

The implications of these data in the interpretation of cytochrome b_5 electron-transfer kinetics are currently being evaluated.

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Electrochemical and Spectral Investigations of Ring-Substituted Bipyridine Complexes of Ruthenium

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Abstract: A spectroelectrochemical study of a series of Ru complexes has been carried out by using an optically transparent thin-layer electrode (OTTLE). The visible spectra of the reduced complexes $\text{Ru}(\text{Bp5COOEt})_3^n$ ($\text{Bp5COOEt} = 5,5'$ -bis(ethoxycarbonyl)-2,2'-bipyridine) and $\text{Ru}(\text{bpy})_3^n$ ($\text{bpy} = \text{bipyridine}$) appear to resemble the spectra of the corresponding ligand radical anion whereas the spectrum of $\text{Ru}(\text{Bp4COOEt})_3^n$ ($\text{Bp4COOEt} = 4,4'$ -bis(ethoxycarbonyl)-2,2'-bipyridine) does not. In the near-IR two types of spectral behavior are observed once the complexes are reduced beyond the 2+ oxidation state: Type A complexes (e.g., $\text{Ru}(\text{bpy})_3$, $\text{Ru}(\text{Bp4Me})_3$ ($\text{Bp4Me} = 4,4'$ -dimethyl-2,2'-bipyridine)) exhibit low-intensity ($\epsilon < 2500$) bands which are similar to the spectra of the reduced free ligand. Type B complexes (e.g., $\text{Ru}(\text{Bp4COOEt})_3^n$, $\text{Ru}(\text{Bp4CONEt}_2)_3^n$ ($\text{Bp4CONEt}_2 = 4,4'$ -bis(diethylcarbonyl)-2,2'-bipyridine)) exhibit broad bands of greater intensity ($1000 < \epsilon < 15000$). Possible origins for type B behavior are discussed. Examination of electrochemical results reveals an almost perfect linear correlation when ligand reduction potentials are plotted against the 2+/1+ couple of the corresponding ruthenium complex (correlation coefficient = 0.9993). The thermodynamic implications of this observation are considered. Both the spectral and electrochemical data support a model of the reduced metal complex having electrons localized in ligand orbitals.

Bipyridine complexes of ruthenium possess several especially interesting chemical and spectral properties. For example, their strong visible absorptions, arising from a metal-to-ligand charge-transfer transition, produce a long-lived excited triplet capable of affecting important redox chemistry.^{1a-d} Also, the inertness of ruthenium to ligand substitution allows the redox chemistry of both the ground and excited state to be studied without complications from ligand exchange reactions.^{1a-d} Developing an understanding of the relationship between the detailed ligand structure and various kinetic and thermodynamic properties of the respective metal complexes is important if desirable properties of these metal complexes are to be optimized. The excited-state electron-transfer rates, the wavelength maximum of the charge-transfer absorption, and the redox potential are all examples of properties which are dependent on the exact nature of the ligand.

Herein we report the systematic spectral and electrochemical study of a variety of bipyridine ligands and their complexes, primarily with ruthenium. A series of substituted bipyridines were employed which differ in the position of substitution, the type of substitution, and reduction potential. The bipyridines most important to this study are shown in Figure 1. The results of our investigations reveal that modest changes in ligand substitution sometimes have dramatic effects on the spectral properties of the metal complexes.

Experimental Section

Equipment. The electrochemical and spectroelectrochemical equipment and cells have been described elsewhere.² Unless otherwise stated all potentials are reported with respect to SCE.

(1) (a) Meyer, T. J. *Acc. Chem. Res.* 1978, 11, 94 and references therein. (b) Sutin, N.; Creutz, C. *Pure Appl. Chem.* 1980, 52, 2717-2738 and references therein. (c) Whitten, D. G. *Acc. Chem. Res.* 1980, 13, 83 and references therein. (d) Balzani, V.; Bolleta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* 1978, 75, 1-64.

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Reagents. Acetonitrile and dimethylformamide (Burdick and Jackson Distilled in Glass) were used without further purification. Tetra-*n*-butylammonium hexafluorophosphate was used as supporting electrolyte.

Coulometry. Coulometric data used for calculating n values were obtained by one or both of the following methods: (1) bulk reduction in a three-compartment H-cell inside a nitrogen atmosphere box or (2) thin-layer coulometry on the reverse potential step (reoxidation) obtained in the optically transparent thin-layer electrode (OTTLE) cell. (Forward potential step data could not generally be used since the generation of highly charged species and the accompanying solution density change causes appreciable stirring at the edges of the OTTLE cell.)

Spectroelectrochemistry. Before each potential step a new solution was drawn into the OTTLE cell and a spectrum of the solution was taken at 0.0 V. The solution was then electrolyzed at the appropriate potential and a spectrum of the reduced species was recorded. After the reverse potential step a spectrum was taken of the reoxidized solution. All reduced species reported exhibit superimposable initial and final spectra, substantiating the chemical reversibility of the electron-transfer processes observed.

Preparation of Free Ligands and N-Alkylated Ligands. Structures and abbreviations of the ligands are shown in Figure 1.

(i) **4,4'-Dimethyl-2,2'-bipyridine (2).** This compound was prepared by the method described by Sasse and Whittle.³ The only modification was the distillation of the 4-picoline from KOH prior to use in the synthesis. Distillation of 100 mL of picoline in the presence of 3 g of KOH yields 80-90 mL of pyrrole-free picoline satisfactory for the bipyridine coupling reaction, mp 170-171 °C.

(ii) **4,4'-Dicarboxy-2,2'-bipyridine (3).** The diacid was obtained following the procedure of Sprintschnik et al.⁴ During the oxidation with potassium permanganate, the starting material steam-distilled into the reflux column. Yields were increased by washing the starting material back into the reaction mixture with permanganate solution. The potassium permanganate initially added to the reaction mixture plus the additional aliquots total approximately a 6-fold molar excess of permanganate.

(iii) **4,4'-Bis(ethoxycarbonyl)-2,2'-bipyridine (4).** Esterification of 3 was done in the presence of sulfuric acid in absolute ethanol. The solution

(3) Sasse, W. H. F.; Whittle, C. P. *J. Am. Chem. Soc.* 1961, 83, 1347.

(4) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* 1977, 99, 4947.

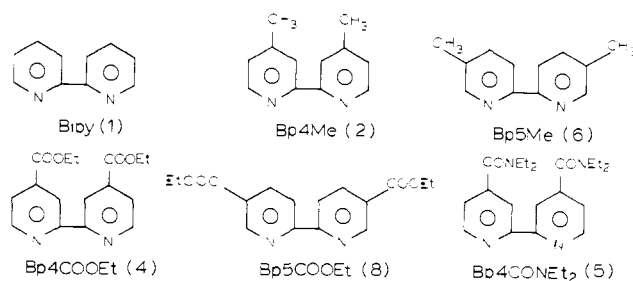


Figure 1. Structures and abbreviations of the bipyridine ligands.

was refluxed for 4 h. Ammonium hydroxide solution was added to the cooled solution until it become alkaline. The resulting white solid was recrystallized from ethanol, mp 157–159 °C.

(iv) **4,4'-Bis(*N,N*-diethylcarbamyl)-2,2'-bipyridine (5)**. **3** (0.5 g) was refluxed for 2 h in 4 mL of thionyl chloride. Excess thionyl chloride was removed by rotary evaporation. Excess diethylamine was added and the mixture was refluxed for 2 h. The solution was then evaporated to dryness. The residue, dissolved in a minimum of chloroform, was loaded on a silica column and eluted with acetone. Evaporation of the solvents yielded a light brown solid. Anal. Calcd for C₂₀H₂₆N₄O₂: C, 67.80; H, 7.34; N, 15.82. Found: C, 67.06; H, 7.24; N, 14.88. (The analysis results indicate the presence of some impurity in the free ligand.)

(v) **5,5'-Dimethyl-2,2'-bipyridine (6)**. This ligand was prepared the same way as **2** except 3-picoline was substituted for 4-picoline. Recrystallization yielded colorless crystals, mp 114–115 °C.

(vi) **5,5'-Dicarboxy-2,2'-bipyridine (7)**. Prepared in the same manner as **3**.

(vii) **5,5'-Bis(ethoxycarbonyl)-2,2'-bipyridine (8)**. Procedures used were the same as those used for the preparation of **4**, except diacid **7** was substituted for **3**. The reaction yielded a white crystalline powder, mp 148–149 °C.

(viii) **1,1'-Dimethyl-2,2'-bipyridinium Bis(hexafluorophosphate) (9)**. 2,2'-Bipyridine, **1** (1 g, Aldrich), 2 mL of ethanol, and 2 mL of methyl iodide were heated in a sealed tube at 90–100 °C for 1 day. After evaporation of the ethanol and excess methyl iodide, the residue was dissolved in water. Aqueous ammonium hexafluorophosphate was added and the white solid obtained was recrystallized from acetonitrile/propanol (1:1) solution.

(ix) **6,7-Dihydrodipyrido[1,2-*a*:2',1'-*c*]Pyrazinedilium Bis(hexafluorophosphate) (10)**, "Diquat". The dibromide salt was prepared as previously described.⁵ This solid was dissolved in a minimum amount of water and an aqueous solution of ammonium hexafluorophosphate was added to produce a white crystalline product.

Preparation of Metal Complexes. (i) **Ru(bpy)₃(PF₆)₂ (11)**. Ruthenium trichloride (0.5 g, Fisher) and 0.76 g of **1** were heated at reflux in 25 mL of DMF for 12 h. The solvent was evaporated under vacuum and the remaining solid was dissolved in a small amount of ethanol. After addition of an ethanol solution of ammonium hexafluorophosphate, the solution was cooled at 0 °C overnight. The orange solid was filtered and recrystallized from ethanol.

(ii) **Ru(Bp4Me)₃(PF₆)₂ (12)**. The complex was prepared following the same procedures used for **11**, substituting **2** for **1**.

(iii) **Ru(Bp5Me)₃(PF₆)₂ (13)**. The procedure followed was the same as that used for **11**, except ligand **6** was used.

(iv) **Ru(Bp4COOEt)₃(PF₆)₂ (14)**. Ruthenium trichloride (100 mg) and 290 mg of **4** were refluxed in ethanol for 2 weeks. An ethanol solution of ammonium hexafluorophosphate was added and the solution was cooled at 0 °C until crystals formed (several days). The final product is a bright red powdered solid. Anal. Calcd for C₄₈H₄₈N₆O₁₂RuP₂F₁₂: C, 44.62; H, 3.72; N, 6.51. Found: C, 44.30; H, 3.61; N, 6.47.

(v) **Ru(Bp4CONEt₂)₃(PF₆)₂ (15)**. Dichlorotetrakis(dimethyl sulfide)ruthenium(II)⁶ (0.10 g) and 0.29 g of **5** were heated at reflux in 10 mL of methanol for 2 h. The solvent was evaporated and the residue was dissolved in a minimum amount of water. An aqueous solution of ammonium hexafluorophosphate was added and the solution cooled until a brown solid formed (several days). Anal. Calcd for C₆₀H₇₈N₁₂O₆RuP₂F₁₂: C, 45.14; H, 4.89; N, 10.53. Found: C, 45.54; H, 5.03; N, 10.51.

(vi) **Ru(Bp5COOEt)₃(PF₆)₂ (16)**. Preparation of this complex is similar to that of **14** except that **8** was refluxed with ruthenium chloride. The final product is a brick-red solid. Anal. Calcd for

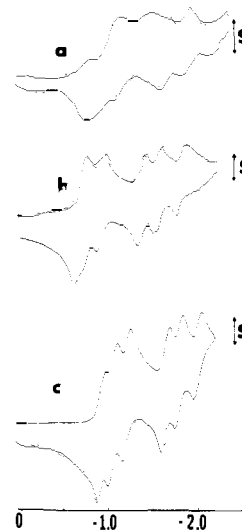


Figure 2. Cyclic voltammograms at a platinum electrode in 0.1 M TBAPF₆/DMF solutions: (a) 1.09×10^{-2} M Ru(Bp4COOEt)₃, $S = 10 \mu\text{A/in.}$, 200 mV/s; (b) 2.24×10^{-4} M Ru(Bp5COOEt)₃, $S = 2 \mu\text{A/in.}$, 200 mV/s; (c) 9.56×10^{-3} M Fe(Bp4COOEt)₃, $S = 10 \mu\text{A/in.}$, 200 mV/s at -25 °C. Both (a) and (b) were done at room temperature.

C₄₈H₄₈N₆O₁₂RuP₂F₁₂: C, 44.62; H, 3.72; N, 6.51. Found: C, 44.46; H, 3.36; N, 6.34.

(vii) **Ru((bpy)₂(Bp4COOH))(PF₆)₂ (17)**. Procedures used to prepare this complex have been described elsewhere.⁴ The starting material, *cis*-dichlorobis(bipyridine)ruthenium, was prepared following the method of Meyer et al.⁷

(viii) **Ru((bipy)₂(Bp4COOEt))(PF₆)₂ (18)**. *cis*-Dichlorobis(bipyridine)ruthenium and a 2-fold molar excess of ligand **4** were dissolved in ethanol. The mixture was heated at reflux for 5 h. The solution was evaporated to dryness and the residue dissolved in a minimum amount of chloroform. The sample was loaded on a neutral alumina column and eluted with a 4:1 chloroform/ethanol solution. The central portion of the orange band was collected and evaporated to dryness. The sample was redissolved in ethanol and an ethanol solution of ammonium hexafluorophosphate was added. The solution was cooled overnight at 0 °C. A red powder precipitated. Anal. Calcd for C₃₆H₃₂N₆O₄RuP₂F₁₂: C, 43.16; H, 3.20; N, 8.39. Found: C, 42.76; H, 2.69; N, 8.21.

(ix) **Fe(Bp4COOEt)₃(PF₆)₂ (19)**. Fe(ClO₄)₂·6H₂O (160 mg) dissolved in ethanol was combined with 400 mg of **4** dissolved in ethanol. The solution was heated gently for several minutes to completely dissolve the ligand. An aqueous solution of ammonium hexafluorophosphate was added and the resultant solution was cooled at 0 °C until crystals formed (1 day). Filtering the solution yielded a dark purple microcrystalline product. Anal. Calcd for C₄₈H₄₈N₆O₁₂FeP₂F₁₂: C, 46.3; H, 3.86; N, 6.75. Found: C, 43.17; H, 3.74; N, 6.31. Analysis results are consistently lower than expected by approximately 1% for C, N, and H. The presence of a small amount of decomposed iron salt could account for this result. Attempts to further purify the compound have not been successful, probably due to the labile nature of the complex formed. The structure was, however, confirmed with NMR spectroscopy and electrochemical results.

Results and Discussion

Electrochemistry. The redox properties of RuL₃²⁺ (L = a 2,2'-bipyridine) are in general characterized by a single, primarily metal-centered, oxidation occurring at a fairly positive potential, and a series of closely spaced, primarily ligand-centered, reductions occurring at fairly negative potentials.⁸ For simple bipyridine and alkyl bipyridine complexes of Ru(II), three reversible one-electron reductions are observable. One additional reduction can be observed at very negative potentials, but the formal RuL₃²⁻ species formed is unstable and fairly rapidly loses bpy⁻. The presence of certain electron-withdrawing substituents on the bipyridine rings has a profound stabilizing effect on low formal oxidation states in these ruthenium complexes.⁹ Consequently,

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(7) Sullivan, B. O.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* 1978, 17, 34.

(8) Saji, T.; Aoyagui, S. *J. Electroanal. Chem.* 1975, 58, 401.

Table I

entry	compd	$E_{1/2}(n_e)^a$ of redox couple, V						
		3+/2+	2+/1+	1+/0	0/1-	1-/2-	2-/3-	3-/4-
1	Ru(bpy) ₃ ⁿ	+1.24	-1.27 (1.10)	-1.46 (1.90)	-1.70 (3.14)			
2	Ru(Bp4COOEt) ₃ ⁿ	+1.54	-0.89 (1.3)	-1.01 (2.26)	-1.19 (3.40)	-1.63 (4.90)	-1.83	-2.15
3	Ru(Bp5COOEt) ₃ ⁿ	+1.53	-0.66 (0.96)	-0.75 (2.72)	-0.91 (3.60)	-1.37 (4.54)	-1.57 (4.92)	-1.82 (5.84)
4	Ru(Bp4Me) ₃ ⁿ	+1.13	-1.37 (1.30)	-1.54 (2.10)	-1.80 (3.12)			
5	Ru(Bp5Me) ₃ ⁿ	+1.15	-1.41	-1.59	-1.80			
6	Ru(Bp4CONEt ₂) ₃ ⁿ	+1.28	-1.12 (0.8)	-1.26 (1.94)	-1.43 (3.14)			
7	Ru(bpy) ₂ (Bp4COOEt) ⁿ	+1.38	-0.93	-1.36	-1.56	-1.90		
8	Fe(Bp4COOEt) ₃ ⁿ	+1.34	-0.91 (0.97)	-1.04	-1.19	-1.62	-1.77	-1.97

^a n_e is the total coulometrically determined number of electrons passed in converting from the formal 2+ oxidation state to the most reduced form of the couple indicated.

Table II

compd	$E_{1/2}$, V	
	first wave	second wave
bpy	-2.10	
Bp4Me	-2.20	
Bp5Me	-2.29	
Bp4COOEt	-1.60	
Bp5COOEt	-1.28	-1.67
Bp4CONEt ₂	-1.90	
diquat	-0.38	-0.78
<i>N,N'</i> -diMebipyridinium	-0.73	
4,4'-diMediquat	-0.48	-0.89
5,5'-diMediquat	-0.48	-0.90

several additional reductions can be observed (compared to the unsubstituted bipyridine complex). A similar effect is observed, but to a lesser degree, for analogous Fe(II) complexes, which are innately more labile. Figure 2 shows the room-temperature cyclic voltammograms (CV) of Ru(Bp5COOEt)₃²⁺, Ru(Bp4COOEt)₃²⁺, and the reduced temperature CV of Fe(Bp4COOEt)₃²⁺. In each case six reversible, chemically stable one-electron reductions are observed. Cyclic voltammogram $E_{1/2}$ potentials for these and all metal complexes considered in this study are listed in Table I. Table II gives the potentials of the corresponding free ligands and data for several *N,N'*-dialkylated bipyridinium cations.¹⁰

A major reason for studying the reductions of RuL₃²⁺ is that RuL₃¹⁺ is generally assumed to be electronically similar to the excited triplet, RuL₃^{2+*}, at least in that the highest energy electron in both species ostensibly resides in the same ligand-based π^* orbital.^{1d,11,12} The experimental evidence supporting this description are various spectral similarities between Ru(bpy)₃¹⁺ and Ru(bpy)₃^{2+*}.^{1d,11,12} Until recently^{13,22} the view has also prevailed that in both of these cases the HOMO is not localized on a single ligand but instead is delocalized over the entire set of three ligands.¹⁴⁻¹⁶ Several aspects of our work indicate that this picture is, however, not correct and that in fact the odd electron is almost completely localized on a single ligand. This is best illustrated by a comparison of the potential of the 2+/1+ couple for the three compounds: Ru(bpy)₃, Ru(Bp4COOEt)₃, and Ru((bpy)₂Bp4COOEt) given in Table I. First, it should be noted that the reduction potentials (Table II) of the two free ligands involved in these complexes differ by 0.50 V, with the unsubstituted bipyridine being the more difficult to reduce. Comparison of entries 2 and 7 in Table I reveal that these two complexes undergo

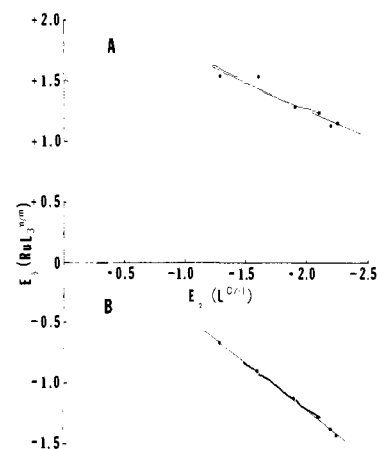


Figure 3. Plots of ligand reduction potential, $E_{1/2}(L^{0/1-})$ vs. the potential of a redox couple for the ruthenium complex, $E_{1/2}(RuL_3^{n/m})$: line A, $n/m = 3+/2+$ and line B, $n/m = 2+/1+$ (cf. Tables I and II).

reduction to the 1+ species at the same potential within experimental error. Furthermore, the second reduction of 7 occurs at (very nearly) the potential of the second reduction of 1. In the case of Ru((bpy)₂Bp4COOEt) the large difference in redox potential of the two ligands would naturally result in the electron being almost totally localized on the single Bp4COOEt ligand (a fact which has been confirmed by ourselves (vide infra) and independently by others.¹⁷) In the symmetrical complex, 2, one would expect that a substantial amount of electron delocalization would produce a first reduction potential significantly more positive than that observed for the localized case, 7. In fact, since the potentials are identical with one another within experimental error, one must deduce that the added electron is almost totally localized on a single ligand in both cases. Spectroscopic results and other electrochemical data presented later confirm the observation that RuL₃¹⁺ species, in general, can best be described with a single-ligand-localized orbital model.

Once delocalization is eliminated as a factor influencing the reduction potential of RuL₃²⁺, the remaining differences between the reduction potentials of the free and complexed ligands can be interpreted in terms of bonding between the metal and individual ligands. Correlations of various sorts have been drawn between the redox chemistry of electrochemically active ligands and their metal complexes.¹⁸ Because these are essentially free energy correlations, several theories have evolved in an effort to explain the experimental results. Previously reported correlations based on bipyridine complexes have been limited primarily to bipyridine and alkyl bipyridines which differ little in redox potential from one another (only 0.2 V).¹⁸ Consideration of the data in Tables I and II shows that the complexes in this study substantially extend the range of ligand reduction potentials. This data set provides a better experimental basis for evaluation of any possible free

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(10) The *N*-alkylated species are included in order to compare the effect of the presence of a positive charge in the compound without the mixing of *d* orbitals.

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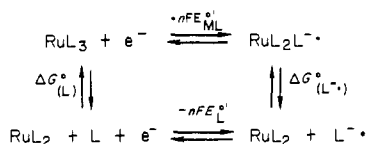
Table III

compd n (α_n)	λ_{\max} (ϵ), nm
Ru(bpy)₃ⁿ	
2+ (0.99+)	422 (12 000), 448 (14 000)
1+ (0.95)	465 (13 000), 494 (14 000), 519 (13 000), 782 (1100), 865 (1200), 988 (900)
0 (0.97)	503 (19 000), 537 (21 000), 782 (1700), 877 (1900), 1000 (1600)
1- (0.99+)	518 (20 000), 544 (21 000), 894 (2300), 994 (2300), 1211 (2000)
Ru(Bp4COOEt)₃ⁿ	
2+ (0.99+)	362 (24 000), 442 (21 000), 471 (25 000)
1+ (0.75)	373 (31 000), 456 (18 000), 501 (19 000), 538 (18 000), 1450 (1200)
0 (0.94)	427 (21 000), 501 (17 000), 541 (19 000), 1273 (3200), 1476 (4200)
1- (0.98)	350 (67 000), 467 (28 000), 515 (28 000), 1300 (7600), 1550 (9000)
2- (0.93)	353 (59 000), 465 (35 000), 1550 (15 000)
3- (0.93)	353 (48 000), 453 (42 000), 1550 (14 000)
4- (0.99+)	350 (45 000), 465 (46 000), 1158 (10 000), 1747 (10 000)
Ru(Bp5COOEt)₃ⁿ	
2+ (0.99+)	465 (8800), 505 (10 000)
1+ (0.71)	387 (19 000), 410 (26 000), 525 (12 000), 552 (12 000)
0 (0.76)	388 (37 000), 415 (53 000), 625 (30 000), 650 [sh] (27 000)
1- (0.99+)	394 (61 000), 416 (65 000), 668 (39 000)
2- (0.93)	400 (52 000), 419 (54 000), 464 (39 000), 510 (63 000), 688 (26 000)
3- (0.98)	363 (48 000), 422 (46 000), 521 (91 000)
4- (0.99+)	362 (41 000), 540 (110 000)
Ru(Bp4Me)₂ⁿ	
2+ (0.99+)	435 (12 000), 462 (13 000)
1+ (0.90)	374 (14 000), 432 (11 000), 462 (13 000), 541 (8400), 750 (1000), 829 (1000), 950 (940)
0 (0.91)	365 (23 000), 475 (13 000), 506 (15 000), 502 (14 000), 750 (1800), 829 (1800), 950 (1300)
1- (0.99+)	365 (33 000), 475 (13 000), 515 (17 000), 550 (18 000), 750 (2000), 850 (2000), 950 (1700), 1200 (1200)
Ru(Bp4CONEt₂)₃ⁿ	
2+ (0.99+)	435 (18 000), 459 (20 000)
1+ (0.88)	471 [sh] (27 000), 505 (19 000), 541 (17 000), 1050 (1800)
0 (0.93)	362 (40 000), 511 (19 000), 547 (20 000), 1050 (2300)
1- (0.90)	344 (67 000), 529 (24 000), 559 (23 000), 1350 (5900)

energy correlations that exist. Figure 3 presents plots of ligand reduction potential vs. the 3+/2+ (line A) and 2+/1+ (line B) couples for ruthenium complexes. For the primarily metal-based 3+/2+ couple (line A), the correlation is fairly crude (correlation coefficient = 0.9810). The ligand-based 2+/1+ reduction, on the other hand, correlates perfectly to within experimental error (correlation coefficient = 0.9993).

Several observations can immediately be drawn from these results. First of all, there is no significant discontinuity within the 2+/1+ series. It follows then that the single-ligand-localized description of the highest occupied molecular orbital must necessarily extend to all six RuL₃¹⁺ complexes used to construct the line. To postulate otherwise would require either a discontinuity or some curvature in the line.¹⁹

The nearly perfect linear correlation in Figure 3B, extending over such a wide potential range, allows for a quasi-thermodynamic interpretation that has implications with respect to the modes of metal-ligand bonding in the complexes. First, in each case studied, the reduction potential is more positive for the metal complex than for the free ligand. Postulating again no delocalization, the following thermochemical cycle can be constructed:



The horizontal steps correspond to the reduction of the metal-

bound ligand (top) and the free ligand (bottom) and the vertical processes correspond to the binding energy of the neutral ligand (left) and the ligand radical anion (right). There are several equivalent ways of considering the data of Figure 3B relative to this cycle. Again, the reduction potential of each complex is more positive than that of the free ligand. This must mean that in each complex, the reduced radical anion is a better ligand and thus bound more tightly than its neutral counterpart. This view is consistent with simple electrostatics and is qualitatively what would be expected if the mode of ligand-metal binding were primarily σ in nature (as it is in these complexes), i.e., the more electron-rich anionic ligand is the better ligand.

The slope of the line in Figure 3B is less than unity, and this fact provides some additional, more subtle insights into the detailed modes of binding in the complexes. The tendency for the various complexes to prefer to bind the reduced ligand, relative to the neutral ligand, decreases as the reduction potential of the ligand becomes more positive. This is the exact opposite of what would be expected from a simple σ bonding interaction. The reduction potential of the ligand becomes more positive as the pyridine rings become more electron deficient and thus less basic. It is important to realize, however, that the data in Figure 3B relate only to the relative binding of L and L⁻ not their absolute binding energy. In all likelihood the absolute binding energy is decreasing as E_L° increases.²⁰ What most likely is being reflected in the slope data of Figure 3B is a change in the relative importance of the σ and π back-bonding interactions. As the ligand becomes more electron deficient, it is less able to donate electron density to the metal though the nitrogen and more able to accept it into the π anti-bonding orbital of the ligand. While reducing the ligand will improve its σ donating abilities, it will likewise reduce its π back-bonding abilities. If the perturbations reflected in the relative

(19) This argument can be extended as follows: The data of Figure 3B is a straight line. The data point for Bp4COOEt is not an extremum within the domain. Since this data point corresponds to zero interligand delocalization (see discussion in text) the only way the line could be straight and the degree of delocalization be nonzero in the other complexes would be if the sign of the delocalization factor were to change as it passes through the Bp4COOEt point. Clearly a negative degree of delocalization has no meaning, therefore it must follow that the delocalization in the other complexes is zero as well.

(20) Ferrous ion, for example, apparently does not form a complex with Bp5COOEt in mixed acetone/H₂O solution, based on the absence of a observable purple color characteristics of intense absorption of the other FeL₃²⁺ complexes.

Table IV

compd <i>n</i>	λ_{\max} (ϵ), nm
bpy ^{<i>n</i>}	
1-	394 (5300), 550 (1600), 581 (1700), 750 (110), 844 (93), 1050 (59), 1229 (68)
2-	unstable
Bp4COOEt ^{<i>n</i>}	
1-	362 (4300), 818 (4500)
2-	unstable
Bp5COOEt ^{<i>n</i>}	
1-	417 (27 000), 437 [sh] (37 000), 450 (59 000), 476 (24 000), 700 [sh] (15 000), 765 (23 000), 811 [sh] (16 000), 900 (3700)
2-	494 (61 000), 529 (95 000)
Bp4Me ^{<i>n</i>}	
1-	392 (3400), 559 (1900), 591 (1900)
2-	unstable
diquat ^{<i>n</i>}	
1	382 (35 000), 433 (4000), 447 (3600), 465 (2600), 825 (3200)
0	382 (10 000), 517 (2700), 544 (2900)

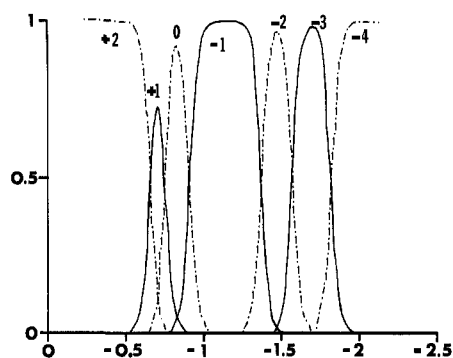


Figure 4. Plots of α_n , the fraction of $\text{Ru}(\text{Bp5COOEt})_3^n$ in a given oxidation state, vs. potential.

contributions of each type of binding to the total bond energy change as ligand reduction potential changes, the relative binding propensity of L and L^- will reflect this change.

Probably the most surprising aspect of the data presented in Figure 3B is the almost perfect linear correlation. This would imply that, while there are major chemical, structural, and steric differences in the various ligands studied, a very simple free energy correlation predominates. This is in clear contrast to the metal-centered process represented in Figure 3A. Here the potential, as would be expected, only roughly parallels that of the ligand.

Visible Spectra. Tables III and IV contain spectral data for selected examples of the metal complexes, ligands, and n -alkyl ligands in various formal oxidation states. Also included are the respective potentials at which each spectrum was obtained and the theoretical calculated fraction of the total present in the major oxidation state at that potential. This information is necessary because some $E_{1/2}$ values are quite close together, making it impossible to generate a solution containing a pure, single oxidation state. As an example, Figure 4 is a plot of α_n , the fraction of the total in oxidation state n , vs. the solution potential for $\text{Ru}(\text{Bp5COOEt})_3^n$. This particular system was chosen as an illustration of a "worst case". The calculated maximum attainable fraction for $n = \alpha_{1+}$ is not better than 0.75 (75%) because of the small separation between the potential for the $2+/1+$ and $1+/0$ redox couples (cf. Figure 1). In most other instances 90% or better is obtainable for the major oxidation state (cf. Table III). The question of actual solution composition is important from two standpoints. First, it has an obvious effect on the quality and accuracy of spectral data (e.g., λ_{\max} and ϵ values). Second, if two or more oxidation states are present in the same solution, intermolecular charge-transfer dimers could hypothetically exist. This second possibility must be carefully considered when attempting to assign low-energy spectral bands (vide infra).

The visible spectra for all seven formal oxidation states ($2+$ through $4-$) of $\text{Ru}(\text{Bp5COOEt})_3^n$ and $\text{Ru}(\text{Bp4COOEt})_3^n$ are presented in Figures 5 and 6, respectively. Spectra of the corresponding reduced free ligands appear in Figures 7 and 8. In

the $n = 2+$ oxidation state the spectra of both of these complexes are similar to that of $\text{Ru}(\text{bpy})_3^{2+}$; they contain a pair of overlapping metal-ligand charge-transfer (MLCT) bands between 450 and 500 nm and a high-energy (<350 nm) band assigned to a ligand-based $\pi \rightarrow \pi^*$ transition.^{21,22} Once reduced beyond the $2+$ oxidation state, however, the spectral similarities of these complexes abruptly end.

The spectral behavior of $\text{Ru}(\text{Bp5COOEt})_3^n$, shown in Figure 5, is similar in many ways to that of $\text{Ru}(\text{bpy})_3^n$ during the initial stages of reduction. As the first three reducing equivalents are introduced into the complex, new bands appear in the spectra which are similar in energy and relative intensity to those of the respective ligand radical anion. Notable also is the fact that, when $n = 1+$, a band ostensible due to the MLCT transition is still present in the spectrum. It is red shifted, reduced in intensity, and appears as a shoulder on the low-energy ligand band, but it is still clearly present in the spectrum. As the next two reducing equivalents are added, the bands resembling the ligand radical increase in intensity (roughly linearly with the number of electrons added) and all evidence of the MCLT disappears from the spectrum.

The three additional oxidation states that are accessible with $\text{Ru}(\text{Bp5COOEt})_3^n$ provide data which complement spectral data obtainable for $\text{Ru}(\text{bpy})_3^n$. Similarities between the ligand radical anion and $1 \leq n \leq -1$ spectra for the simple bipyridine complex have been noted previously.¹³ The smooth spectral transitions for $\text{Ru}(\text{Bp5COOEt})_3^n$ between $n = 2+$ and $4-$ are also consistent with residence by each of the added electrons in localized ligand orbitals over the entire range of accessible oxidation states.

The spectral behavior of the $\text{Ru}(\text{Bp4COOEt})_3^n$ system is interesting in contrast to that of the $\text{Ru}(\text{Bp5COOEt})_3^n$ system. The free ligand can be reduced in two successive one-electron processes, but only the first reduction is chemically reversible. Because of its instability the spectrum of the second reduction product could not be obtained even at reduced temperature. The ruthenium complex, however, is stable enough (on the time scale of thin-layer electrode experiment) to obtain spectra of all seven oxidation states ($n = 2+$ to $4-$). Surprisingly, spectra of reduced $\text{Ru}(\text{Bp4COOEt})_3^n$ (Figure 5) bear little or no resemblance either to the reduced ligand (Figure 8) or to the reduced $\text{Ru}(\text{Bp5COOEt})_3^n$ complex. A complicated region of overlapping bands between 400 and 500 nm tends to grow and change shape in a relatively smooth fashion over the course of six electron reduction steps. A high-energy (350 nm) band first grows in and then disappears again reaching a maximum intensity when $n = -1$. The visible spectra of the $\text{Ru}(\text{Bp4COOEt})_3^n$ complexes are unique among those ruthenium complexes that we have studied in any detail. It is the only case where there is no resemblance between the reduced ligand and the reduced metal complex.

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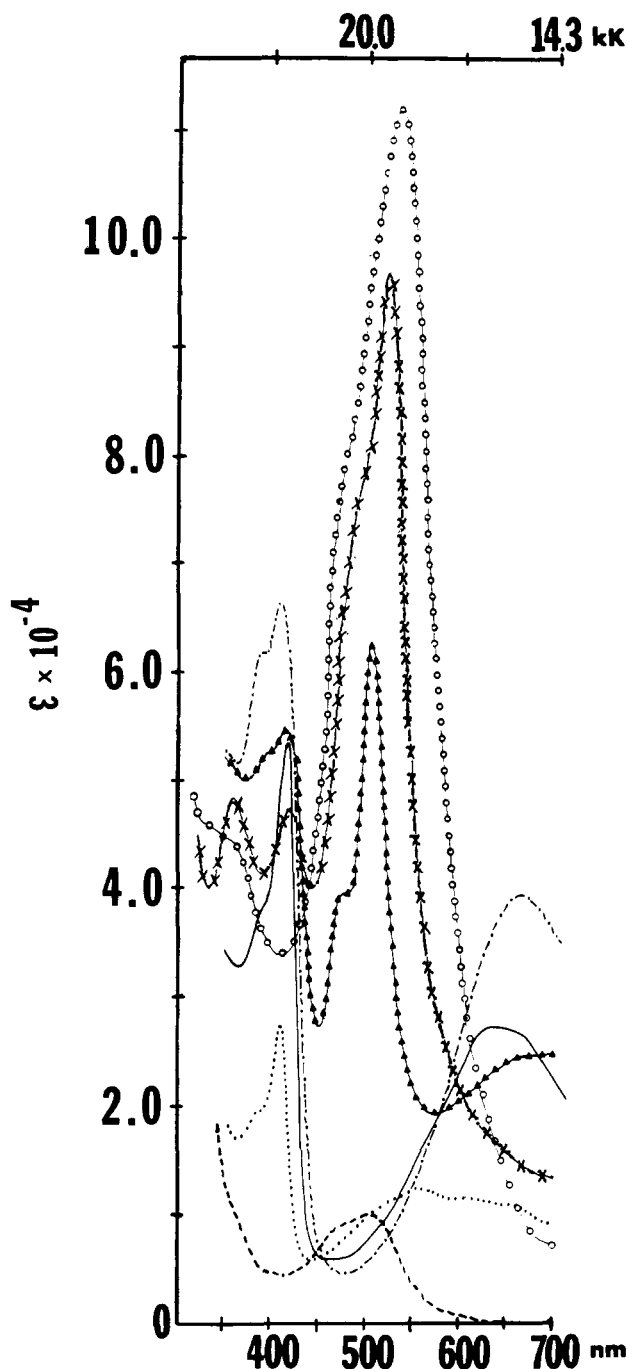


Figure 5. Visible spectra of $\text{Ru}(\text{Bp5COOEt})_3^n$ in DMF with 0.1 M TBAPF_6 measured in a 5.4×10^{-3} cm OTTLE cell, $n = 2+$, $---$; $1+$, \cdots ; 0 , $—$; $1-$, $---$; $2-$, $\blacktriangle-\blacktriangle-\blacktriangle$; $3-$, $\times-\times-\times$; $4-$, $\text{O}-\text{O}-\text{O}$.

Spectral differences as pronounced as those observed between $\text{Ru}(\text{Bp5COOEt})_3^n$ and $\text{Ru}(\text{Bp4COOEt})_3^4$ are especially surprising. For compounds that seem otherwise quite similar, more subtle differences might have been expected.

Near-Infrared Spectra. Spectral differences among these compounds is not limited to the visible region. The near-infrared spectra of all compounds presented in Table I were examined in each accessible, stable oxidation state. There were no observable ($\epsilon > 50$) near-IR transitions ($\lambda > 800$ nm) in either the $2+$ or $3+$ formal oxidation states for any of the compounds studied. However, when reduced beyond the $2+$ oxidation state ($n < 2$), there are, generally, concentration-independent low-energy transitions present. On the basis of the shape, intensity, and λ_{max} of these bands, we have chosen to divide the compounds into two functionally defined classes: type A, which are characterized by relatively low-intensity ($\epsilon < 2500$) highly structured bands which tail down into the near-IR from the visible region, and type B,

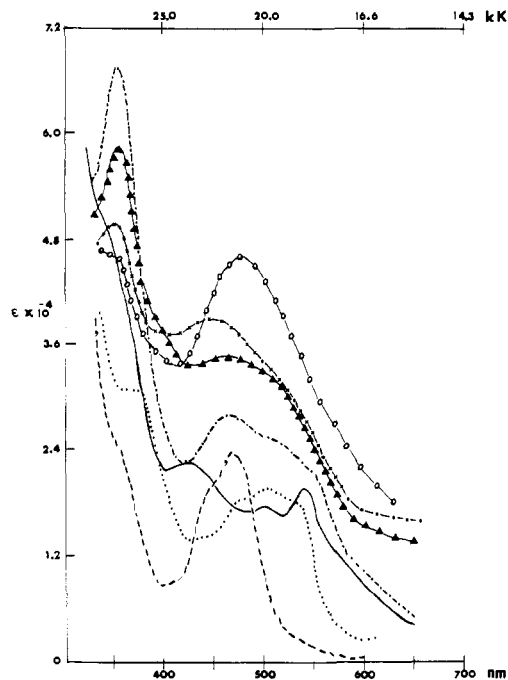


Figure 6. Visible spectra of $\text{Ru}(\text{Bp4COOEt})_3^n$ in DMF with 0.1 M TBAPF_6 measured in a 5.4×10^{-3} cm OTTLE cell, $n = 2+$, $---$; $1+$, \cdots ; 0 , $—$; $1-$, $---$; $2-$, $\blacktriangle-\blacktriangle-\blacktriangle$; $3-$, $\times-\times-\times$; $4-$, $\text{O}-\text{O}-\text{O}$.

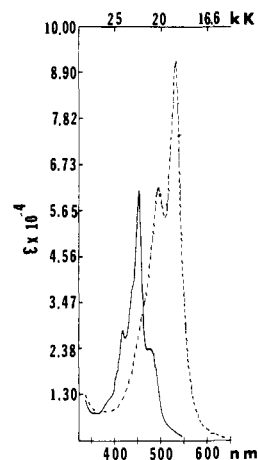


Figure 7. Visible spectra of $(\text{Bp5COOEt})_3^n$ in DMF with 0.1 M TBAPF_6 measured in a 5.4×10^{-3} cm OTTLE cell, $n = 1-$, $---$; $2-$, $---$.

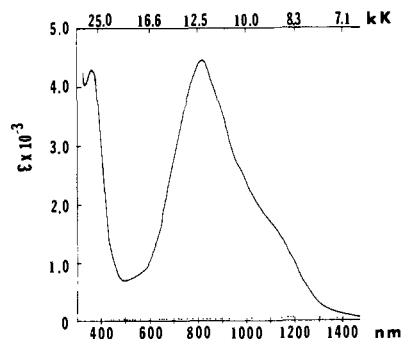


Figure 8. Visible and near-IR spectra of $(\text{Bp4COOEt})_3^n$ in DMF with 0.1 M TBAPF_6 measured in a 5.4×10^{-3} cm OTTLE cell, $n = 0$, \cdots ; $1-$, $---$.

which are very broad, lower energy bands with generally very large extinction coefficients ($1000 < \epsilon < 15000$). Figure 9 presents two examples of each type of spectrum. With a single exception, namely $\text{Ru}(\text{Bp5COOEt})_3^n$, some transition below 800 nm has been observed for every metal complex studied. Reduced type A

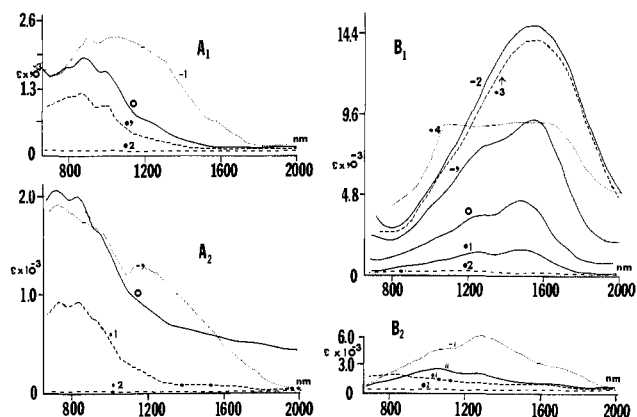


Figure 9. Near-IR spectra in DMF with 0.1 M TBAPF₆: (A₁) Ru(bpy)₃ⁿ; (A₂) Ru(Bp4Me)₃ⁿ; (B₁) Ru(Bp4COOEt)₃ⁿ; (B₂) Ru(Bp4CONEt₂)₃ⁿ. Spectra A₁ were measured in 0.1-cm cell after bulk electrolysis in an inert atmosphere box. A₂, B₁, and B₂ were measured in a 5.4 × 10⁻³ cm OTTLE cell.

complexes produce near-IR spectra that closely resemble the spectrum of the corresponding ligand radical anion. The near-IR spectra of type B complexes, on the other hand, differ from those of the reduced free ligand. The transitions above 800 nm in reduced Ru(bpy)₃ⁿ (a type A complex by our definition) have been assigned previously to simple electronic excitations of ligand which tail down to low energies.¹³ We agree with this assignment and propose that it is appropriate for all of the complexes in this study that exhibit type A behavior. The origin of the fine structure in these bands is very likely vibrational in nature. The transitions in type B systems, on the other hand, appear to be quite different. Their energy maximum, width, and absorbance intensity suggest origins other than those proposed for type A complexes.

Of those complexes studied only four fit into the type B category: Ru(Bp4COOEt)₃ⁿ, Fe(Bp4COOEt)₃ⁿ, Ru(Bp4CONEt₂)₃ⁿ, and Ru((bpy)₂(Bp4COOEt))ⁿ. The presence in the complex of at least one of either a 4,4'-bis(ethoxycarbonyl) or 4,4'-bis(*N,N*-diethylcarbamyl)bipyridine seems to be sufficient to produce type B behavior. Several facts are conspicuous. First, since very similar behavior is observed for both iron and ruthenium complexes of 4,4'-bis(ethoxycarbonyl)bipyridine, the transitions are almost certainly ligand based. Second, the transitions are observed only in the metal complexes not in the reduced free ligand; at least they are not observable at energies similar to those found for the metal complexes. Third, substitution in the pseudopara positions seems to be essential to producing the behavior. Finally, the type of substitution is also important, since complexes containing either 4,4'-dimethylbipyridine or 4,4'-dicarboxylate ion bipyridine are type A.

When we first observed these low-energy bands in Ru(Bp4COOEt)₃ⁿ, we suggested that the transitions might be an interligand charge-transfer process⁹ where the electron could be thought of as "hopping" between the localized ligand π* orbitals within the complex. The present results show that this interpretation is clearly incorrect. Careful examination of Figure 9B shows that while the extinction coefficient at λ_{max} increases linearly with the first two reducing electrons, as would be expected if the transition were interligand in nature, it also increases after the third electron is added. Our original model would predict, at the very least, a major shift in the band energy when the third electron is added since now the excitation process would require double electron occupancy of a ligand π* orbital. Equally damning to this interpretation are the spectral results obtained for the mixed complex, Ru((bpy)₂(Bp4COOEt))ⁿ. Reduction by one electron produces a species having a near-IR spectrum that is, within experimental error, identical with that of Ru(Bp4COOEt)₃ⁿ. With the second reduction of the mixed ligand complex (to *n* = 0) virtually no change in the low energy spectrum is observed. These two observations leave little doubt that the transitions must be almost exclusively intraligand in nature (i.e., the electrons involved in an individual transition are localized on a single ligand although

transitions in more than one ligand are likely contributing to the intensity when *n* = 0 or -1).

Type B behavior could have at least two reasonable origins. On one hand, the transitions could simply be between closely spaced orbitals with accidental near degeneracy (e.g., π₁* → π₂* or π₁* → *n*, etc.).²³ The difficulty with this interpretation lies in explaining the absence of an energetically similar transition in the reduced free ligand. It also seems rather coincidental that groups as electronically different as COOEt and CONEt₂ (as is evident by the difference in the redox potentials of the ligands, cf. Table II) should have such similar spectral transitions that differ in energy by only about 1000 cm⁻¹.

An alternate possibility for the origin of these transitions is that they are effectively intraligand charge-transfer processes. If for the anion the HOMO and LUMO of the bound ligands are localized to a significant extent on the carboxyl functions, one could conceive of a transition occurring between the plus and minus combination of carbonyl π* type orbitals. The separation between such orbitals would depend largely on the degree of interaction between the carbonyls, which would, in turn, be dependent on the relative orientation of the carbonyls with respect to each other and their orientation with respect to the bipyridine plane. This argument is exactly analogous to the one appropriate for the intervalence charge-transfer transition in the Ru²⁺-Ru³⁺ Creutz and Taube ion²⁴ except that in the former case the transition is between combinations of π* orbitals and in the latter it is between combinations of d orbitals.

Finally, the intraligand charge-transfer picture is consistent with the absence of analogous transitions in the reduced free ligand and Ru(Bp5COOEt)₃⁺ complex. First, the lack of steric constraint in the free reduced ligand (Bp4COOEt⁻) undoubtedly could alter the modes of interaction of the carbonyls. For the Bp5COOEt complex, examination of models clearly reveals very different (compared to the Bp4COOEt complex) steric factors with respect to the ester function. Additionally, the different substitution position alone should have a major influence on the bipyridine π systems ability to mediate electronic interaction between the two ester groups. This should affect the orbital separation (which should be smaller) and the oscillator strength of the transition (which should be weakened).

On the basis of available data, however, neither of these explanations can be discounted. Nonetheless, the spectral behavior of type B complexes is unusual. Whatever the exact origin of the low-energy transition in complexes of this type, both the functional identity and position of substitution on the bipyridine ring are critical for producing them.

Summary

In the series of bipyridine complexes studied, spectral differences for the formal 2+ oxidation state are relatively subtle. Changes in the energy of the charge-transfer bands as a function of bipyridine ligand (for a given metal) are moderate to small. Once the complex is reduced beyond the 2+ oxidation state, the situation is quite different. Within the limits that the excited-state triplet and the formal 1+ oxidation state can be considered to be energetically similar, these ligand-dependent spectral differences could have profound importance. In other words, while the excitation process (MLCT) appears to be roughly similar in energy and, to a lesser extent, oscillator strength for all of the complexes, the triplet states, once produced, may be chemically different. Altering the ligand structure could potentially produce desirable chemical properties without significantly altering the primary photochemical properties (i.e., λ_{max} and ε).

Finally, the spectral and electrochemical data obtained here are uniformly consistent with a model of reduced metal complex having the electrons localized in individual ligand orbitals. Given the structural and spectral differences within the series of com-

(23) We carried out extended Hückel calculations on several of the systems considered herein. With respect to the low energy transitions, in particular, there was no correlation between the experimental data and calculated results either for energies or oscillator strengths.

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pounds studied, the degree of correlation between the first reduction potential of the ligand and that of the metal complex is impressive.

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Registry No. 2, 1134-35-6; 3, 6813-38-3; 4, 1762-42-1; 5, 83605-42-9; 6, 1762-34-1; 7, 1802-30-8; 8, 1762-46-5; 9, 83605-43-0; 10, 67994-94-9; 11, 60804-74-2; 12, 83605-44-1; 13, 83605-45-2; 14, 75324-94-6; 15, 83605-47-4; 16, 83605-48-5; 17, 64189-98-6; 18, 83605-49-6; 19, 83605-83-8; Ru(Bp5COOEt)₃³⁺, 83605-50-9; Ru(Bp5COOEt)₃⁴⁺, 83605-51-0; Ru(Bp4Me)₃³⁺, 47837-95-6; Ru(Bp4Me)₃⁴⁺, 65605-26-7; Ru(Bp4Me)₃, 83605-52-1; Ru(Bp4Me)₃⁻, 83605-53-2; Ru(Bp5Me)₃³⁺, 47837-83-2; Bpy, 37275-48-2; Ru(Bp5Me)₃⁺, 83605-54-3; Ru(Bp5Me)₃,

83605-55-4; Ru(Bp5Me)₃⁻, 83605-56-5; Ru(Bp4CONEt₂)₃³⁺, 83615-44-5; 4,4'-diMediquat, 16651-71-1; Ru(Bp4CONEt₂)₃⁺, 83605-57-6; Ru(Bp4CONEt₂)₃, 83605-58-7; Ru(Bp4CONEt₂)₃⁻, 83605-59-8; Ru((bpy)₂Bp4COOEt)₃³⁺, 83605-60-1; Ru((bpy)₂Bp4COOEt)₃⁺, 83605-61-2; Ru((bpy)₂Bp4COOEt), 83605-62-3; Ru((bpy)₂Bp4COOEt)₃⁻, 83605-63-4; Ru((bpy)₂Bp4COOEt)₃²⁻, 83605-64-5; Fe(Bp4COOEt)₃³⁺, 83605-65-6; Fe(Bp4COOEt)₃⁺, 83605-66-7; Fe(Bp4COOEt)₃, 83605-67-8; Fe(Bp4COOEt)₃⁻, 83605-68-9; Fe(Bp4COOEt)₃²⁻, 83605-69-0; Fe(Bp4COOEt)₃³⁻, 83605-70-3; Fe(Bp4COOEt)₃⁴⁻, 83605-71-4; Ru((bpy)₃)³⁺, 18955-01-6; Ru((bpy)₃)⁺, 56977-24-3; Ru((bpy)₃), 74391-32-5; Ru((bpy)₃)⁻, 56977-23-2; Ru(Bp4COOEt)₃³⁺, 83605-72-5; Ru(Bp4COOEt)₃⁺, 83605-73-6; Ru(Bp4COOEt)₃, 83605-74-7; Ru(Bp4COOEt)₃⁻, 83605-75-8; Ru(Bp4COOEt)₃²⁻, 83605-76-9; Ru(Bp4COOEt)₃³⁻, 83605-77-0; Ru(Bp4COOEt)₃⁴⁻, 83605-78-1; Ru(Bp5COOEt)₃³⁺, 83615-45-6; Ru(Bp5COOEt)₃⁺, 79374-05-3; Ru(B5COOEt)₃, 83605-79-2; Ru(Bp5COOEt)₃⁻, 83605-80-5; Ru(Bp5COOEt)₃²⁻, 83605-81-6; 5,5'-diMediquat, 16651-72-2; diethylamine, 109-89-7; 3-picoline, 108-99-6; 4-picoline, 108-89-4.

Photophysical and Photochemical Behavior of Tetrahydridobis(bis(1,2-diphenylphosphino)ethane)-molybdenum and -tungsten: Optical Emission and Photoreduction of Alkenes

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Abstract: The complexes H₄M(DPPE)₂ and D₄M(DPPE)₂ (M = Mo, W; DPPE = bis(1,2-diphenylphosphino)ethane) exhibit emission of visible light upon photoexcitation at 77 K in 2-methyltetrahydrofuran. The emission lifetime at 77 K for the W species (~13 μs) is shorter than for the Mo species (~90 μs) and is independent of whether the substance is the ¹H or ²H species. The shorter lifetime for the W species is consistent with an emissive triplet state that is antibonding with respect to M-H₂ interactions, since the solution photochemistry at 298 K is dominated by H₂ loss. While the lifetime of the ¹H and ²H species is the same, the quantum yield for emission for M = Mo is higher for the ²H species (0.28) than for the ¹H species (0.21). The data are consistent with an effect from ²H that diminishes nonradiative decay from the singlet excited state reached by direct absorption. This diminished nonradiative decay allows intersystem crossing to be more competitive, yielding the emissive triplet with higher efficiency. Irradiation of the H₄M(DPPE)₂ species in the presence of an alkene (e.g., 1-pentene, *cis*-2-pentene, 3,3-dimethyl-1-pentene, cyclopentene) results in stoichiometric reduction to form an alkane; i.e., each H₄M(DPPE)₂ molecule yields two molecules of alkane. Irradiation of H₄M(DPPE)₂ in the presence of alkene and 10 psi of H₂ yields photoassisted alkane formation, yielding many alkane molecules per H₄M(DPPE)₂ initially present, as illustrated with the reduction of 1-pentene. The intriguing finding concerning the photoreduction of 1-pentene or *cis*-2-pentene is that the reduction occurs without detectable isomerization to *cis*- and *trans*-2-pentene or 1- and *trans*-2-pentene, respectively, an unprecedented result for such photoassisted alkene reactions using polyhydride precursors.

While studying the photophysical properties of H₄Re₄(CO)₁₂,² we discovered that H₄W(DPPE)₂ (DPPE = bis(1,2-diphenylphosphino)ethane) and H₄Mo(DPPE)₂ exhibit visible light emission when excited by ultraviolet or high-energy visible light. This afforded us an opportunity to further examine the effect of replacing ¹H with ²H on the excited-state decay properties of transition-metal hydride complexes. As in earlier studies of hydrogen isotope effects on the excited-state decay of organic molecules and inorganic complexes,²⁻⁴ the importance of these

studies rests in the fact that replacement of ¹H by ²H results in little change in the electronic structure or geometry of the molecules while the vibrational energies are altered significantly. Thus, the importance of high-energy vibrations on the rates of nonradiative excited-state decay can be probed by replacing ¹H with ²H.

Often, the highest energy vibrations are found to be important in nonradiative decay, but for metal complexes where the excited

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