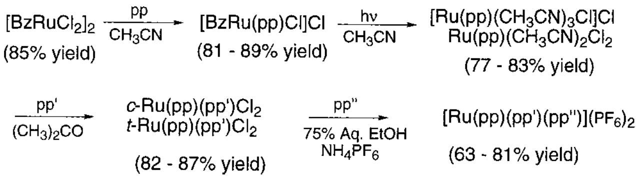
[Ru(Me$_2$bpy)(phen)(Me$_2$phen)][PF$_6$]$_2$. $Ru(Me_2bpy)(phen)Cl_2$ (0.120 g, 0.224 mmol) and 4,7-dimethyl-1,10-phenanthroline (0.512 g, 0.246 mmol) were added to a three-necked flask under an argon purge and dissolved in 20 mL of 75% ethanol/water. The solution was purged with argon and then refluxed for 16 h. Over the first 8 h, the dark purple solution gradually faded to a reddish-orange color. The solution was cooled, and the volume was reduced to ca. 5 mL under reduced pressure. Addition of an excess of NH_4PF_6 precipitated the product, which was filtered and washed with diethyl ether. The product was purified by chromatography on a ca. 15 cm alumina column with acetonitrile as the eluent. The product was the rapidly eluting reddish-orange band followed by a slower-eluting dark band. Addition of diethyl ether to the acetonitrile solution and cooling overnight precipitated the product as bright reddish-orange microcrystals, which were filtered and washed with diethyl ether (0.176 g, 81.5% yield). Anal. Calcd for $C_{38}H_{32}F_{12}N_6P_2Ru{\cdot}H_2O$: C, 46.48; H, 3.50; N, 8.56. Found: C, 46.34; H, 3.10; N, 8.51. FAB-MS *m/e*: 819.2 ($Ru(Me_2bpy)(Me_2phen)(phen)PF_6^+$), 673.2 ($Ru(Me_2bpy)(Me_2phen)(phen)^{2+}$).

[Ru(bpy)(Me$_2$bpy)(phen)][PF$_6$]$_2$. $Ru(bpy)(Me_2bpy)Cl_2$ (0.120 g, 0.234 mmol) and 1,10-phenanthroline monohydrate (0.051 g, 0.258 mmol) were treated the same as above to yield 0.135 g of reddish-orange microcrystals (63.2% yield). Anal. Calcd for $C_{34}H_{28}F_{12}N_6P_2Ru{\cdot}H_2O$: C, 44.79; H, 3.10; N, 9.22. Found: C, 44.61; H, 3.30; N, 8.99. FAB-MS *m/e*: 767.1 ($Ru(bpy)(Me_2bpy)(phen)PF_6^+$), 621.1 ($Ru(bpy)(Me_2bpy)(phen)^{2+}$).

Results and Discussion

Our route to $[Ru(pp)(pp')(pp'')]^{2+}$ complexes is outlined in Scheme 1. The $[BzRuCl_2]_2$ dimer is prepared as previously reported[15,16] in high yield. Refluxing $[BzRuCl_2]_2$ in acetonitrile solution with either 2,2′-bipyridine (bpy) or 4,4′-dimethyl-2,2′-bipyridine (Me$_2$bpy) cleaves the dimer to give [BzRu(pp)Cl]Cl in high yield. Both complexes prepared here are slightly soluble in acetonitrile and are isolated by simply filtering the reaction mixture. ^1H NMR spectra of these complexes are identical to spectra of the same complexes prepared by a previously reported route.[4,18]

Scheme 1



In the second step, the η^6-benzene ligand is displaced by photolysis of [BzRu(pp)Cl]Cl in acetonitrile solution. Photolysis is required in this step because thermal displacement of the η^6-benzene ligand in a refluxing acetonitrile solution does not occur. The low solubility of the benzene complex in acetonitrile is not problematic as long as the solution is stirred vigorously during photolysis. The use of an immersion well photolysis apparatus allowed the efficient conversion of 1 g of starting material. Reducing the volume of the photolyte followed by the addition of diethyl ether precipitates the product as a dark red solid. The photoproduct is reasonably stable as long as it is stored under dry conditions. The photoproduct was characterized by UV−vis spectroscopy (the spectrum is shown in the Supporting Information). The two main bands that are observed at 436 and 502 nm are at positions essentially identical to those previously reported for the mixture of $[(bpy)Ru(CH_3CN)_3Cl]^+$ and $(bpy)Ru(CH_3CN)_2Cl_2$ produced by the photolysis of $bpyRu(CO)_2Cl_2$ in acetonitrile solution.[19] We have also observed that these two complexes may be photochemically interconverted. (Please see the Supporting Information for details.) The [BzRu(Me$_2$bpy)Cl]Cl photoproduct gave a similar spectrum with peaks at 436 and 492 nm.

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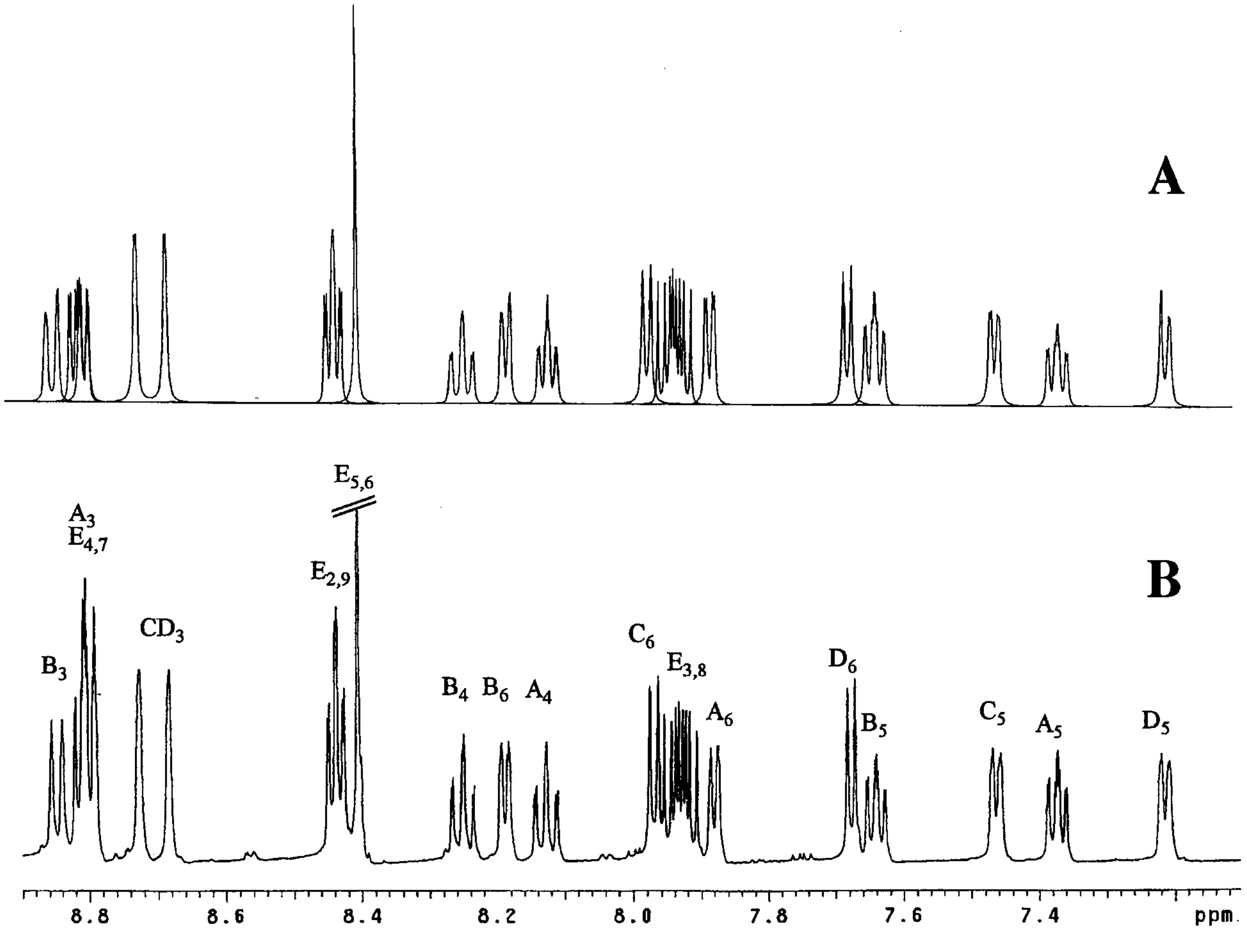

Figure 1. (A) Simulation of ^{1}H NMR spectrum of $[Ru(bpy)(Me_2bpy)(phen)][PF_6]_2$. (B) 500 MHz ^{1}H NMR spectrum of $[Ru(bpy)(Me_2bpy)(phen)][PF_6]_2$ in d_6-acetone. Labels refer to those in Figure 3.

Introduction of the second polypyridyl ligand (pp′) into the coordination sphere of the ruthenium is clearly the key step for the efficient synthesis of heteroleptic ruthenium tris-chelates. The second polypyridyl ligand (pp′) is readily introduced by refluxing the mixture of $[(pp)Ru(CH_3CN)_3Cl]Cl$ and $(pp)Ru(CH_3CN)_2Cl_2$ with the desired ligand in acetone solution. $Ru(bpy)(Me_2bpy)Cl_2$ and $Ru(Me_2bpy)(phen)Cl_2$ (phen = 1,10-phenanthroline) were prepared with a ca. 85% isolated yield by this route with no evidence of ligand scrambling. The $Ru(pp)(pp')Cl_2$ products are essentially insoluble in acetone and were isolated by simple filtration of the reaction mixture. Washing the solid products with acetonitrile and diethyl ether and drying in vacuo gave analytically pure material as the monohydrate (the presence of the water of hydration was confirmed by ^{1}H NMR spectroscopy) in excellent yield. Although the elemental analyses of both products were consistent with the neutral dichloride complex, there were clearly two complexes present (*cis* and *trans* isomers, vide infra). The major product was soluble (for $Ru(bpy)(Me_2bpy)Cl_2$), while the minor product was slightly soluble in dichloromethane; the minor product for $Ru(Me_2bpy)(phen)Cl_2$ was completely insoluble. An ^{1}H NMR spectrum of the $Ru(bpy)(Me_2bpy)Cl_2$ mixture showed the presence of two compounds in a ca. 2:1 ratio. The number of resonances in the aromatic region indicated that each polypyridyl ligand is symmetrical in the minor product (*trans* isomer) while the two halves of each ligand are in different magnetic environments in the major product (*cis* isomer). Over 24 h, the peaks for the minor product decreased in intensity concomitant with an increase in the intensity of the peaks for the major product. These data are consistent with the slow thermal conversion of the minor product *t*-$Ru(bpy)(Me_2bpy)Cl_2$ to the major product *c*-$Ru(bpy)(Me_2bpy)Cl_2$. ^{1}H NMR data, the low solubility of the *trans* vs that of the *cis* isomer, and the *trans*-to-*cis* isomerization are all consistent with the behavior of previously reported *cis* and *trans* $Ru(pp)_2Cl_2$ complexes.[20,21]

To complete the synthesis of the tris-heteroleptic polypyridyl complexes, the third ligand (pp″) is introduced by a standard route.[22] Refluxing of $Ru(pp)(pp')Cl_2$ with pp″ in 75% EtOH/H_2O followed by addition of NH_4PF_6 yields the tris-heteroleptic polypyridyl complexes as the PF_6^- salts after purification by column chromatography. $[Ru(bpy)(Me_2bpy)(phen)][PF_6]_2$ and $[Ru(Me_2bpy)(phen)(Me_2phen)][PF_6]_2$ (Me_2phen = 4,7-dimethyl-1,10-phenanthroline) were prepared from $Ru(bpy)(Me_2bpy)Cl_2$ and $Ru(Me_2bpy)(phen)Cl_2$, respectively.

Characterization of $[Ru(pp)(pp')(pp'')]PF_6]_2$ Complexes. Although the tris-heteroleptic polypyridyl complexes gave acceptable elemental analyses, UV−vis absorption and emission spectra, and cyclic voltammograms, a significant concern in the preparation of these complexes is the possibility of ligand scrambling to produce a mixture of products that would give similar data for these techniques. To thoroughly discount this possibility, we also investigated the mass spectra and ^{1}H NMR

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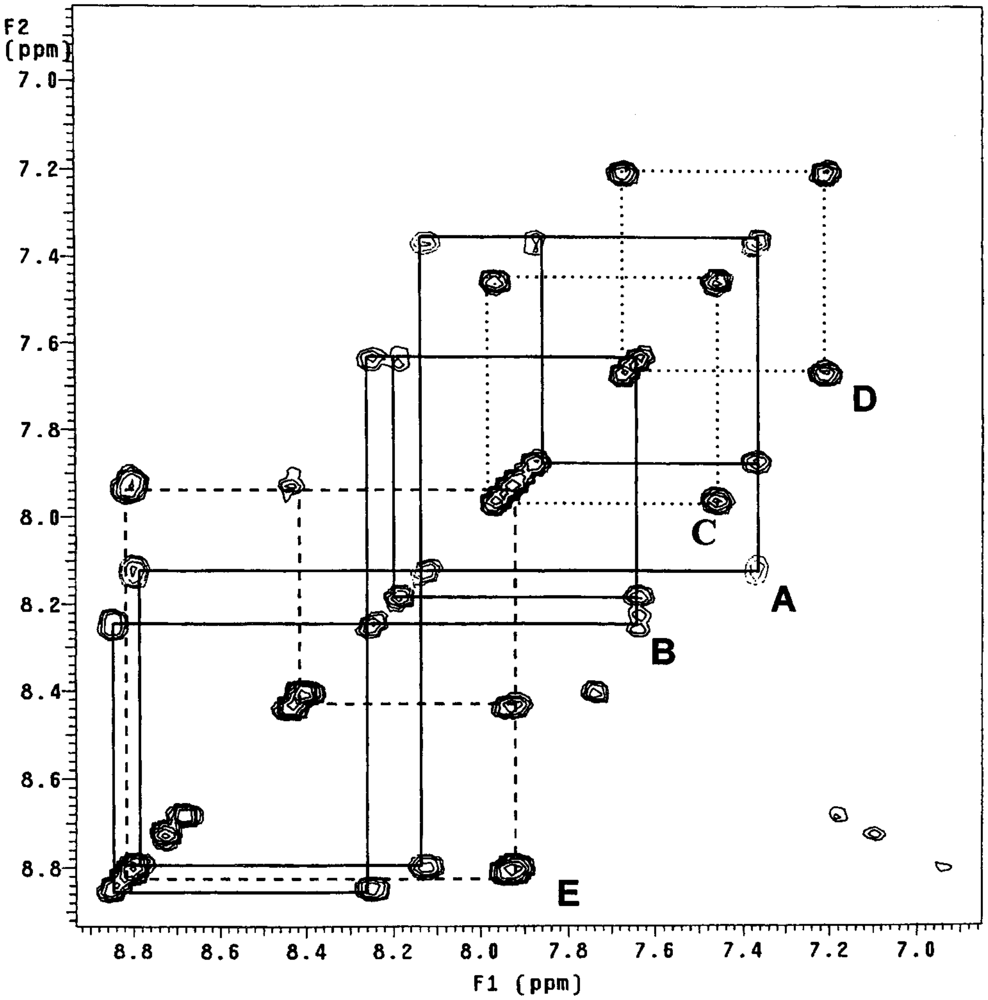

Figure 2. 500 MHz H,H-COSY spectrum of [Ru(bpy)(Me_2bpy)(phen)][PF_6]$_2$. Labels refer to those in Figure 3.

spectra of these complexes. The only major features observed at high *m*/*e* in the FAB-MS of both complexes were peaks consistent with the [Ru(pp)(pp′)(pp″)]PF_6^+ and [Ru(pp)(pp′)(pp″)]$^{2+}$ ions. Ions with scrambled ligand sets were not observed; additionally, the experimental isotopic distributions matched well with those calculated for tris-heteroleptic complexes. These results provide strong evidence that the complexes are the pure tris-heteroleptic species with little or no contamination from other mixed ligand species.

Further evidence of complex purity is provided by the clean ^{1}H NMR spectra obtained for these complexes and the successful simulation of the complicated coupling patterns observed. Both complexes have low symmetry (C_1 point group), which requires the nonequivalence of all six pyridyl rings. We were able to make a partial, detailed assignment of the one-dimensional (1D) ^{1}H NMR spectra by collecting additional data (500 MHz 1D ^{1}H NMR and H,H-COSY NMR). The H,H-COSY spectra were particularly helpful for assigning each of the six separate spin systems observed for a particular pyridyl ring. The H,H-COSY spectra were also helpful in deconvoluting several overlapping resonances in the 1D spectra and for determining the coupling patterns. We discuss in detail the assignment of the spectra obtained for [Ru(bpy)(Me_2bpy)(phen)][PF_6]$_2$. The details of the NMR assignments for [Ru(bpy)(Me_2bpy)(phen)][PF_6]$_2$ and [Ru(Me_2bpy)(phen)(Me_2phen)][PF_6]$_2$ are given in the Supporting Information.

The aromatic regions of the 1D and H,H-COSY spectra of [Ru(bpy)(Me_2bpy)(phen)][PF_6]$_2$ are shown in Figures 1 and 2, respectively. Also shown in Figure 1 is our simulation of the 1D spectra. The label above each peak on the 1D spectrum refers to the pyridyl rings labeled A−E (E refers to the entire phen ligand) in Figure 3. A total of 21 signals in the 1D spectrum were observed. An accidental degeneracy occurs between the $H^{5,6}$ hydrogens on phen. Five separate spin systems were identified in the H,H-COSY spectrum. Separate spin systems could be identified for each of the pyridyl rings on the bpy and Me_2bpy ligands. Although we observe separate peaks for the pseudosymmetrical protons on the phen ligand (except for H^5 and H^6), we were not able to assign peaks to specific spin systems because the chemical shift differences were too small to resolve by COSY. Greater differences are observed for the

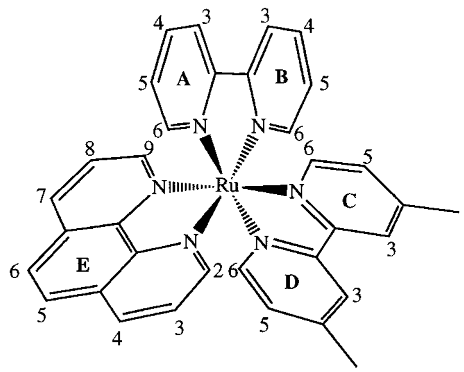

Figure 3. Sketch of [Ru(bpy)(Me_2bpy)(phen)]$^{2+}$.

Table 1. Cyclic Voltammetry and UV−Vis Absorption and Emission Data for $[Ru(pp)(pp')(pp'')]^{2+}$ Complexes[a]

complex	$E°$ (V)[a] ox	$E°$ (V)[a] red	absorption[b] λ_{max} (nm), ($\epsilon \times 10^{-4}$)	emission λ_{max} (nm)
$[Ru(bpy)(Me_2bpy)(phen)]^{2+}$	1.27	−1.33, −1.55, −1.81	451 (1.7)	623
$[Ru(Me_2bpy)(phen)(Me_2phen)]^{2+}$	1.20	−1.37, −1.61, −1.84	449 (2.0)	623
$[Ru(bpy)_3]^{2+,c}$	1.26	−1.35, −1.54, −1.77	452 (1.40)	626

[a] Data reported for ca. 1 mM solutions in CH_3CN with $TBAPF_6$ as the supporting electrolyte. Scan rate was 100 mV/s. Aqueous Ag/AgCl was used as a reference; see Experimental Section for details. [b] Units for ϵ are M^{-1} cm^{-1}. [c] Data taken from ref 9.

magnetic environments of the two rings of bpy and Me_2bpy in comparison to those in phen. As shown in Figure 3, the two rings of a given ligand are differentiated by the rings *cis* and *trans* to the ring of interest. For instance, ring A of the bpy ligand in Figure 3 is *trans* to an Me_2bpy ring and *cis* to two phen rings and an Me_2bpy ring. Ring B is *trans* to a phen ring and *cis* to two Me_2bpy rings and a phen ring. Apparently, a bpy-type ring and a phen ring create significantly different magnetic environments. In contrast, both rings of the phen ligand are *cis* and *trans* to bpy-type rings, leading to only small chemical shift differences. We assigned the peaks for rings A and B on bpy and rings C and D on Me_2bpy by considering the likely differences between the anisotropic ring current effects caused by bpy and phen ligands. Previous workers have shown that $H^{5,5',6,6'}$ of the pp rings of $[Ru(pp)_3]^{2+}$ complexes undergo a significant upfield shift relative to the free ligands due to interactions with the anisotropic ring currents of the *cis* pyridyl ring.[23] For instance, H^6 on ring A in Figure 3 will be shielded by the anisotropic ring currents from the phen ligand. The assignments in Figure 1 were made by assuming that the more extensive aromatic system of the phen ligand induces a greater upfield shift relative to a bpy-type ligand. This assignment is supported by comparison of the coordination-induced shift of Me_2bpy ring C in $[Ru(bpy)(Me_2bpy)(phen)]^{2+}$ to the analogous shifts for the Me_2bpy protons in the $[Ru(Me_2bpy)(phen)(Me_2phen)]^{2+}$ where both rings of the Me_2bpy ligand are *cis* to a phen-type ring.

For completeness, we also investigated the UV−vis absorption and emission spectra as well as the electrochemistry of the tris-heteroleptic polypyridyl complexes. These data are compiled in Table 1. Both complexes exhibit an intense, visible absorption band, which is assigned to a $d\pi \rightarrow \pi^*$ (polypyridyl) metal-to-ligand charge transfer (MLCT) transition. Excitation of the MLCT band produces the expected intense, orange emission from both complexes. Not surprisingly, the maxima and general appearance of the absorption and emission bands for the two tris-heteroleptic complexes are very similar to each other and to those for $Ru(bpy)_3{}^{2+}$ itself. The energy of the MLCT excited states in $[Ru(pp)_3]^{2+}$ complexes is principally dependent on the energy of the π^* orbitals on the polypyridyl ligands. On the basis of the absorption spectra of the $[Ru(pp)_3]^{2+}$ parent complexes[8] and E_L, the ligand electrochemical parameter developed by Lever,[24] it is expected that the MLCT states localized on bpy, Me_2bpy, phen, and Me_2phen ligands will all have similar energies.

The electrochemical behavior of these complexes is similar to that exhibited by previously studied $[Ru(pp)_3]^{2+}$ complexes.[8,25,26] Cyclic voltammograms of both complexes show a reversible one-electron oxidation at ca. 1.24 V assigned to the oxidation of Ru(II) to Ru(III) and series of three reversible one-electron ligand-based reductions. Due to the similarity between the ligands used here, our data do not allow the order in which the ligands are reduced for either complex to be determined.

Conclusions

We have described a high-yield preparation and thorough characterization of two tris-heteroleptic ruthenium polypyridyl complexes. All of the synthetic reactions take place under relatively mild conditions that avoid ligand-scrambling reactions and use reagents that require no special purification. The route uses the standard synthon for $[Ru(pp)_3]^{2+}$ complexes, in this case $Ru(pp)(pp')Cl_2$, and should be applicable to the synthesis of complexes containing a wide variety of polypyridyl ligands. The mild reaction conditions should allow this route to be extended to the preparation of complexes containing polypyridyl ligands with reactive substituents and to supramolecular assemblies of Ru(II) polypyridine complexes.

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Supporting Information Available: Tables of H,H-COSY NMR data and a discussion of the photochemistry of [BzRu(bpy)Cl]Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

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