Inorg. Chem. **1995**, *34*, 821−829 **821**

Ground- and Excited-State Properties of Ruthenium(II) Complexes Containing Tridentate Azine Ligands, Ru(tpy)(bpy)L^{2+}, Where L Is a Polymerizable Acetylene

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Received July 15, 1994⊗

A series of polypyridyl ruthenium(II) complexes containing monodentate pyridyl- and cyano-substituted acetylenes have been prepared. Complexes of the type Ru(tpy)(bpy)L^{2+} (where tpy = 2,2′:6′:2″-terpyridine ($C_{15}H_{11}N_3$), bpy = 2,2′-bipyridine ($C_{10}H_8N_2$), and L = pyridine (py) (C_5H_5N), pyridylacetylene (PA) (C_7H_5N), phenylpyridylacetylene (PPA) ($C_{13}H_9N$), dipyridylacetylene (DPA) ($C_{12}H_8N_2$), CH_3CN, cyanoacetylene (CA) (C_3HN), and cyanophenylacetylene (CPA) (C_9H_5N)) have been prepared, and their synthesis and characterization are reported herein. The complexes [Ru(tpy)(bpy)(PPA)]$(PF_6)_2\cdot(CH_3)_2CO$, [Ru(tpy)(bpy)(PA)]$(PF_6)_2\cdot(CH_3)_2CO$, and [Ru(tpy)(bpy)(CH_3CN)]$(PF_6)_2$ have been crystallized and the crystal structures determined. [Ru(tpy)(bpy)(CH_3CN)]$(PF_6)_2$ crystallizes in the monoclinic $P2_1/c$ space group with $a = 19.419(5)$ Å, $b = 10.702(4)$ Å, $c = 16.380(5)$ Å, $\beta = 112.09(2)°$, $Z = 4$, $R = 0.0725$, and $R_w = 0.0933$. [Ru(tpy)(bpy)(PA)]$(PF_6)_2\cdot(CH_3)_2CO$ crystallizes in the triclinic $P\bar{1}$ space group with $a = 9.936(2)$ Å, $b = 10.261(2)$ Å, $c = 19.270(3)$ Å, $\alpha = 77.65(1)°$, $\beta = 85.19(1)°$, $\gamma = 84.69(1)°$, $Z = 2$, $R = 0.0427$, and $R_w = 0.0492$. [Ru(tpy)(bpy)(PPA)]$(PF_6)_2\cdot(CH_3)_2CO$ crystallizes in the triclinic $P\bar{1}$ space group with $a = 10.235(3)$ Å, $b = 13.094(1)$ Å, $c = 16.593(2)$ Å, $\alpha = 79.55(1)°$, $\beta = 80.76(2)°$, $\gamma = 89.01(2)°$, $Z = 2$, $R = 0.0456$, and $R_w = 0.0602$. The inclusion of the functionalized acetylene groups makes these complexes possible precursors to metal-coordinated polyacetylenes.

Introduction

Polyacetylene, $(CH)_x$, was first synthesized in 1955, but due to its form and properties, detailed characterization was unsuccessful.[1,2] Then, in the early 1970s, advancements in polymerization techniques led Shirakawa and co-workers to produce polyacetylene as a lustrous silvery film.[1−4] This new form was soon found to exhibit high conductivities when doped with oxidative or reductive sources.[2−18] For example, upon doping with iodine, polyacetylene shows the highest conductivity of any organic polymer and closely approaches that of copper metal.[2−9,19]

Due to these highly conductive properties, and its simple empirical formula, polyacetylene has been considered the prototype of conducting polymers and is still the most extensively studied of these systems.[2,3,9−11,20−23] Unfortunately, polyacetylene still exhibits many poor characteristics which restrict both its possible applications and its continuing characterization. Most notable of these defects are its decomposition in the presence of oxygen and its lack of solubility in conventional solvents.[1−3,8,17−20]

The addition of a covalently bonded metal center to the polyacetylene chain could improve both the stability and solubility of the compound without losing the desired conductive capabilities. To achieve this, we have prepared precursor ruthenium acetylene monometallic complexes by reaction of the

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[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1995.

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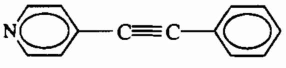
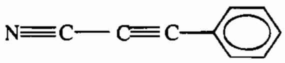
0020-1669/95/1334-0821$09.00/0

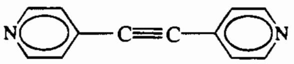
well-characterized complex [Ru(tpy)(bpy)Cl]PF_6 (where tpy = 2,2′:6′2″-terpyridine and bpy = 2,2′-bipyridine),[24,25] with a variety of monodentate substituted acetylene ligands:



PPA



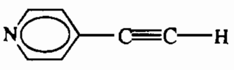
CPA



DPA

$N\equiv C-C\equiv C-H$

CA



PA

Substituted acetylenes such as phenylacetylene have already been shown to polymerize analogously to acetylene and have similar enhanced conductivity properties when doped with I_2.[26-30] Phenylacetylene itself has the added bonus of possessing enhanced photoconductivity upon exposure to visible light.[26] The ligands depicted above should retain these characteristics, thus enabling the active acetylene unit of these monometallics to be polymerized to produce metalated homo- or copolymers by known polymerization techniques.[29-32]

To characterize the complex ions $Ru(tpy)(bpy)L^{2+}$, absorption and emission spectral measurements, electrochemical studies, excited-state-lifetime measurements, and single-crystal X-ray structure determinations were initiated. The two parents, of which these complexes are a mixture, are $Ru(tpy)_2{}^{2+}$ [33-42] and $Ru(bpy)_3{}^{2+}$.[35-37,40-50] The $Ru(bpy)_3{}^{2+}$ complex has a relatively long-lived excited state at room temperature (0.85 μs, CH_3CN; ~0.62 μs, H_2O)[38-45] and at 77 K (5.2 μs, MeOH/EtOH).[36-40,42,48] The $Ru(tpy)_2{}^{2+}$ ion has a slightly longer lifetime than the tris-bpy analog at 77 K (~11 μs, MeOH/EtOH)[36-40] but a very short lifetime at room temperature (250 ps, H_2O).[51,52] The exact reason for the extremely short lifetime of the $Ru(tpy)_2{}^{2+}$ ion is still being debated; however, on the basis of the work of McMillin and co-workers, the data are consistent with excited-state decay through a low-lying ligand field state at room temperature.[39,52-54] In this report, we describe the preparation of these complexes and will compare the excited-state and structural properties of the parent and mixed-ligand systems.

Experimental Section

Materials. Materials for this study were reagent grade and were used without further purification, unless noted. The ruthenium trichloride was supplied by Johnson-Matthey, Inc. 2,2′-Bipyridine (bpy), phenylacetylene, propiolic acid, 4-bromopyridine hydrochloride, and diethylamine were all purchased from Aldrich Chemical Co. The ligand 2,2′:6′,2″-terpyridine (tpy) was purchased from Sigma. Literature procedures were used to prepare CuI[55] and $(PPh_3)_2PdCl_2$.[56] *o*-Dichlorobenzene (Aldrich), used in the cyanoacetylene synthesis, was distilled from phosphorus pentoxide, deoxygenated, and stored under argon.

The spectroquality acetonitrile (Burdick and Jackson) used in the electrochemical and spectroscopic studies was dried over activated molecular sieves. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAH), prepared by the addition of HPF_6 to an aqueous solution of tetrabutylammonium bromide (Aldrich). The crude electrolyte was then recrystallized from ethanol and stored in a vacuum desiccator. The adsorption alumina used for column chromatography was 80–200 mesh and was purchased from Fisher Scientific. All other chemicals were Fisher Scientific reagent grade and were used without further purification.

Syntheses. $Ru(tpy)Cl_3$,[57] cyanophenylacetylene (CPA),[58] pyridylacetylene (PA),[59] and dipyridylacetylene (DPA)[60] were prepared by literature methods. All ligands were prepared using anaerobic Schlenk techniques.

Phenylpyridylacetylene. PPA was prepared previously by Katritzky *et al.*[61,62] Their preparation required multiple synthetic steps and included little characterization. Our synthesis is a single-step procedure with a greater overall yield.

In our preparation, PPA was prepared by a modification of the synthesis of 2-methyl-4-(4-pyridyl)-3-butyn-2-ol, substituting the reagent phenylacetylene (3.06 g, 3.29 mL, 30.0 mmol) for 2-methyl-3-butyn-2-ol.[59] Phenylacetylene, 4-bromopyridine hydrochloride (4.85 g, 25.0 mmol), CuI (0.0250 g, 0.130 mmol), and $(PPh_3)_2PdCl_2$ (0.175 g, 0.250 mmol) were added to 50 mL of diethylamine in a dry Schlenk flask under argon. This mixture was allowed to stir at room temperature for 16 h, during which time the mixture changed from light yellow to dark brown. The solvent was removed under vacuum, and 50 mL of H_2O was added. This mixture was extracted with two 50 mL portions of anhydrous diethyl ether, and the palladium salts were eliminated by passing these combined ether solutions down a short (~7.5 cm) alumina column. The eluted band was light brown, and removal of solvent by rotary evaporation produced 3.11 g of a solid light tan product. A typical yield for this reaction was 69%. The product analyzed well for $C_{13}H_9N$. Anal. Calcd: C, 87.1; H, 5.1; N, 7.8. Found: C, 87.3; H, 5.1; N, 7.5. Mp: 85.5–86.5 °C. ^{13}C NMR ($CDCl_3$): δ 131.2 (py C_{ipso}), 125.4 (py C_o), 149.6 (py C_m), 121.9 (ph C_{ipso}), 131.7 (ph C_o), 128.3 (ph C_m), 129.1 (ph C_p), 86.5 (py $C_{acetylene}$), 93.8 (ph $C_{acetylene}$). ^1H NMR ($CDCl_3$): δ 7.33 (m, 4H), 7.53 (m, 3H), 8.57 (m, 2H). IR

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(KBr): 2221 cm^{-1} (−C≡C−). Electrochemistry (CH$_3$CN, V vs SCE): −1.91 (E_p^a), −2.18 (E_p^c), −2.05 ($E_{1/2}$). UV−vis (EtOH) (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 326 (3.0×10^3), 300 (2.3×10^4), 283 (2.5×10^4). MS (*m/e* (relative intensity)): 179.2 (100).

Cyanoacetylene. Cyanoacetylene (CA) was prepared by modifications of previous literature methods.[63−65] Propiolic acid (5.00 g, 4.42 mL, 71.4 mmol) was dissolved in 10 mL of absolute methanol. This solution was cooled in an ice−water bath, and concentrated sulfuric acid (1.43 g, 0.809 mL, 14.6 mmol) was added dropwise to the mixture with stirring. The resultant solution was maintained at room temperature for 2 days, after which time it was added to 25 mL of ice-cold water and extracted with diethyl ether. The ether layers were washed with NaHCO$_3$ to remove any unreacted propiolic acid and dried with MgSO$_4$. Then the ether was removed under vacuum to give methyl propiolate as a pale yellow liquid. This intermediate product was then added to a Schlenk flask and frozen; the flask was evacuated, after which 30 mL of liquid ammonia was distilled into the flask and the resulting solution stirred at −45 °C for 10 h. The volatile components were removed to yield the propiolamide as an off-white powder. Phosphorus pentoxide (10.5 g, 73.8 mmol) was added followed by 30 mL of dry *o*-dichlorobenzene. This mixture was frozen, and the flask was evacuated, thawed, and heated in an oil bath at 120 °C for 2 h. The product was isolated by vacuum transfer to yield 1.62 g of a clear, colorless liquid. **CAUTION!** *Cyanoacetylene is air-sensitive, a lachrymous, pyrophoric, and potentially explosive.* A typical yield for this reaction was 45%. ^{13}C NMR (CDCl$_3$): δ 104.3 (nitrile), 73.9 (acetylene), 56.8 (acetylene). ^{1}H NMR (CDCl$_3$): δ 2.68 (s, 1H).

Chloro(2,2′-bipyridine)(2,2′:6′,2″-terpyridine)ruthenium(II) Hexafluorophosphate. [Ru(tpy)(bpy)Cl]PF$_6$ was prepared by modification of previous literature methods.[24,25] Ru(tpy)Cl$_3$ (0.500 g, 1.13 mmol), the ligand bpy (0.177 g, 1.13 mmol), and LiCl (0.200 g, 5.00 mmol) were added to 100 mL of a 3:1 (v/v) ethanol/water solvent mixture. Triethylamine (1 mL) was added as a reductant, and the mixture was heated at reflux with stirring for 4 h. This solution was concentrated to 25 mL by rotary evaporation and added dropwise to 100 mL of saturated, aqueous KPF$_6$. The resulting precipitate was separated from solution by vacuum filtration, washed with four 10 mL portions of chilled 3 M HCl and 50 mL of diethyl ether, and dried under vacuum. This crude product was then purified by alumina chromatography using a 1:1 (v/v) acetone/toluene solvent mixture as the eluant. The desired product eluted first as a purple band, which was then concentrated by rotary evaporation, dissolved in a minimal amount of acetonitrile, and precipitated by addition to 200 mL of diethyl ether. The precipitate was again isolated by vacuum filtration and washed with diethyl ether. This procedure produced 0.520 g of a dry purple solid. A typical yield for this method was 69%. The solid analyzed well by UV−visible absorption spectroscopy and cyclic voltammetry for [Ru(tpy)(bpy)Cl]PF$_6$ as prepared by Meyer and coworkers.[24,25]

(Triflato)(2,2-bipyridine)(2,2′:6′,2″-terpyridine)ruthenium(II) Triflate. [Ru(tpy)(bpy)(CF$_3$SO$_3$)]CF$_3$SO$_3$ was prepared by the addition of [Ru(tpy)(bpy)Cl]PF$_6$ (0.500 g, 0.745 mmol) to 50 mL of *o*-dichlorobenzene under an argon atmosphere. Trifluoromethanesulfonic acid (1 mL, 11.3 mmol) was then added and the mixture heated at reflux for 4 h. The reaction mixture was then cooled to 0 °C, and precipitation was effected by addition to 0 °C diethyl ether. The resulting red precipitate was collected by vacuum filtration and washed with diethyl ether. This procedure produced 0.547 g of product. A typical yield for this reaction was 93%. Upon addition to acetonitrile, the solution analyzed well for Ru(tpy)(bpy)(CH$_3$CN)$^{2+}$ by UV−visible absorption spectroscopy and cyclic voltammetry.

(Acetonitrile)(2,2′-bipyridine)(2,2′:6′,2″-terpyridine)ruthenium(II) Hexafluorophosphate. [Ru(tpy)(bpy)(CH$_3$CN)](PF$_6$)$_2$ was prepared by the addition of [Ru(tpy)(bpy)(CF$_3$SO$_3$)]CF$_3$SO$_3$ (0.120 g, 0.160 mmol) to 20 mL of acetonitrile and allowed to stand for 3 days. Aqueous, saturated KPF$_6$ (20 mL) was then added, and the solution was allowed to evaporate. The resulting precipitate was collected by vacuum filtration and washed with water. This orange solid was crystallized by slow evaporation of a 1:1 CH$_3$CN/H$_2$O solution to produce 0.128 g of red parallelepiped crystals. A typical yield for this reaction was 97%. This complex analyzed well for [Ru(tpy)(bpy)(CH$_3$CN)](PF$_6$)$_2$ as previously reported by McMillin and co-workers[66] and Deutsch *et al.*[67] Anal. Calcd: C, 39.5; H, 2.7; N, 10.2. Found: C, 39.4; H, 2.7; N, 10.1.

(2,2′-Bipyridine)(pyridine)(2,2′;6′,2″-terpyridine)ruthenium(II) Hexafluorophosphate. [Ru(tpy)(bpy)(py)](PF$_6$)$_2$ was prepared as above by substituting pyridine (0.9 mL, 11.2 mmol) in 20 mL of 100% ethanol for acetonitrile. This complex was further purified by alumina chromatography using a 2:1 (v/v) toluene/acetonitrile solvent mixture as the eluant. A single orange band was collected and precipitated by addition to diethyl ether. The resulting precipitate was collected by vacuum filtration and washed with diethyl ether. This procedure produced 0.13 g of an orange-red solid. A typical yield for this reaction was 73%. This complex analyzed well for [Ru(tpy)(bpy)(py)](PF$_6$)$_2$·H$_2$O as previously reported by McMillin and co-workers[66] and Calvert and Meyer.[68] Anal. Calcd: C, 41.1; H, 3.0; N, 9.6. Found: C, 41.3; H, 2.9; N, 9.6.

(2,2′-Bipyridine)(phenylpyridylacetylene)(2,2′:6′,2″-terpyridine)ruthenium(II) Hexafluorophosphate. [Ru(tpy)(bpy)(PPA)](PF$_6$)$_2$ was prepared by combining [Ru(tpy)(bpy)Cl]PF$_6$ (0.50 g, 0.745 mmol) with the ligand PPA (0.533 g, 2.98 mmol) in 60 mL of a 1:1 (v/v) ethanol/water solvent mixture and heating at reflux with stirring for 4 h. The reaction mixture was added dropwise to 100 mL of saturated aqueous KPF$_6$, and the resulting precipitate was isolated by vacuum filtration. This crude product was dissolved in a minimum amount of acetone and reprecipitated by addition to 200 mL of diethyl ether to remove excess water. The product was purified by alumina chromatography using a 1:1 (v/v) acetone/toluene solvent mixture as the eluant. A small amount of unreacted ruthenium starting material eluted first as a purple band, followed by an orange band containing the desired product. This band was concentrated by rotary evaporation to induce precipitation, dissolved in a minimal amount of acetone, and again precipitated by addition to 200 mL of diethyl ether. The resulting precipitate was isolated by vacuum filtration and dried under vacuum to produce 0.472 g of a dry orange solid. A typical yield for this reaction was 66%. The complex analyzed well for [Ru(tpy)(bpy)(PPA)](PF$_6$)$_2$·C$_3$H$_6$O. Anal. Calcd: C, 48.4; H, 3.4; N, 8.3. Found: C, 48.2; H, 3.3; N, 8.3. IR (KBr): 2221 cm^{-1} (−C≡C−).

(2,2′-Bipyridine)(pyridylacetylene)(2,2′:6′,2″-terpyridine)ruthenium(II) Hexafluorophosphate. [Ru(tpy)(bpy)(PA)](PF$_6$)$_2$ was prepared and purified as above by substituting the ligand PA (0.307 g, 2.98 mmol) for the ligand PPA to produce 0.382 g of an orange solid. A typical yield for this reaction was 58%. The complex analyzed well for [Ru(tpy)(bpy)(PA)](PF$_6$)$_2$·C$_3$H$_6$O. Anal. Calcd: C, 44.6; H, 3.2; N, 8.9. Found: C, 44.6; H, 3.2; N, 8.9. IR (KBr): 2215 cm^{-1} (−C≡C−).

(2,2′-Bipyridine)(cyanophenylacetylene)(2,2′:6′,2″-terpyridine)ruthenium(II) Hexafluorophosphate. [Ru(tpy)(bpy)(CPA)](PF$_6$)$_2$ was prepared and purified as above by substituting the ligand CPA (0.378 g, 2.98 mmol) for the ligand PPA to produce 0.203 g of an orange solid. A typical yield for this reaction was 30%. The complex analyzed for [Ru(tpy)(bpy)(CPA)](PF$_6$)$_2$·H$_2$O. Anal. Calcd: C, 44.1; H, 2.8; N, 9.0. Found: C, 44.3; H, 3.2; N, 8.5.

(2,2′-Bipyridine)(dipyridylacetylene)(2,2′:6′,2″-terpyridine)ruthenium(II) Hexafluorophosphate. [Ru(tpy)(bpy)(DPA)](PF$_6$)$_2$ was prepared and purified as above by substituting the ligand DPA (0.536 g, 2.98 mmol) for the ligand PPA. Unlike the other acetylene complexes, this ligand forms both a mono- and bimetallic species. Therefore, following the elution of the orange band containing the monometallic species, a dark red-purple band was eluted containing a small amount of the bimetallic complex. This procedure produced 0.501 g of the monometallic species as an orange solid. A typical yield for this reaction was 70%. The complex analyzed well for [Ru(tpy)(bpy)-

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Table 1. Crystal Data for Ru(tpy)(bpy)L^{2+}

	L		
	CH_3CN	PA	PPA
formula	$C_{27}H_{22}N_6F_{12}P_2Ru$	$C_{35}H_{30}N_6OF_{12}P_2Ru$	$C_{41}H_{34}N_6OF_{12}P_2Ru$
fw	821.51	941.66	1017.75
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	19.419(5)	9.936(2)	10.235(3)
b, Å	10.702(4)	10.261(2)	13.094(1)
c, Å	16.380(5)	19.270(3)	16.593(2)
α, deg		77.65(1)	79.55(1)
β, deg	112.09(2)	85.19(1)	80.76(2)
γ, deg		84.69(1)	89.01(2)
V, Å3	3154(2)	1906.8(6)	2158.3(7)
Z	4	2	2
D_{calc}, g cm^{-3}	1.73	1.64	1.57
μ, mm^{-1}	0.69	0.58	0.53
transm coeff	0.86−1.00	0.89−1.00	0.84−1.00
no. of obsd data ($I > 3\sigma(I)$)	3060	3864	4855
$R(F_o)$[a]	0.0725	0.0427	0.0456
$R_w(F_o)$[b]	0.0933	0.0492	0.0602

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

(DPA)]$(PF_6)_2$·C_3H_6O. Anal. Calcd: C, 47.2; H, 3.3; N, 9.6. Found: C, 46.9; H, 3.3; N, 9.6. IR (KBr): 2235 cm^{-1} (−C≡C−).

(2,2′-Bipyridine)(cyanoacetylene)(2,2′:6′,2″-terpyridine)ruthenium(II) Hexafluorophosphate. [Ru(tpy)(bpy)(CA)]$(PF_6)_2$ was prepared as follows: [Ru(tpy)(bpy)(CF_3SO_3)]CF_3SO_3 (0.500 g, 0.634 mmol) was added to a clean, dry Schlenk flask, which was then evacuated. The ligand, CA (2.50 mL, 2.04 g, 40.0 mmol), was added by vacuum transfer and the mixture allowed to stir for 24 h. Saturated, aqueous KPF_6 (30 mL) was then added, and the resulting precipitate was separated from solution by vacuum filtration, washed with diethyl ether, and dried under vacuum. This crude product was then purified as above. This procedure produced 0.316 g of a dry orange solid. A typical yield for this reaction was 60%. The complex analyzed well for [Ru(tpy)(bpy)(CA)]$(PF_6)_2$·$2(CH_3)_2CO$. Anal. Calcd: C, 43.0; H, 3.4; N, 8.9. Found: C, 42.5; H, 3.3; N, 8.9.

Spectroscopy. Absorption spectra were recorded using two, matched, 1 cm quartz cells on a Shimadzu UV-3100 spectrophotometer interfaced to a Shimadzu PC computer. Samples were prepared gravimetrically as acetonitrile solutions and studied at room temperature. Extinction coefficients were calculated by the collection of the adsorption values for five different micromolar solutions. These values were then plotted vs their respective concentrations, and the resulting slope was used for the coefficient values.

Emission spectra were recorded on a Spex Fluorolog spectrofluorometer, utilizing an uncooled Hamamatsu R928 photomultiplier tube. All measurements were made in 1 cm fluorescence cuvettes at right angles to the incident beam. Samples were prepared from single crystals which were washed with ether to remove any residual powder from the crystal exterior. The crystal was then prepared as an argon-purged acetonitrile or methylene chloride solution and studied at room temperature. Emission spectra were collected using an excitation wavelength of 459 nm and reported as uncorrected values. Excitation spectra were independent of the monitoring wavelength.

Emission lifetimes were measured using a PAR LN 1000 nitrogen laser (337 nm) as the excitation source. The excitation source was passed through a PRA L-OT photodiode trigger and through the sample, which was prepared in deoxygenated CH_2Cl_2 at a concentration to give a 0.2 absorbance at the excitation maximum. The emission was collected through a filter and an ISA Model H-10 monochromator. The detector used was an uncooled Hamamatsu R928 photomultiplier tube. The PMT output was fed into a SR250 gated integrator and boxcar averager. The data were then transferred to a 386 PC, and data manipulation was performed with a software package developed by Stanford Research Systems. Low-temperature emission and lifetime measurements were taken at 77 K on samples which were argon-purged 1:1 methanol/ethanol glasses.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [Ru(tpy)(bpy)CH_3CN]$(PF_6)_2$

	x	y	z	U_{eq}[a]
Ru(1)	2548(1)	2755(1)	3832(1)	42(1)
P(1)	−1048(2)	2559(4)	827(2)	72(2)
P(2)	5745(2)	2022(4)	1673(2)	68(1)
F(1)	−1043(8)	1427(18)	289(10)	245(11)
F(2)	−1045(7)	3739(10)	1363(10)	170(8)
F(3)	−504(7)	3268(16)	473(9)	190(9)
F(4)	−1587(7)	1933(12)	1181(7)	154(7)
F(5)	−362(6)	2099(13)	1588(8)	178(7)
F(6)	−1741(7)	3009(18)	47(9)	219(9)
F(7)	5740(7)	668(10)	2040(6)	157(6)
F(8)	5819(6)	3338(11)	1312(7)	144(6)
F(9)	4987(4)	1775(11)	876(4)	110(4)
F(10)	6509(5)	2262(9)	2488(5)	102(4)
F(11)	6186(5)	1529(12)	1112(5)	136(5)
F(12)	5323(5)	2555(13)	2234(6)	154(6)
N(1)	2260(5)	1268(8)	2967(5)	50(4)
N(2)	2968(4)	1372(8)	4645(5)	47(4)
N(3)	2971(4)	3734(9)	5012(5)	47(4)
N(4)	2019(4)	4113(8)	2918(5)	48(3)
N(5)	1529(4)	2775(8)	3921(5)	47(3)
N(6)	3561(5)	2939(9)	3751(5)	51(4)
C(1)	1850(6)	1268(12)	2092(7)	63(5)
C(2)	1679(7)	201(14)	1595(8)	77(6)
C(3)	1933(7)	−936(13)	1996(9)	73(6)
C(4)	2335(6)	−946(11)	2890(8)	60(5)
C(5)	2490(6)	126(10)	3361(7)	51(5)
C(6)	2915(6)	198(11)	4329(7)	53(5)
C(7)	3222(6)	−802(12)	4884(7)	63(5)
C(8)	3586(7)	−533(14)	5777(8)	73(6)
C(9)	3636(6)	670(13)	6090(7)	66(5)
C(10)	3321(5)	1624(12)	5516(6)	53(4)
C(11)	3307(5)	2958(11)	5725(6)	47(4)
C(12)	3606(6)	3472(14)	6567(7)	69(6)
C(13)	3561(7)	4721(14)	6696(8)	72(6)
C(14)	3226(7)	5465(13)	5980(9)	73(6)
C(15)	2933(6)	4942(11)	5149(8)	58(5)
C(16)	2295(6)	4720(12)	2390(7)	64(5)
C(17)	1871(7)	5402(13)	1689(8)	74(6)
C(18)	1122(8)	5520(13)	1516(8)	81(6)
C(19)	825(6)	4962(12)	2066(8)	72(5)
C(20)	1277(5)	4252(10)	2765(7)	51(4)
C(21)	1026(5)	3609(10)	3380(6)	50(4)
C(22)	357(6)	3794(13)	3464(8)	73(6)
C(23)	188(7)	3167(14)	4085(9)	78(6)
C(24)	680(6)	2306(14)	4608(8)	73(6)
C(25)	1335(6)	2127(12)	4501(7)	62(5)
C(26)	4174(7)	3052(12)	3839(6)	61(5)
C(27)	4962(6)	3240(17)	3962(8)	88(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Infrared spectra were recorded on a Nicolet 5DX spectrometer interfaced to a Nicolet 620 processor and a Hewlett Packard 7470A plotter. Samples were prepared as KBr pellets (2 mg of sample/100 mg of KBr), and the sample compartment was purged with nitrogen for 10 min prior to each scan.

Electrochemistry. Cyclic voltammograms were recorded on an EG&G Princeton Applied Research potentiostat/galvanostat, Model 373. Measurements were made at a sweep rate of 100 mV/s at a current range of 1 mA. The three-electrode system consisted of a platinum disk working electrode, a platinum disk auxiliary electrode, and a saturated calomel reference electrode. Millimolar solutions of the samples were prepared by dissolution in Burdick and Jackson high-purity acetonitrile dried over molecular sieves. The supporting electrolyte was 0.1 M TBAH (tetrabutylammonium hexafluorophosphate). The solutions were deoxygenated by bubbling with nitrogen for 15 min prior to each scan and blanketed with nitrogen during the scan. The platinum disk working electrode was manually cleaned and polished prior to each individual scan.

NMR. NMR spectra were recorded on a Bruker AC 300 MHz NMR spectrometer. Samples were prepared in 5 mm NMR tubes as

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for $[Ru(tpy)(bpy)(PA)](PF_6)_2 \cdot (CH_3)_2CO$

	x	y	z	U_{eq}[a]
Ru(1)	1236(1)	3001(1)	2722(1)	33(1)
P(1)	2871(2)	3467(2)	5642(1)	52(1)
P(2)	1136(2)	7432(2)	316(1)	61(1)
F(1)	1341(4)	3520(5)	5942(3)	83(2)
F(2)	3058(4)	4823(4)	5887(2)	67(2)
F(3)	2680(5)	2102(5)	5399(3)	86(2)
F(4)	3290(5)	2628(4)	6402(2)	82(2)
F(5)	2455(5)	4279(5)	4892(2)	89(2)
F(6)	4419(4)	3390(5)	5360(3)	89(2)
F(7)	1996(6)	8376(7)	602(4)	151(4)
F(8)	1350(8)	6405(8)	1019(4)	175(4)
F(9)	−176(6)	8048(8)	621(4)	167(4)
F(10)	1036(8)	8302(8)	−432(4)	179(4)
F(11)	2537(6)	6800(6)	20(3)	122(3)
F(12)	313(7)	6429(7)	51(3)	131(3)
O(1)	4579(10)	−88(9)	2064(5)	151(5)
N(1)	2135(5)	2797(5)	1737(3)	38(2)
N(2)	483(5)	1373(5)	2606(3)	39(2)
N(3)	112(4)	2528(5)	3685(3)	38(2)
N(4)	2187(5)	4657(5)	2862(3)	38(2)
N(5)	2907(5)	2099(5)	3241(3)	38(2)
N(6)	−471(5)	4110(5)	2246(2)	36(2)
C(1)	3009(7)	3559(7)	1316(4)	53(3)
C(2)	3498(9)	3337(8)	656(4)	73(3)
C(3)	3068(9)	2292(8)	420(4)	72(3)
C(4)	2182(8)	1480(7)	840(4)	60(3)
C(5)	1726(6)	1733(6)	1499(3)	44(2)
C(6)	771(6)	922(6)	1995(3)	42(2)
C(7)	177(8)	−187(7)	1894(4)	59(3)
C(8)	−657(8)	−849(7)	2440(5)	67(3)
C(9)	−947(7)	−383(7)	3057(4)	61(3)
C(10)	−357(6)	735(6)	3141(3)	45(2)
C(11)	−536(6)	1376(6)	3764(6)	44(2)
C(12)	−1272(7)	891(8)	4385(4)	63(3)
C(13)	−1391(8)	1553(9)	4939(4)	71(3)
C(14)	−755(7)	2684(8)	4863(4)	63(3)
C(15)	17(7)	3155(7)	4239(3)	55(3)
C(16)	1815(7)	5959(6)	2604(4)	51(3)
C(17)	2523(7)	6969(7)	2712(4)	62(3)
C(18)	3631(8)	6656(7)	3122(4)	65(3)
C(19)	4027(7)	5352(7)	3395(4)	56(3)
C(20)	3300(6)	4355(6)	3248(3)	38(2)
C(21)	3695(6)	2918(7)	3471(3)	42(2)
C(22)	4779(7)	2405(8)	3876(4)	56(3)
C(23)	5085(7)	1044(8)	4053(4)	63(3)
C(24)	4298(7)	220(8)	3813(4)	63(3)
C(25)	3234(6)	767(6)	3407(3)	50(2)
C(26)	−805(7)	4116(6)	1582(3)	46(2)
C(27)	−1962(7)	4729(7)	1299(3)	51(3)
C(28)	−2878(6)	5411(6)	1695(3)	41(2)
C(29)	−2533(7)	5473(7)	2364(3)	56(3)
C(30)	−1349(6)	4817(7)	2621(3)	50(2)
C(31)	−4148(6)	6010(7)	1429(3)	47(2)
C(32)	−5181(7)	6521(7)	1212(4)	64(3)
C(33)	5593(12)	346(11)	1724(6)	100(5)
C(34)	6143(15)	−153(13)	1070(7)	151(7)
C(35)	6201(11)	1538(11)	1896(6)	106(5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

chloroform-*d* solutions containing 1% (v/v) TMS. ^1H spectra were referenced to trimethylsilane and ^{13}C spectra were referenced to the center peak of the chloroform-*d* triplet.

Crystallography. X-ray quality parallelepiped crystals of $[Ru(tpy)(bpy)(CH_3CN)](PF_6)_2$ were obtained by slow evaporation of a water/acetonitrile solution. X-ray quality parallelepiped crystals of $[Ru(tpy)(bpy)(PPA)](PF_6)_2 \cdot (CH_3)_2CO$ and $[Ru(tpy)(bpy)(PA)](PF_6)_2 \cdot (CH_3)_2CO$ were obtained by layering diethyl ether onto an acetone solution of the metal complex in a sealed glass tube.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for $[Ru(tpy)(bpy)(PPA)](PF_6)_2 \cdot (CH_3)_2CO$

	x	y	z	U_{eq}[a]
Ru(1)	530(1)	2961(1)	−2006(1)	33(1)
P(1)	7351(2)	3507(2)	−4553(1)	79(1)
P(2)	4721(2)	7150(2)	−180(1)	55(1)
F(1)	8120(6)	2491(5)	−4658(5)	183(4)
F(2)	8267(6)	3655(5)	−3918(4)	150(3)
F(3)	8250(7)	4115(6)	−5285(4)	209(4)
F(4)	6335(6)	3175(7)	−5074(4)	185(4)
F(5)	6326(6)	2899(4)	−3787(3)	136(3)
F(6)	6556(6)	4505(4)	−4425(4)	156(3)
F(7)	5573(5)	6537(5)	−774(4)	151(3)
F(8)	3865(6)	6113(3)	190(3)	119(2)
F(9)	3725(5)	7401(4)	−840(3)	115(2)
F(10)	3738(5)	7708(4)	426(3)	117(2)
F(11)	5396(7)	8203(4)	−546(4)	154(3)
F(12)	5621(5)	6912(4)	486(3)	134(3)
O(1)	639(14)	8507(10)	−2418(7)	270(8)
N(1)	1386(4)	2905(3)	−3213(2)	41(1)
N(2)	2065(4)	3901(3)	−2124(3)	38(1)
N(3)	304(4)	3323(3)	−822(2)	36(1)
N(4)	−963(4)	1837(3)	−1892(2)	41(1)
N(5)	1450(4)	1634(3)	−1523(2)	44(2)
N(6)	−612(4)	4253(3)	−2393(2)	39(1)
C(1)	989(6)	2384(4)	−3752(3)	53(2)
C(2)	1689(7)	2409(5)	−4538(4)	70(3)
C(3)	2838(7)	2966(5)	−4780(4)	69(3)
C(4)	3259(6)	3525(5)	−4246(4)	59(2)
C(5)	2519(5)	3494(4)	−3463(3)	47(2)
C(6)	2889(5)	4094(4)	−2865(3)	46(2)
C(7)	3906(6)	4811(5)	−2969(4)	63(2)
C(8)	4079(6)	5300(5)	−2316(4)	67(3)
C(9)	3259(5)	5059(4)	−1554(4)	58(2)
C(10)	2243(5)	4338(4)	−1470(3)	43(2)
C(11)	1295(5)	3951(3)	−715(3)	39(2)
C(12)	1399(6)	4160(4)	64(3)	53(2)
C(13)	491(6)	3718(5)	737(3)	63(2)
C(14)	−527(6)	3115(4)	615(3)	55(2)
C(15)	−597(5)	2934(4)	−159(3)	43(2)
C(16)	−2134(5)	1980(4)	−2164(3)	53(2)
C(17)	−3016(6)	1178(6)	−2106(4)	71(3)
C(18)	−2722(8)	206(5)	−1744(5)	83(3)
C(19)	−1524(7)	43(5)	−1472(4)	73(3)
C(20)	−639(6)	859(4)	−1557(3)	49(2)
C(21)	685(6)	761(4)	−1321(3)	48(2)
C(22)	1162(7)	−155(5)	−900(4)	74(3)
C(23)	2410(8)	−172(5)	−688(5)	82(3)
C(24)	3158(7)	707(5)	−892(4)	71(3)
C(25)	2677(6)	1605(4)	−1308(3)	55(2)
C(26)	−1742(5)	4453(4)	−1905(3)	43(2)
C(27)	−2482(5)	5323(4)	−2068(3)	48(2)
C(28)	−2073(5)	6062(4)	−2785(3)	43(2)
C(29)	−936(5)	5850(4)	−3302(3)	49(2)
C(30)	−251(5)	4953(4)	−3092(3)	46(2)
C(31)	−2793(6)	7004(4)	−2969(3)	54(2)
C(32)	−3370(6)	7793(4)	−3115(3)	55(2)
C(33)	−4070(6)	8742(4)	−3290(3)	55(2)
C(34)	−5194(6)	8942(5)	−2761(4)	69(2)
C(35)	−5855(8)	9876(6)	−2938(6)	91(4)
C(36)	−5371(10)	10607(6)	−3623(6)	100(4)
C(37)	−4298(11)	10415(6)	−4127(6)	121(5)
C(38)	−3629(9)	9499(6)	−3966(5)	98(3)
C(39)	635(20)	9155(13)	−3802(10)	233(11)
C(40)	1075(15)	8412(13)	−3096(7)	162(7)
C(41)	2079(16)	7541(13)	−3162(10)	192(9)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The crystal structures were solved by direct methods. The refinements were performed by full-matrix least squares. All calculations

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(69) Sheldrick, G. M. *SHELXTL, Crystallographic Computing System*; Nicolet Instruments Division: Madison, WI, 1986.

(70) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2B.

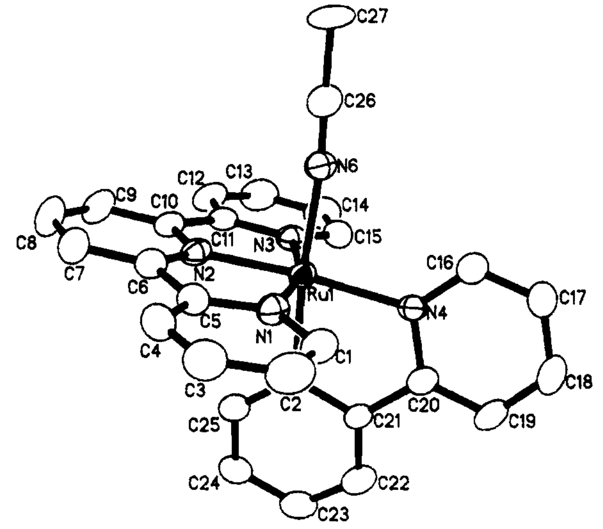

Figure 1. Thermal ellipsoid plot of Ru(tpy)(bpy)(CH$_3$CN)$^{2+}$.

Table 5. Selected Bond Lengths (Å) for Ru(tpy)(bpy)L^{2+} Cations

	L		
atoms	CH$_3$CN	PPA	PA
Ru(1)−N(1)	2.063(9)	2.066(4)	2.073(5)
Ru(1)−N(2)	1.952(8)	1.976(4)	1.954(5)
Ru(1)−N(3)	2.077(8)	2.081(4)	2.073(5)
Ru(1)−N(4)	2.062(8)	2.103(4)	2.095(5)
Ru(1)−N(5)	2.040(9)	2.057(4)	2.052(5)
Ru(1)−N(6)	2.030(10)	2.101(4)	2.114(4)
N(6)−C(26)	1.150(16)	1.352(6)	1.347(8)
C(26)−C(27)	1.479(18)	1.366(7)	1.356(9)
N(6)−C(30)		1.345(6)	1.346(8)
C(30)−C(29)		1.376(7)	1.376(9)
C(27)−C(28)		1.402(6)	1.376(9)
C(28)−C(29)		1.387(7)	1.376(10)
C(28)−C(31)		1.436(7)	1.436(8)
C(31)−C(32)		1.187(8)	1.175(9)
C(32)−C(33)		1.431(8)	
C(33)−C(34)		1.383(8)	
C(33)−C(38)		1.377(9)	
C(34)−C(35)		1.394(10)	
C(35)−C(36)		1.376(11)	
C(36)−C(37)		1.320(14)	
C(37)−C(38)		1.376(12)	

were performed using the SHELXTL PLUS program package.[69] An empirical absorption correction was applied to the data for all of the compounds. Neutral atom scattering factors were those of Cromer and Waber,[70] and the real and imaginary anomalous dispersion corrections were those of Cromer.[71] Relevant crystal data are given in Table 1, and atomic coordinates are given in Tables 2−4.

Results and Discussion

The X-ray crystal structure of the cation Ru(tpy)(bpy)(CH$_3$CN)$^{2+}$ is shown in Figure 1. Atomic coordinates are listed in Table 2, and selected bond angles and distances are given in Tables 5 and 6. The coordination sphere of this complex shows asymmetric bond distances to the varying ligands. Most noticeable is the short Ru−N distance to the central nitrogen of the terpyridine ligand. To optimize the chelation of this ligand, this bond shortens while the terminal Ru−N bonds lengthen to relieve strain and retain a typical terpyridine bite angle of ~79°.[34,66,72−77] This results in more than a 0.1 Å difference between the Ru−N bonds and is consistent with the strain intrinsic to the metal−terpyridine moiety as seen in Ru(tpy)$_2^{2+}$ [72] and other Ru(tpy)L$_3^{n+}$ complexes.[34,66,73−75] The asymmetric bonding of the bipyridine (Ru(1)−N(4) = 2.062(8), Ru(1)−N(5) = 2.040(9) Å) is consistent with that seen in other Ru(tpy)(bpy)L^{n+} complexes.[64,74,75]

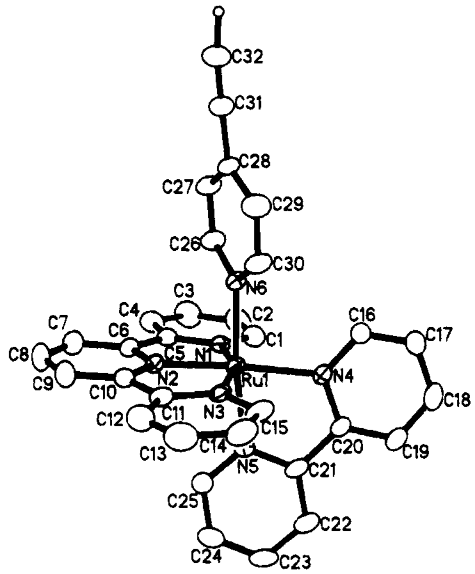

Figure 2. Thermal ellipsoid plot of Ru(tpy)(bpy)(PA)$^{2+}$.

Table 6. Selected Bond Angles (deg) for Ru(tpy)(bpy)L^{2+} Cations

	L		
atoms	CH$_3$CN	PPA	PA
N(1)−Ru(1)−N(2)	79.6(3)	79.9(2)	79.0(2)
N(1)−Ru(1)−N(4)	96.5(3)	97.6(2)	99.7(2)
N(1)−Ru(1)−N(5)	92.1(3)	93.4(2)	92.6(2)
N(1)−Ru(1)−N(6)	92.8(4)	92.1(1)	91.4(2)
N(2)−Ru(1)−N(3)	80.2(3)	79.2(2)	80.0(2)
N(2)−Ru(1)−N(5)	97.3(4)	96.1(2)	97.4(2)
N(2)−Ru(1)−N(6)	87.2(4)	89.1(2)	88.3(2)
N(3)−Ru(1)−N(4)	103.5(3)	102.9(1)	101.0(2)
N(3)−Ru(1)−N(5)	89.0(3)	86.4(2)	87.7(2)
N(3)−Ru(1)−N(6)	87.6(3)	96.1(2)	90.4(2)
N(4)−Ru(1)−N(5)	79.2(3)	78.6(2)	78.3(2)
N(4)−Ru(1)−N(6)	96.6(3)	96.4(2)	96.0(2)
Ru(1)−N(6)−C(26)	169.8(8)	120.0(3)	124.2(4)
N(6)−C(26)−C(27)	178.1(14)	124.1(4)	124.3(6)
Ru(1)−N(6)−C(30)		123.8(3)	120.3(4)
C(26)−N(6)−C(30)		116.1(4)	115.4(5)
N(6)−C(30)−C(29)		123.5(4)	123.3(6)
C(30)−C(29)−C(28)		119.9(4)	120.0(6)
C(26)−C(27)−C(28)		119.3(4)	120.0(6)
C(29)−C(28)−C(27)		117.0(4)	117.0(6)
C(29)−C(28)−C(31)		121.6(4)	121.4(6)
C(27)−C(28)−C(31)		121.4(4)	121.6(6)
C(28)−C(31)−C(32)		178.7(7)	178.9(8)
C(31)−C(32)−C(33)		179.8(5)	
C(32)−C(33)−C(34)		120.5(5)	
C(32)−C(33)−C(38)		121.7(6)	
C(38)−C(33)−C(34)		117.8(6)	
C(33)−C(38)−C(37)		121.5(7)	
C(33)−C(34)−C(35)		119.6(6)	
C(34)−C(35)−C(36)		120.3(7)	
C(35)−C(36)−C(37)		120.1(8)	
C(38)−C(37)−C(36)		120.8(8)	

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(71) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.

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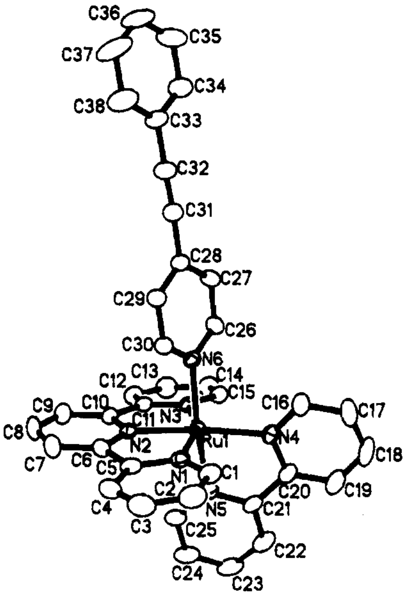

Figure 3. Thermal ellipsoid plot of Ru(tpy)(bpy)(PPA)$^{2+}$.

The X-ray crystal structures of the cations Ru(tpy)(bpy)(PA)$^{2+}$ and Ru(tpy)(bpy)(PPA)$^{2+}$ are illustrated in Figures 2 and 3, respectively. Atomic coordinates are listed in Tables 3 and 4, and selected bond angles and distances are given in Tables 5 and 6, respectively.

Like the CH_3CN complex, both acetylene structures show asymmetric bonding within the coordination sphere. In the PA complex, this bonding follows the same form as in the CH_3CN complex and matches very well with the complex Ru(tpy)(bpy)(py)$^{2+}$ previously reported by McMillin.[66] This shows that the addition of the acetylene group to the pyridine has little effect on the bonding of the other ligands within the coordination sphere.

The bonding of the Ru(tpy)(bpy)(PPA)$^{2+}$ complex differs considerably from that of the Ru(tpy)(bpy)(py)$^{2+}$ complex. Most noticeable is the distortion in the planarity of the terpyridine ligand. This is likely caused by a packing effect in which the terpyridine rings of neighboring cations overlap and then must bend out of plane to relieve steric crowding. The ring-to-ring distance of this packing is approximately 3.45 Å as compared to 3.55 Å in the [Ru(tpy)(bpy)(PA)]$^{2+}$ complex. This distortion of planarity pushes the terpyridine rings closer to the bpy ring *cis* to tpy and *trans* to the PPA ligand. Repulsion between these ligands could explain the atypical bonding of the bpy ligand in comparison to the other Ru(tpy)(bpy)L^{n+} complexes.[66,74,75] The Ru−N bonds of the bpy ligand are considerably longer, with the Ru−N bond of the bpy ring oriented *trans* to tpy lengthened to 2.103(4) Å in comparison to the normal Ru−N bond length (2.056(6) Å) observed in [Ru(bpy)$_3$](PF$_6$)$_2$,[78] possibly due to attempted reduction of this repulsion.

Table 7. Cyclic Voltammetric Data for Ruthenium Nitrile Complexes[a]

complex	$E_{1/2}$, V (ΔE, mV)[b]
[Ru(tpy)(bpy)(CH$_3$CN)](PF$_6$)$_2$	1.29 (90) −1.27 (90) −1.54 (120)
[Ru(tpy)(bpy)(CA)](PF$_6$)$_2$	1.29 (70) −1.29 (80) −1.52 (110)
[Ru(tpy)(bpy)(CPA)](PF$_6$)$_2$	1.31 (80) −1.28 (60) −1.59 (70)

[a] All potentials vs SCE. Data obtained from room-temperature CH_3CN solutions with 0.1 M TBAH as supporting electrolyte. [b] $E_{1/2} = (E_{ox} + E_{red})/2$; $\Delta E = E_{ox} - E_{red}$.

Table 8. Cyclic Voltammetric Data for Ruthenium Pyridyl Complexes[a]

complex	$E_{1/2}$, V (ΔE, mV)[b]
[Ru(tpy)(bpy)(py)](PF$_6$)$_2$	1.26 (80) −1.27 (100) −1.55 (120)
[Ru(tpy)(bpy)(PA)](PF$_6$)$_2$	1.26 (60) −1.25 (110) −1.52 (130)
[Ru(tpy)(bpy)(PPA)](PF$_6$)$_2$	1.24 (80) −1.26 (70) −1.57 (110) −1.79 (140)
[Ru(tpy)(bpy)(DPA)](PF$_6$)$_2$	1.26 (90) −1.25 (90) −1.47 (130) −1.77 (100)

[a] All potentials vs SCE. Data obtained from room-temperature CH_3CN solutions with 0.1 M TBAH as supporting electrolyte. [b] $E_{1/2} = (E_{ox} + E_{red})/2$; $\Delta E = E_{ox} - E_{red}$.

Tables 7 and 8 summarize the electrochemical data for the series of pyridyl- and nitrile-coordinated acetylene complexes. Electrochemically, we observe a single metal-centered oxidation in the positive potential region and successive ligand-based reductions in the negative potential region. These reductions correspond to the formation of radical anions as electrons are added to the π^* orbitals of the polypyridyl ligands.[25,79] Comparing these results with those of Ru(bpy)$_3{}^{2+}$,[35,42,43,68] Ru(tpy)$_2{}^{2+}$,[35] previous Ru(tpy)(bpy)L^{n+} complexes,[25,68] and with those for the reductions of the free ligands, we have assigned these observed electrochemical processes as follows:

$$\begin{array}{c}
[\mathrm{Ru^{III}(tpy)(bpy)L}]^{3+} \\
-1e^- \Updownarrow +1e^- \\
[\mathrm{Ru^{II}(tpy)(bpy)L}]^{2+} \\
-1e^- \Updownarrow +1e^- \\
[\mathrm{Ru^{II}(tpy^{\bullet-})(bpy)L}]^{+} \\
-1e^- \Updownarrow +1e^- \\
[\mathrm{Ru^{II}(tpy^{\bullet-})(bpy^{\bullet-})L}]^{0} \\
-1e^- \Updownarrow +1e^- \\
[\mathrm{Ru^{II}(tpy^{\bullet-})(bpy^{\bullet-})L^{\bullet-}}]^{1-}
\end{array}$$

Meyer and co-workers have also suggested that the tpy-based initial reduction is supported by comparison of the MLCT transition energies in the visible spectra of Ru^{II}−bpy and −tpy complexes, from which it seems the lowest π^* levels are in the order tpy < bpy.[25] The last process, the reduction of L, is only seen in the PPA and DPA complexes. In the other complexes, the reduction potentials of L are too negative to be observed within the solvent window.

Figure 4 displays the cyclic voltammogram of Ru(tpy)(bpy)(PPA)$^{2+}$. This complex exhibits a quasi-reversible ruthenium III/II oxidative couple with a half-wave potential of 1.26 V, in conjunction with three quasi-reversible ligand-based reductions with half-wave potentials of −1.26, −1.57, and −1.79 V.

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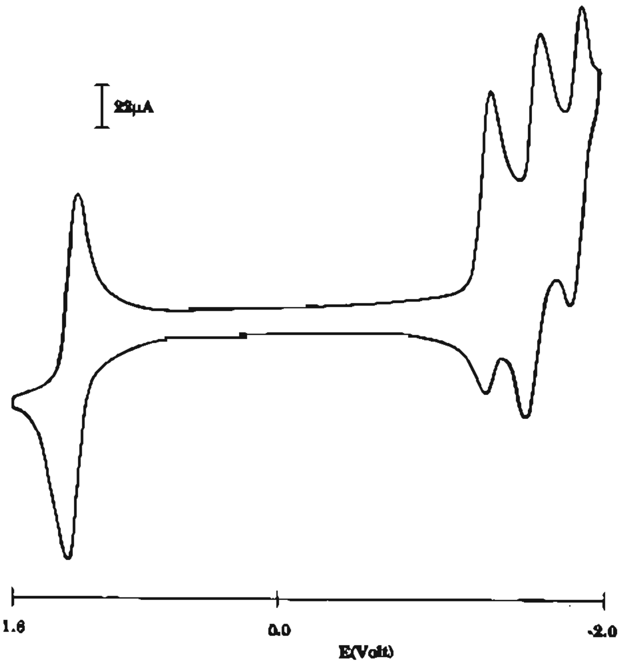
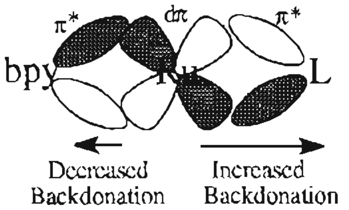


Figure 4. Cyclic voltammogram of Ru(tpy)(bpy)(PPA)$^{2+}$ in CH_3CN/0.1 TBAH.

In the complexes containing pyridyl-bound acetylenes, we observed a close similarity in the ruthenium oxidative potentials (all at approximately 1.26 V). Likewise, the tpy reductions are similarly spaced, exhibiting reductions at about −1.26 V. Of interest, though, is the scattering of the bpy reductions, ranging from −1.47 V in the DPA complex to −1.57 V in the PPA complex. The geometries of these complexes show that the changing monodentate ligands (L) are *trans* to one ring of the bipyridine ligand, while all three rings of the terpyridine are in a *cis* orientation with respect to L. Thus, bpy should feel any electronic variations due to the changing ligands (L) to a greater extent than tpy. As the π-electron-withdrawing nature of the monodentate in increased, there is a increased stabilization of Ru(II) and an increased effective nuclear charge. The extent of π-back-donation to the other ligands is then reduced, thus decreasing the destabilization of their π* orbitals.[80]



Therefore, as the π-withdrawing ability increases in the order PPA < py < PA < DPA, the bpy reduction decreases to less negative potential. With the small changes in the monodentate ligands, this stabilization is minor enough to only exhibit small decreases in the bpy reduction potentials, without any noticeable effect on the oxidation potentials of the metal or the reduction potentials of tpy.

In the nitrile series, we see similar results with both the Ru(III/II) and tpy couples remaining fairly constant. Because of the differing σ-donating/π-withdrawing abilities of the nitrile ligands compared to the pyridine ligands, the ruthenium oxidative couple has shifted to the more positive potential of 1.29 V. Again, the bpy reductions range from −1.54 V for the CH_3CN complex to −1.59 V for the CPA complex, following the trend seen in the pyridyl series. As π withdrawing increases in the order CPA < CH_3CN < CA, the bpy π* orbital is stabilized and the reductions shift to lower negative potential.

Table 9. Electronic Spectral Data for a Series of Ruthenium(II) Complexes Containing Monodentate Nitrile Ligands[a]

complex	λ_{max}^{abs}, nm	$10^{-3}\epsilon$, $M^{-1}\,cm^{-1}$	λ_{max}^{em}, nm	τ, ns
[Ru(tpy)(bpy)(CH_3CN)](PF_6)$_2$	240	22		
	286	42		
	306	37		
	455	11		
[Ru(tpy)(bpy)(CA)](PF6)$_2$	286	40	604	26
	307	37		
	453	9.5		
[Ru(tpy)(bpy)(CPA)](PF_6)$_2$	289	27	604	18
	309	23		
	456	6.0		

[a] Absorption spectra obtained from room-temperature CH_3CN solutions using matched 1 cm quartz cells. Room-temperature emission and lifetime data obtained from CH_2Cl_2 solutions, at an excitation of 459 nm.

Table 10. Electronic Spectral Data for a Series of Ruthenium(II) Complexes Containing Monodentate Pyridyl Ligands[a]

complex	λ_{max}^{abs}, nm	$10^{-3}\epsilon$, $M^{-1}\,cm^{-1}$	λ_{max}^{em}, nm	τ, ns
[Ru(tpy)(bpy)(py)](PF_6)$_2$	234	30	604	15
	282	30		
	311	34		
	415 (sh)	6.5		
	466	7.8		
[Ru(tpy)(bpy)(PA)](PF6)$_2$	240	35	604	19
	286	37		
	311	35		
	353 (sh)	8.8		
	422	9.6		
	464 (sh)	8.2		
[Ru(tpy)(bpy)(PPA)](PF_6)$_2$	290	54	604	22
	310	56		
	356	13		
	422	14		
	471 (sh)	10		
[Ru(tpy)(bpy)(DPA)](PF_6)$_2$	283	54	604	<30[b]
	308	36		
	373	9.8		
	426	14		
	473 (sh)	9.6		

[a] Absorption spectra obtained from room-temperature CH_3CN solutions using matched 1 cm quartz cells. Room-temperature emission and lifetime data obtained from CH_2Cl_2 solutions, at an excitation of 459 nm. [b] Estimated from fast-lived componant on decay trace.

Tables 9 and 10 summarize the electronic spectral data for the pyridyl- and nitrile-coordinated acetylene complexes, as well as the pyridine and acetonitrile complexes for comparison. The absorption spectra are dominated by intense ligand-based (π−π*) bands in the ultraviolet region, while charge-transfer bands are observed in the visible region of the spectrum. These lowest energy transitions in the nitrile complexes are similar in both shape and wavelength to that of the CH_3CN complex. In the pyridyl series, we see first a distinct peak at approximately 422 nm, followed by a shoulder at about 470 nm. This shoulder in the acetylene complexes corresponds well with the lowest energy transition of the pyridine complex at 466 nm. The pyridine complex also exhibits a weak shoulder at 415 nm, which corresponds well with the more intense transition of the acetylene complexes at 422 nm. McMillin and co-workers assign the shoulder at 415 nm in the pyridine complex as Ru^{II} → py MLCT, and they see enhancement of this transition when

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[80] Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1986**, *124*, 152.

a phenyl substituent is added to the *para* position of the py, due to conjugation with the aryl substituent.[66] With addition of the acetylene unit, this transition is enhanced to even a greater degree, making it more intense than the unresolved transitions to tpy and bpy at lower energy. The intensity of this transition is further enhanced by addition of phenyl or pyridyl substituents in the PPA and DPA complexes, presumably due to increased conjugation.[66,81] McMillin's assignment is also consistent with the visible spectrum of the protonated DPA complex. Upon protonation of the remote nitrogen of the DPA ligand with HPF_6, we see a red shift of this transition from 426 to 440 nm.

All of the complexes of both series, with the exception of the CH_3CN complex, show room-temperature emission in CH_2Cl_2 at approximately 604 nm and have lifetimes in the 15–30 ns range. Emission studies were carried out in CH_2Cl_2 due to a noticeable enhancement in the emission intensity, in comparison with the CH_3CN studies, and because of the noncoordinating properties of CH_2Cl_2, which minimizes the possibility of the photosubstitution observed in similar ruthenium polypyridyl complexes.[39,66,82,83] Photolysis of these complexes, though, showed no noticeable spectral changes in the presence of CH_3CN. Electrochemistry and detailed spectroscopic studies are consistent with the lowest excited state being assigned as a $Ru^{II} \rightarrow$ tpy MLCT excited state.[84] At 77 K, the emission intensity is increased and the low-temperature lifetimes are considerably longer than those recorded at room temperature, a property of Ru(II) polypyridyl complexes that has been widely documented.[37,43,50,85] Within each series, changing the sixth ligand site little affects the apparent emission maxima. Meyer and co-workers have shown that an expected feature of MLCT states is the correlation of E_{em} with $\Delta E_{1/2}$ (for these complexes, $\Delta E_{1/2} = E_{1/2}(Ru^{III/II}) - E_{1/2}(tpy^{0/-})$).[86] As shown in Tables 7 and 8, there is little change in the Ru and tpy electrochemical couples within each series, and the emission maxima would therefore be expected to be relatively invariant.

The complexes reported here have considerably enhanced lifetimes in comparison to $Ru(tpy)_2^{2+}$,[51,52] but these are still much shorter than the lifetime of $Ru(bpy)_3^{2+}$.[38-45] In the absence of temperature-dependent lifetime data, it is difficult to determine the extent of LF state intervention in the mono-tpy series considered here. Such LF state intervention, however, is expected to be less severe in this case, since the bpy and monodentate ligands are less geometrically strained.[39,56] The N–Ru–N angles in $Ru(tpy)_2^{2+}$ involving *trans* nitrogens are ~157°,[72] while the bpy and monodentate ligands in these complexes coordinate more favorably with a *trans* N–Ru–N angle of ~175°. This reduction in strain should result in an increased ligand field strength, decrease the $d\sigma^*-d\pi$ mixing, and destabilize the LF states, thus extending the lifetimes of these complexes.

Initially, we believed that the lifetime of the excited state of the $Ru(tpy)(bpy)(DPA)^{2+}$ ion was much longer lived and the emission intensity much greater than the others in the series. However, there was no indication in the electronic spectrum or the electrochemical studies that the DPA complex was different from the others in the series. Since the DPA ligand does contain a remote pyridyl nitrogen, we decided to look at the emission again in the presence of HPF_6, to see the effect of protonation of this pyridyl nitrogen on the observed emission maximum. What we observed was that protonation greatly red-shifted the MLCT transition in the visible spectrum but had no effect on the emission spectrum. From this observation and through comparison of the excitation spectra of the DPA complex and $Ru(bpy)_3^{2+}$, we concluded that the enhanced emission and extended lifetime were due to a small amount of $Ru(bpy)_3^{2+}$ not removed through repeated chromatography and recrystallization. Comparison of the emission intensities leads us to believe this impurity is less than 1.3%, which would be undetectable in the elemental analysis or characterization presented here. Close examination of the decay trace of this sample does show a fast-lived component with a lifetime of less than 30 ns, which we believe to be the true lifetime of the DPA complex.

Conclusion

Substituted acetylenic ligands bound through a pyridyl or a nitrile group to a $Ru(tpy)(bpy)^{2+}$ metal center can be prepared and characterized in the solution and solid states. The acetylenic function does very little to change the electronic and structural properties of the metal complexes, and the properties of these systems are similar to the non-acetylenic parent ions, $Ru(tpy)(bpy)(py)^{2+}$ and $Ru(tpy)(bpy)(CH_3CN)^{2+}$. The excited-state properties of the $Ru(tpy)(bpy)L^{2+}$ complexes lie between those of the parent $Ru(bpy)_3^{2+}$ and $Ru(tpy)_2^{2+}$ ions. The acetylenic compounds can now be used as monomeric starting materials in preparing metal-substituted polyacetylene complexes. The lack of perturbation of the acetylenic functionality on the properties of the ruthenium center suggests that the polymer will have ruthenium(II) centers with their typical excited-state properties close to the polymeric backbone.

Acknowledgment. The authors thank Dr. David Thompson for helpful discussions. J.D.P. and J.W.K. thank the Petroleum Research Fund, administered by the American Chemical Society, for support of the initial portions of this work. J.D.P. acknowledges partial support of the Office of Basic Energy Sciences, Department of Energy (Contract DE-FG09-87ER137568).

Supplementary Material Available: For $[Ru(tpy)(bpy)(CH_3CN)](PF_6)_2$, $[Ru(tpy)(bpy)(PA)](PF_6)_2\cdot(CH_3)_2CO$, and $[Ru(tpy)(bpy)(PPA)](PF_6)_2\cdot(CH_3)_2CO$, tables of complete cyrstallographic data, full bond lengths and angles, anisotropic displacement coefficients, and hydrogen atom parameters, as well as packing diagrams for the PA and PPA complexes (17 pages). Ordering information is given on any current masthead page.

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