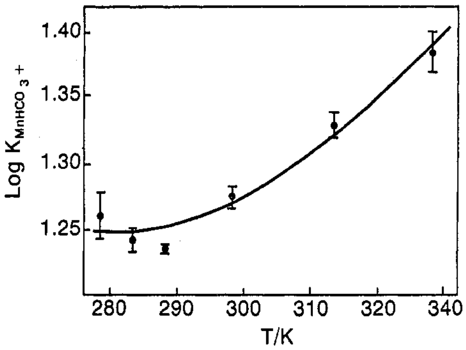

Figure 1. Log *K* formation of $MnHCO_3^+$ vs. temperature in Kelvin. Solid line represents the equation $\log K = -80.629 + 28.405 \log T + 3462.5/T$.

estimates of $\Delta G°$, $\Delta H°$, and $\Delta C_p°$ while requiring only three parameters.

The thermodynamic data listed in Tables III–V for the manganese bicarbonate species indicate that eq 4 is an endothermic reaction made possible by favorable entropy changes.

$$Mn^{2+}(aq) + HCO_3^-(aq) = MnHCO_3^+(aq) \qquad (4)$$

It should be pointed out that there is nothing in the thermodynamic data to indicate the type of ion pairing, inner or outer sphere, present in the manganese bicarbonate species.

Previous research[3,4] indicated that purely electrostatic bonding predominated in the $CaHCO_3^+$ and $MgHCO_3^+$ ion pairs. Purely electrostatic bonding can be expected to predominate in ion pairs formed from cations with a noble gas configuration such as Ca^{2+} or Mg^{2+}. However, cations such as Mn^{2+} or Zn^{2+} which have a half-filled and filled d subshell, respectively, are more polarizable than Ca^{2+} or Mg^{2+} and are more apt to form ion pairs which have some covalent character.

The work of ion pair formation may be regarded as consisting of two parts: W_{env} representing long range electrostatic forces dependent upon environment and increasing with temperature, and W_{non} representing short-range or quantum mechanical forces, insensitive to environment and independent of temperature.[10] The factors that determine the magnitudes of W_{env} and W_{non} are quite separate and independent, and there is no reason why a small W_{non} should not be accompanied by a large W_{env} or a large W_{non} accompanied by a small W_{env}.[11]

If W_{env} is zero or near zero, then the ion pair behavior should be described by W_{non} and thus be independent of temperature. This is clearly not the case in the present study. Gurney[11] has shown that the term W_{env} can be considered to be almost entirely electrostatic in nature and may be represented by W_{el} which is proportional to the dielectric constant, ϵ, of the solvent. If we now consider the case of pure electrostatic forces, that is $W_{non} = 0$, the values of log *K* would lie on a curve passing through a minimum at 219 K, the characteristic constant for water. Analysis of the experimental data via eq 1 indicates a minimum at 277 K.

Therefore, the behavior or the $MnHCO_3^+$ ion pair cannot be fully described by simple electrostatic interactions. Gurney[11] found that the addition of a nonelectrostatic contribution W_{non} to W_{el} will shift the position of the minimum to a higher temperature, that is to say, toward room temperature. With this as a criterion, it can be said that the bonding in the $MnHCO_3^+$ ion pair is a composite of both electrostatic and nonelectrostatic interactions.

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Registry No. $MnHCO_3^+$, 68013-64-9.

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Mixed Phosphine 2,2′-Bipyridine Complexes of Ruthenium

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Two types of mixed complex, e.g., $[(bpy)_2Ru(PPh_3)Cl^+]$ and $[(bpy)_2Ru(Ph_2PCH_2PPh_2)]^{2+}$, have been prepared from the appropriate group 5 ligand and $(bpy)_2RuCl_2$ (bpy = 2,2′-bipyridine). A complete study of the electronic spectral and redox properties indicates that phosphorus ligands stabilize the Ru(II) forms of these ions to a greater extent than pyridine-type ligands, which is consistent with the greater π-acid nature of the tertiary phosphine ligands. The impressive chemical stability and high reduction potentials for the Ru(III) form of these ions in acetonitrile solution make them ideal candidates as stoichiometric oxidants in inorganic or organic syntheses.

In the known mono- and diphosphine, -arsine, and -stibine complexes of ruthenium, the remaining ligands in the inner coordination sphere are usually the strong π-acid ligands of organometallic chemistry, i.e., CO, NO, phosphine, arsine, and unsaturated hydrocarbons,[1] or the hydride ligand.[2,3] Considerably fewer complexes have been reported which contain both group 5 ligands and ligands like NH_3, 2,2′-bpy or 1,10-phen which are more normally associated with classical coordination complexes. Complexes of the latter kind which have been reported, e.g., $[Ru_2Cl_2(P(C_6H_5)_3)_4(bpy)_2]Cl_2$,[4] *mer*-$(bpy)Ru(P)Cl_3$ ($P = P(C_6H_5)_3$),[5] and $(bpy)_2Ru(P)Cl^+$ [5] ($P = P(C_6H_5)_3$, $As(C_6H_5)_3$), have been prepared by the displacement of ligands from *trans*-P_3RuCl_2 or *trans*-P_4RuCl_2.

We describe here the preparations of mono- and bis-substituted complexes of the types $(bpy)_2Ru(P)Cl^+$ and $(bpy)_2RuP_2^{2+}$ (where P is tertiary phosphine, arsine or stibine) which are based on the known chemistry of *cis*-$(bpy)_2RuCl_2$ developed previously by ourselves[6,7] and by Dwyer and his co-workers.[8,9] There is by now a considerable synthetic chemistry of bis(bipyridyl)ruthenium(II) complexes, and electrochemical and spectral studies have given insight into the nature of the Ru(II)–ligand bond. One of the goals of this

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work was to use the $(bpy)_2Ru$ chemical system and the results of spectral and electrochemical studies to obtain information about the nature of the Ru–group 5 ligand bond. A second was to develop a synthetic chemistry which would provide the basis for a series of di(tertiary phosphine)-bridged Ru–Ru dimers. In past experiments, using the mixed-valence dimers $[(bpy)_2ClRu(L)RuCl(bpy)_2]^{3+}$ (L is pyrazine, 4,4′-bpy, and *trans*-$NC_5H_4CH{=}CHC_5H_4N$) it has been possible to demonstrate the presence of localized valences and to verify the Hush treatment for optical electron transfer in localized valence, mixed-valence complexes.[10–12] Given the background information available, it should be possible to use dimeric mixed-valence systems based on $(bpy)_2ClRu$ as a probe to investigate the role of bridging ligand on the extent of metal–metal interaction.

Experimental Section

Measurements. Ultraviolet, visible, and near-infrared spectra were recorded using either a Cary Model 14 or Bausch and Lomb Model 210 spectrophotometer. Molar extinction coefficients were obtained from absorbance measurements on at least two different concentrations of complex. Proton NMR spectra were determined with a 100-MHz Varian Fourier transform spectrometer with Me_4Si as an internal standard. Electrochemical measurements were made vs. the saturated sodium chloride calomel electrode (ssce) at 25 ± 2 °C and are uncorrected for junction potential effects. The $E_{1/2}$ values for reversible couples were calculated from half the difference between E_p values for the anodic and cathodic waves from cyclic voltammetry. $E_{1/2}$ values are used as formal reduction potentials assuming differences in diffusion coefficients for oxidized and reduced species are negligible. The measurements were made using a PAR Model 173 potentiostat for potential control with a PAR Model 175 universal programmer as a sweep generator for voltammetry measurements. Values for n, where n is the total number of electrons transferred in exhaustive oxidative electrolysis at constant potential, were calculated after measuring the total area under current vs. time curves for the complete reaction. These reactions were considered complete after the current had fallen to 1% of the initial value. Values of n for the re-reduction of the oxidized product were determined by the same criterion. All coulometry measurements were performed at platinum screen electrodes using MCB Spectrograde acetonitrile as the solvent and 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the electrolyte. Elemental analyses were performed by Integral Microlabs, Raleigh, N.C.

Materials. TBAH was prepared in accordance with previously published techniques,[13] recrystallized from hot ethanol–water three times, and vacuum-dried at 70 °C for 10 h. Acetonitrile (MCB Spectrograde) was dried over Davison 4-Å molecular sieves for electrochemical experiments and used without drying for spectral measurements. Deuterioacetonitrile (99.9%) was purchased from Stohler Isotope Chemicals. Water was deionized and then distilled from alkaline permanganate. All solvents used for preparations were reagent grade and used without further purification. Ligands were purchased from either Aldrich or Strem Chemical and were used as received.

Preparations. ***cis*-$(bpy)_2RuCl_2{\cdot}2H_2O$.** The following modification of the preparation of this complex developed by Weaver[14] was utilized to give good yields of the complex.

Commercial $RuCl_3{\cdot}3H_2O$ (7.8 g, 29.8 mmol), bipyridine (9.36 g, 60.0 mmol), and LiCl (8.4 g, 2 mmol) were heated at reflux in reagent grade dimethylformamide (50 mL) for 8 h. The reaction was stirred magnetically throughout this period. After the reaction mixture was cooled to room temperature, 250 mL of reagent grade acetone was added and the resultant solution cooled at 0 °C overnight. Filtering yielded a red to red-violet solution and a dark green-black microcrystalline product. The solid was washed three times with 25-mL portions of water followed by three 25-mL portions of diethyl ether, and then it was dried by suction. Yields ranged from 65 to 70% based on starting ruthenium.

General Preparation of $[Ru(bpy)_2(L)Cl](PF_6)$ (L = tertiary phosphine, arsine, or stibine). Two methods were used for the synthesis of these complexes. In a typical preparation *cis*-$Ru(bpy)_2Cl_2{\cdot}2H_2O$ (262 mg, 5×10^{-4} mol) was suspended in 50 mL of a 1:1 ethanol–water solution (by volume), and a 50–100% molar excess of the appropriate ligand was added. The resulting mixture was deaerated with N_2 for ca. 15 min using a syringe needle. The mixture was heated at reflux for 3–6 h with vigorous stirring using a magnetic stirrer. After the reflux period, the dark red to orange solution was evaporated to ca. one-third of the initial volume and 35 mL of water was added. At this point unreacted ligand (in the case of solids) was removed by filtration. An excess of NH_4PF_6 was added and the flocculent orange to red precipitate which appeared was collected. The product was washed copiously with water followed by ether and then air-dried. Either direct crystallization from acetone–ether at ~10 °C or column chromatography on alumina utilizing benzene–acetonitrile as eluent followed by recrystallization from acetone–ether gave crystalline complexes. Yields varied between 47 and 88% based upon ruthenium.

A second method involving the use of the complex $[Ru(bpy)_2Cl(CH_3COCH_3)]^+$ as an intermediate was also employed. An acetone solution (~50 mL) was deaerated with N_2 using a syringe needle. To the deaerated solution was added 262 mg of *cis*-$Ru(bpy)_2Cl_2$ and 104 mg of $AgClO_4$. The resulting mixture was stirred with a magnetic stirrer for 1.5 h under N_2 and then filtered by gravity (in the air). A 50–100% molar excess of ligand was added to the solution of the monoacetone complex, and the resultant mixture was again deaerated and stirred for ca. 24 h. Purification of the product was accomplished as described above.

General Preparation of $[Ru(bpy)_2(L\text{-}L)](ClO_4)_2$ or $[Ru(bpy)_2(L\text{-}L)](PF_6)_2$ (L-L is two monodentate or one bidentate phosphine or arsine). The aqueous preparation technique was used exactly as previously described. The use of $Ru(bpy)_2(CH_3COCH_3)_2{}^{2+}$ proved to be easier and more efficient for the synthesis of some of the dicationic complexes and therefore was the method of choice. In a typical experiment 262 mg of *cis*-$Ru(bpy)_2Cl_2{\cdot}2H_2O$ and 208 mg of $AgClO_4$ were added to 50 mL of N_2-deaerated acetone. The resultant mixture was stirred magnetically for 3 h and filtered by gravity. To the clear red-brown solution was added a 50–100% molar excess of ligand, the solution was deaerated by N_2 bubbling, and then the solution was heated as described above. Purification of the complexes was carried out as described above.

$[(bpy)_2Ru(L)Cl](PF_6)$ (L = $(C_6H_5)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$). To a nitrogen-deaerated ethanol–water mixture (ca. 40 mL, 80% ethanol, 20% water) was added 262 mg (0.5 mmol) of *cis*-$(bpy)_2RuCl_2{\cdot}2H_2O$ and the ligand (~0.7 mmol). The mixture was heated at reflux for 8 h. After this period, the reaction mxture was reduced to ca. one-third the original volume by rotary evaporation followed by the addition of 20 mL of distilled water. The solution was then filtered by suction to give a solid precipitate consisting of unreacted ligand and a clear red to orange filtrate. To the filtrate was added an excess of NH_4PF_6 which resulted in the formation of an orange to red-orange flocculent precipitate. Purification was achieved by dissolving the precipitate in a minimum of acetone and filtering, followed by slow addition of ether to the filtrate. This process was repeated to obtain salts which were analytically pure. The complexes were dried by suction. Yields were about 70% (based upon ruthenium) for all the salts.

$\{(bpy)_2Ru[(CH_3(CH_2)_3)_3P]Cl\}(PF_6)$. The same procedure was followed as described for the triaryl–group 5 complexes. Chromatography was necessary to obtain the complex in acceptable purity. The crude PF_6^- salt was dissolved in a minimum of a CH_3CN–C_6H_6 mixture (30:70 by volume) followed by elution on a 1 × 20 cm column of alumina; the eluent was also 3:7 CH_3CN–C_6H_6. The first band was the red-brown complex. A second smaller yellow band also appeared followed by a third band that was green. The other two products were not investigated further. The former is probably the di(phosphine) disubstitution product and the latter is possibly a Ru(III) species, perhaps containing a bridging oxo ligand.[15] The desired product was purified further by removing the solvent, followed by dissolution in acetone and reprecipitation with ether. Dark red-brown crystalline prisms of the complex could be grown from acetonitrile–ether. The total yield was 65%.

$\{(bpy)_2Ru[(C_6H_5)_2PCH_3]Cl\}(PF_6)$. The ethanol–water procedure was followed for this preparation using 500 mg of the phosphine. The reflux time was 6 h. Chromatography with 3:1 C_6H_6–CH_3CN solution gave a bright orange band which was the complex. A slower moving lemon yellow band which contained the disubstituted product $\{(bpy)_2Ru[(C_6H_5)_2PCH_3]_2\}(PF_6)_2$ was eluted next. The yields of the two salts were 69 and 11%, respectively. Recrystallization was carried out by slow evaporation of an ether–acetone solution.

$(bpy)_2)Ru[(C_6H_5)_2AsCH_2As(C_6H_5)_2]Cl(PF_6)$. The same procedure was followed in the case of the diarsine ligand, except that 650 mg of the ligand was used. After precipitation of the crude orange brown salt, the product was chromatographed on alumina with 7:3 C_6H_6–CH_3CN as previously described. The first large orange-red band was collected and from it was obtained the salt in 45% yield after precipitation from acetone–ether.

$\{(bpy)_2Ru[(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2]Cl\}(ClO_4)$. Thirty milliliters of degassed acetone, 262 mg (0.5 mmol) of *cis*-$(bpy)_2RuCl_2{\cdot}2H_2O$, and 104 mg (0.5 mmol) of $AgClO_4$ were stirred magnetically for 1.5 h under nitrogen. After this period, the reaction mixture was filtered by gravity and 390 mg of the diphosphine was added. The reaction mixture was degassed by bleeding N_2 through the solution for ca. 15 min. The reaction was stirred for 18 h under nitrogen. At this time the solvent was removed by rotary evaporation and the red residue was dissolved in a minimum of acetonitrile. Suction filtration of this solution gave a solid precipitate consisting largely of unreacted ligand. Ether was added to the filtrate until complete precipitation of the red-orange salt was achieved. The complex was dissolved and reprecipitated twice more to achieve good product purity. The yield was 59%.

$\{(bpy)_2Ru[$*cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2]\}(PF_6)_2$. The ethanol–water technique was applied using 262 mg of *cis*-$(bpy)_2RuCl_2{\cdot}2H_2O$ and 440 mg of the diphosphine. Addition of NH_4PF_6 to the final aqueous solution gave a flocculent light-yellow solid which was purified by dissolution in acetonitrile and precipitation with ether. The yield was 82%.

$[(bpy)_2Ru(L\text{-}L)](ClO_4)_2$ ($L\text{-}L = (C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$, n = 1, 3). To 50 mL of N_2-degassed acetone were added 262 mg of *cis*-$(bpy)_2RuCl_2{\cdot}2H_2O$ and 208 mg of $AgClO_4$. The mixture was stirred magnetically under a nitrogen blanket for 3 h at which time it was filtered by gravity. The diphosphine was added (220 mg) and the solution degassed by bleeding nitrogen through the solution for 15 min. The reaction mixture was refluxed under an N_2 blanket for 6 h and then cooled to room temperature, and the solvent was removed by rotary evaporation. After partial removal of the solvent (~30 mL), a yellow solid was deposited which was filtered from the reaction mixture giving a product of high purity. The rest of the solvent was removed leaving a dirty yellow solid which was purified from acetonitrile–ether solutions as previously described. The total yield was 72% for the methanophosphine and 65% for the propanophosphine.

$\{(bpy)_2Ru[(p\text{-}CH_3C_6H_4)_3P]_2\}(ClO_4)_2$. The preparation was carried out as in the previous synthesis except that 750 mg of the free ligand was used and the reflux time was extended to 14 h. The total yield was only 32% perhaps because of steric inhibition of complex formation because of the bulky triarylphosphine groups.

Results and Discussion

Syntheses. The monosubstituted complexes $[Ru(bpy)_2(L)Cl]^+$ were prepared by reaction of the free ligand either with $[Ru(bpy)_2Cl(H_2O)]^+$ or with $[Ru(bpy)_2Cl(CH_3COCH_3)]^+$ (eq 1–4). Both the monoaquo and monoacetone complexes[16] are known to be valuable synthetic intermediates. The use of silver ion to produce the acetone complex provides an alternative to the ruthenium–nitrosyl–azide method previously described (eq 5).[16] The preparation

$$cis\text{-}Ru(bpy)_2Cl_2 \xrightarrow[\Delta]{EtOH/H_2O} [Ru(bpy)_2Cl(H_2O)]^+ + Cl^- \quad (1)$$

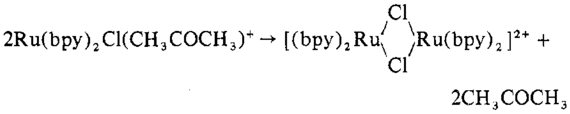
$$[Ru(bpy)_2Cl(H_2O)]^+ + L \rightarrow [Ru(bpy)_2Cl(L)]^+ + H_2O \quad (2)$$

$$cis\text{-}[Ru(bpy)_2Cl_2] + AgClO_4 \xrightarrow{acetone} [Ru(bpy)_2Cl(CH_3COCH_3)]^+ + ClO_4^- + AgCl \quad (3)$$

$$[Ru(bpy)_2Cl(CH_3COCH_3)]^+ + L \rightarrow [Ru(bpy)_2Cl(L)]^+ + CH_3COCH_3 \quad (4)$$

$$[Ru(bpy)_2Cl(NO)]^{2+} + N_3^- \xrightarrow{acetone} [Ru(bpy)_2Cl(CH_3COCH_3)]^+ + N_2O + N_2 \quad (5)$$

of the monoacetone complex must be carefully timed. At short reaction times (<1.5 h) the complex is not completely formed, the limiting factor being the rate of dissolution of *cis*-$Ru(bpy)_2Cl_2{\cdot}2H_2O$ in acetone. At long reaction times (>1.5 h) a dark, red-brown precipitate begins to form. Isolation of this complex showed it to be identical with the dimer $[(bpy)_2RuCl]_2(ClO_4)_2$ (by cyclic voltammetry and electronic absorption spectroscopy)[17] (see eq 6).



$$2Ru(bpy)_2Cl(CH_3COCH_3)^+ \rightarrow [(bpy)_2Ru(\mu\text{-}Cl)_2Ru(bpy)_2]^{2+} + 2CH_3COCH_3 \quad (6)^{17}$$

Isolation of the monosubstitution products was achieved by two methods: (1) addition of NH_4PF_6 to the aqueous solution when the aquo complex was used as intermediate followed by filtration of the flocculent precipitates which appeared or (2) evaporation of the acetone solution when the acetone complex was used. The crude solid obtained by the latter method always contained unreacted ligand as the predominant impurity. Purification of the crude products was accomplished in most cases by reprecipitation from an acetone solution by adding diethyl ether. In several preparations, pure complexes were obtained only following column chromatography. Crystallization could be accomplished in most cases from an equivolume mixture of acetone–ether by letting the solution sit for several days in a fume hood. Over longer periods of time the crystals redissolved due to enrichment of the acetone content of the solution.

The colors of the complexes varied from red-brown to orange depending upon the group 5 ligand and the counterion. Hexafluorophosphate salts appeared generally lighter in color than perchlorate salts. The overall yields (based upon ruthenium) varied from ca. 50 to 90% depending upon the method of synthesis and seemingly the steric requirements of the phosphine ligand.

The procedures involved for disubstitution in *cis*-$(bpy)_2RuCl_2$ by the phosphine ligands were analogous to those utilized for monosubstitution. The route involving aqueous

$$cis\text{-}(bpy)_2RuCl_2 \xrightarrow[\Delta]{H_2O,\ 2P} cis\text{-}(bpy)_2Ru(P_2)^{2+} + 2Cl^- \quad (7)$$

$$cis\text{-}(bpy)_2RuCl_2 + 2AgClO_4 \xrightarrow{acetone} cis\text{-}(bpy)_2Ru(CH_3COCH_3)_2{}^{2+} + 2AgCl$$

$$cis\text{-}(bpy)_2Ru(CH_3COCH_3)_2{}^{2+} + 2P \rightarrow cis\text{-}(bpy)_2Ru(P)_2{}^{2+} + 2\,CH_3COCH_3 \quad (8)$$

solution (eq 7) could only be used effectively for chelating phosphines. The route involving the bis(acetone) complex (eq 8) was the most efficient method for the preparation of the bis(phosphine) complex $(bpy)_2Ru[(p\text{-}tol)_3P]_2{}^{2+}$. No attempt was made to isolate the bis(acetone) complex because it is moisture sensitive. Figure 2 compares the electronic absorption spectrum (in acetone) of the two intermediates $[(bpy)_2Ru(CH_3COCH_3)Cl]^+$ and $[(bpy)_2Ru(CH_3COCH_3)_2]^{2+}$. As expected for a dication, both of the low-energy metal-to-bpy CT bands are shifted to higher energy relative to the bands in $(bpy)_2Ru(CH_3COCH_3)Cl^+$ (see below).

While monosubstituted complexes of both $(C_6H_5)_3As$ and $(C_6H_5)_3Sb$ were isolated, we were unable to prepare disubstituted complexes. This is almost surely due in part to the considerable steric requirements of the ligands. It was possible to isolate the monosubstituted complexes $(bpy)_2Ru(P\text{-}P)Cl^+$ [$P\text{-}P = (C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$, n = 1, 3] and to obtain from them the di(tertiary phosphine) substitution products by chelate ring closure in polar solvents (eq 9). It is almost

$$[(bpy)_2Ru(P\text{-}P)Cl]^+ \xrightarrow[\Delta]{EtOH/H_2O} [(bpy)_2Ru(P\text{-}P)_2]^{2+} + Cl^- \quad (9)$$

certain that the monodentate complexes are intermediates in the direct syntheses of the chelate complexes (eq 7), but they

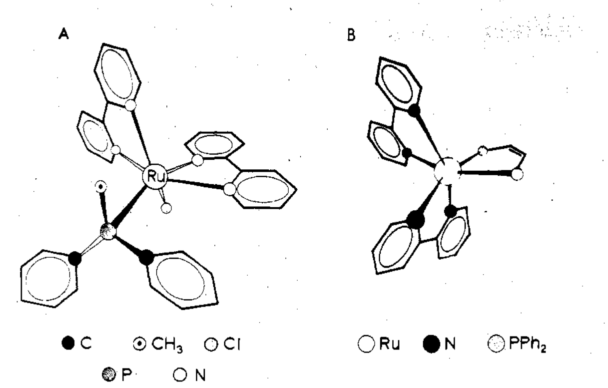


Figure 1. Structures of the two types of bipyridylphosphine complexes: (A) $[(bpy)_2Ru(Ph_2MeP)Cl]^+$, (B) $[(bpy)_2Ru(\textit{cis}\text{-}Ph_2PCH{=}CHPPh_2)]^{2+}$.

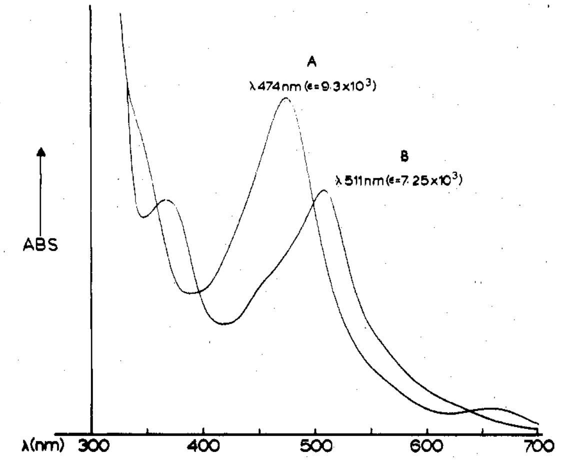


Figure 2. Electronic spectra for the complexes as PF_6^- salts in acetone solution: (A) $(bpy)_2Ru(CH_3COCH_3)_2^{2+}$, (B) $(bpy)_2Ru(CH_3COCH_3)Cl^+$.

were not observed as intermediates.

The colors of the disubstituted products ranged from yellow to pale yellow. Yields were all close to 75% for the cyclic bidentate products and below 40% for the monodentate products. In preparations of the latter, the solution color became green during the course of the reaction. The origin of the green color was not investigated but it may arise from the product of a side reaction which was responsible for the relatively low yields.

The assumed structures (Figure 1A,B) for the two different kinds of complexes prepared here are based on the method of synthesis, cyclic voltammetry and coulometry, ^1H NMR spectral data, electronic absorption spectral data, and elemental analyses (see Table I). Stephenson et al.[5] had previously reported preparations, colors, and elemental analyses for the complexes $[Ru(bpy)_2(L)Cl]^+$ ($L = (C_6H_5)_3P$ and $(C_6H_5)_3As$) and our results are in agreement with theirs.

Thin-Layer and Column Chromatography. In order to obtain products of high purity, it was necessary in some cases to use column chromatography. Thin-layer chromatography was attempted in order to determine efficient supports and eluent compositions. Our results are described here in some detail because they may be of general interest in separations involving other cationic coordination compounds.

Cellulose TLC was carried out using Eastman plates with either THF or CH_2Cl_2–C_6H_6 mixtures as eluents. Due to excessive tailing, this partition technique proved unsatisfactory. The use of Eastman alumina TLC plates was, in general, very satisfactory. A 2:1 mixture of benzene and acetonitrile provided sharp, slightly fan-shaped spots which had convenient R_f values. Application of differing concentrations of complex (e.g., $\{(bpy)_2Ru[(C_6H_5)_3P]Cl\}(PF_6)$) to a plate revealed a striking dependence of R_f values on concentration. (The R_f values could be varied from 0.4 to ~0.7.)

Table I. Elemental Analyses for Salts of the Complexes

		Analysis		
		% C	% H	% N
$[(bpy)_2Ru(Ph_3P)Cl](PF_6)$	calcd	53.05	4.07	6.51
	found	52.91	3.55	6.20
$\{(bpy)_2Ru[(p\text{-}MeC_6H_4)_3P]Cl\}(PF_6)$	calcd	53.45	4.78	6.08
	found	53.91	4.15	5.68
$\{(bpy)_2Ru(MePh_2P)Cl\}(PF_6)$	calcd	49.90	3.15	7.05
	found	50.05	3.31	7.19
$\{(bpy)_2Ru[(CH_3(CH_2)_3)_3P]Cl\}(PF_6)$	calcd	48.27	4.02	7.03
	found	48.03	4.05	6.94
$[(bpy)_2Ru(Ph_2PC{\equiv}CPPh_2)Cl](ClO_4)\cdot H_2O^a$	calcd	57.21	3.95	5.81
	found	57.26	3.48	5.72
$\{(bpy)_2Ru[Ph_2P(CH_2)_3PPh_2]Cl\}(PF_6)$	calcd	43.92	3.17	5.54
	found	43.79	3.40	5.50
$[(bpy)_2Ru(Ph_3As)Cl](PF_6)$	calcd	50.47	3.83	6.19
	found	50.54	3.48	5.80
$[(bpy)_2Ru(Ph_3Sb)Cl](PF_6)$	calcd	47.97	3.68	5.89
	found	47.95	3.64	5.61
$[(bpy)_2Ru(Ph_2AsCH_2AsPh_2)Cl](PF_6)$	calcd	49.65	3.66	5.15
	found	49.56	3.35	5.15
$\{(bpy)_2Ru[(p\text{-}MeC_6H_4)_3P]_2\}(PF_6)_2\cdot 2H_2O$	calcd	48.78	5.37	4.42
	found	48.51	4.90	4.14
$[(bpy)_2Ru(Ph_2PCH_2PPh_2)](PF_6)_2\cdot H_2O$	calcd	49.99	3.84	5.03
	found	50.48	3.75	4.68
$[(bpy)_2Ru(\textit{cis}\text{-}Ph_2PCH{=}CHPPh_2)](PF_6)_2\cdot H_2O$	calcd	49.15	3.32	4.99
	found	49.53	3.28	4.81
$[(bpy)_2Ru(Ph_2P(CH_2)_3PPh_2)](PF_6)_2$	calcd	52.96	4.32	5.26
	found	53.33	4.10	4.88
$\{(bpy)_2Ru(MePh_2P)\}(PF_6)_2$	calcd	48.04	4.37	5.10
	found	48.19	4.51	5.28

[a] Chlorine analysis: calcd 7.47; found 7.98.

Silica gel TLC (Eastman) was unsatisfactory due to an extremely tenacious association of the complexes with the support. Only elution with pure CH_3CN or MeOH resulted in an appreciable R_f value (~0.3). Since SiO_2 is known to act as an ion exchanger, it could be that the formation of cation–hydroxyl anion pairs is the source of this behavior.

For the reasons cited above, column chromatography was performed with alumina (Baker) as the support with ca. 2:1 C_6H_6–CH_3CN as the eluent. The PF_6^- salts of all complexes were soluble in the mixture, and clean separations of dicationic products from monocationic products were obtained. The complex of lower charge always eluted first. Traces of other materials were found in some of the preparations, especially for the chelated phosphine complexes. No effort was made to investigate the side products.

^1H NMR Spectra. Representative ^1H NMR data[19] were obtained for four of the complexes, two of which were monocations and two dications. For $\{(bpy)_2Ru[P(n\text{-}Bu)_3]Cl\}(PF_6)$ a complex series of resonances extending from τ 0.20 to 2.96 (area 16) was assigned to the aromatic protons on 2,2′-bipyridine. The bound phosphine showed three resonances centered at τ 8.53 (multiplet, area 6), τ 8.93 (multiplet, area 12), and τ 9.26 (triplet, area 9). The resonances can be assigned to the methylene group bound to phosphorus, the two insulating methylene groups, and the terminal methyl group, respectively. The relative ratio of aromatic protons to phosphine protons is 16:27, as is expected for the proposed structural assignment. The molecule possesses no symmetry so that the 16 bipyridine protons are expected to be unique. A first-order coupling scheme predicts eight doublets and eight triplets.

The complex $\{(bpy)_2Ru[(p\text{-}tol)_3P]Cl\}(PF_6)$ showed a complicated pattern of resonances from τ 0.17 to 2.39. The observed pattern can be assigned as a superposition of the aromatic protons on the bipyridine with those on the tolyl phosphine. The para-methyl group exhibited a sharp singlet

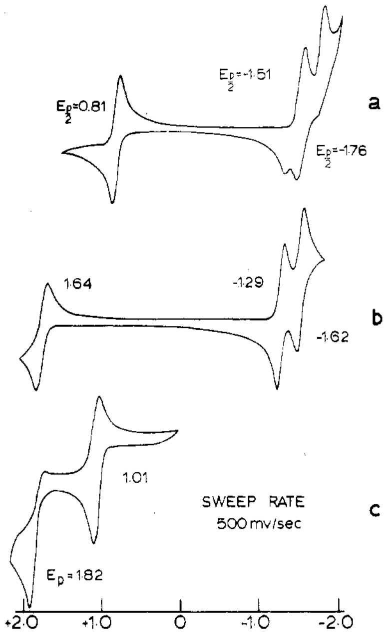


Figure 3. Representative cyclic voltammograms for the phosphine complexes: (a) $\{(bpy)_2Ru[P(n\text{-}Bu)_3]Cl\}PF_6$, (b) $[(bpy)_2Ru(Ph_2PCH_2PPh_2)](PF_6)_2$, (c) $[(bpy)_2Ru(Ph_2PC{\equiv}CPPh_2)Cl](PF_6)$. All were taken in CH_3CN with 0.1 M TBAH as supporting electrolyte.

at τ 6.95. The relative ratio of aromatic protons to the methyl protons was 36 to 6 as expected for the proposed structure.

For the dication $\{(bpy)_2Ru[(p\text{-tol})_3P]_2\}(ClO_4)_2$ a series of simple, distinguishable resonances appeared in the aromatic region. Resonances that occurred at τ 1.50 (doublet, area 4), τ 2.06 (doublet, area 4), τ 2.14 (triplet, area 4), and τ 2.64 (triplet, area 4) were assigned to the bipyridine ligand. Two higher field groups were assigned to the aromatic protons on the tolyl phosphine: one at τ 2.99 (doublet, area 12) and one at τ 4.03 (sextet, area 12). The methyl protons of the ligands occurred as a sharp singlet at τ 6.85 (area 18). The relative area of the bipyridine protons to phosphine aromatic protons to phosphine methyl protons was 16:24:18. For the chelate $\{(bpy)_2Ru(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2\}(ClO_4)_2$ the composite resonances of the bipyridine and phenyl protons extended from τ 1.48 to 3.82 in a complicated pattern. An unsymmetrical complex multiplet at τ 7.04 can be assigned to overlapping methylene resonances from the CH_2 groups on the chelating phosphine. The relative ratio of aromatic to methylene protons was 36:6.

Both of the dication types, e.g., $\{(bpy)_2Ru[(p\text{-tol})_3P]_2\}(PF_6)_2$, and the chelates should have C_2 symmetry. In the C_2 point group a twofold axis of rotation interconverts the bipyridine ligands. There is no operation, however, which results in equivalence of the two pyridine rings on a given bipyridine unit, and there should be eight distinct bpy proton environments observable in the ^1H NMR spectra. A first-order coupling scheme predicts four of these to be doublets and four of these to be triplets. Such splitting patterns have been observed for *cis*-$(bpy)_2RuCl_2$[20] and cis-$(dmbp)_2Ru(NH_3)_2^{2+}$ (dmbp is 5,5′-dimethyl-2,2′-bipyridine).[21] The overlap of the phenyl protons from the phosphine ligand makes the aromatic region for $[(bpy)_2Ru(Ph_2P(CH_2)_3PPh_2)](ClO_4)_2$ very complicated. The di-*p*-tolylphosphine complex, however, displays an unexpectedly high symmetry.[41] In this case two doublets and two triplets can be assigned to the bpy ligand. The protons ortho to the phosphorus atom result in a sextet which can be interpreted as an intermediate case of ABX coupling ($J_{AB} \approx J_{BX} \approx 8$ Hz and $J_{AX} = 0$).[22]

Redox Properties. The results of cyclic voltammetry experiments in CH_3CN solution with 0.1 M TBAH as supporting electrolyte for both the monocations and dications are given in Table II. For both types of complex a reversible oxidation and two reversible or quasi-reversible reductions are observed (see Figure 3A,B). In the series of monocations the oxidative process occurs from ~0.8 to ~1.0 V (vs. the ssce at 22 ± 2 °C). In the dications the oxidative process occurs from ~1.5 to ~1.75 V. The reductions in the monocations occur at ~-1.5 and ~-1.7 V and in the dications at -1.3 and -1.5 V. The general increase in both oxidation and reduction potentials going from the series of monocations to the dications presumably results from both the increase in charge on the complexes and the replacement of a π-donor ligand, Cl^-, with a π-acceptor group 5 ligand.

Table II. Cyclic Voltammetry Results for Complexes of the Types $(bpy)_2Ru(P)Cl^+$ and $(bpy)_2RuP_2^{2+}$

complex	$E_{1/2}$,[a] V
$[(bpy)_2Ru(Ph_3P)Cl](PF_6)$	+0.94, −1.29, −1.47, −1.67
$\{(bpy)_2Ru[(p\text{-}MeC_6H_4)_3P]Cl\}(PF_6)$	+0.94, (1.00, 0.95),[c] −1.32, −1.53, −1.68
$\{(bpy)_2Ru(MePh_2P)Cl\}(PF_6)$	+0.91, −1.33,[b] −1.59, −1.71
$\{(bpy)_2Ru[\{CH_3(CH_2)_3\}_3P]Cl\}(PF_6)$	+0.81, −1.32,[b] −1.51, −1.76
$[(bpy)_2Ru(Ph_2PC{\equiv}CPPh_2)Cl](ClO_4)$	+1.75,[b] +1.01, −1.33,[b] −1.47, −1.65
$\{(bpy)_2Ru[Ph_2P(CH_2)_3PPh_2]Cl\}(PF_6)$	+0.91, −1.31,[b] −1.51, −1.68
$[(bpy)_2Ru(Ph_3As)Cl](PF_6)$	+0.93 (1.00, 0.96),[c] −1.35,[b] −1.49, −1.63
$[(bpy)_2Ru(Ph_3Sb)Cl](PF_6)$	+0.93 (1.02, 0.90),[c] −1.37,[b] −1.45, −1.61
$[(bpy)_2Ru(Ph_2AsCH_2AsPh_2)Cl](PF_6)$	+1.08,[b] +0.90, −1.29,[b] −1.49, −1.69
$\{(bpy)_2Ru(MePh_2P)\}(PF_6)_2$	+1.50 (2.30, 0.75),[c] −1.33, −1.53
$[(bpy)_2Ru(Ph_2P(CH_2)_3PPh_2)](PF_6)_2$	+1.62, −1.30, −1.50
$[(bpy)_2Ru(cis\text{-}Ph_2PCH{=}CHPPh_2)](PF_6)_2$	+1.75 (1.05, 1.05),[c] −1.28, −1.51
$[(bpy)_2Ru(Ph_2PCH_2PPh_2)](PF_6)_2$	+1.63, −1.29, −1.54
$\{(bpy)_2Ru[(p\text{-}MeC_6H_4)_3P]_2\}(PF_6)_2$	+1.51, −1.34, −1.54

[a] In CH_3CN solution with 0.1 M TBAH as supporting electrolyte. [b] Irreversible peak potential. [c] Coulometry was carried out 200 mV above $E_{1/2}$ for an oxidation [Ru(II) → Ru(III)] and 200 mV below for a reduction [Ru(III) → Ru(II)]. The first value refers to the *n* value for oxidation, and the second value the *n* value for re-reduction. $E_{1/2}$ values were calculated from the average of the anodic and cathodic peak potentials, $E_{1/2} = E_{pa} + E_{pc/2}$. Where easily measured, the peak current ratios i_c/i_a were 0.95–1.05. ΔE_p, the difference in potential between anodic and cathodic peak currents, varied from 60 to 90 mV and appeared to be largely independent of sweep rate.

An additional irreversible oxidation is observed in $[(bpy)_2Ru(Ph_2PC{\equiv}CPPh_2)Cl]^+$ which could be due either to a Ru(III)–Ru(IV) couple of transient stability or to a phosphine-localized oxidation (to give a short-lived coordinated phosphenium cation) (Figure 3C). All of the monocationic complexes exhibited a small irreversible oxidation at ca. -1.3 V. This was shown to be a product from the second reduction process and in part explains its irreversibility. No attempt was made to investigate the decomposition product. This behavior was not observed for the dications.

Controlled-potential coulometry showed that the oxidations in both the monocationic and dicationic complexes were one-electron transfer processes (Table II). The potentials for oxidation of the monocationic and dicationic complexes are all at higher potentials than their corresponding pyridine analogues under the same conditions. For the couples $[(bpy)_2Ru(py)Cl]^{2+/+}$,[23] $[(bpy)_2Ru(py)_2]^{3+/2+}$,[23] and $[(bpy)_3Ru]^{3+/2+}$,[24] formal reduction potentials are 0.77, 1.29, and 1.29 V.

Table III. Electronic Absorption Spectra for the $(bpy)_2Ru^{II}(P)Cl^+$ Complexes in CH_3CN Solution

	λ_{max}, nm (log ϵ_{max}) (*f*)				
complex	Ia	IIa	IIIa	IVa	Va
$[(bpy)_2Ru(Ph_3P)Cl](PF_6)$	454 (3.79) (9.23×10^{-2})	328 (3.85) *a*	292 (4.60) (2.47×10^{-1})	231 (4.60) *a*	>207 (>4) *a*
$\{(bpy)_2Ru[(p\text{-}MeC_6H_4)_3P]Cl\}(PF_6)$	462 (3.83) (9.12×10^{-2})	~332 (3.83) *a*	295 (4.63) (2.56×10^{-1})	239 (4.70) *a*	>209 (>4) *a*
$[(bpy)_2Ru(MePh_2P)Cl](PF_6)$	464 (3.79) (7.50×10^{-2})	333 (3.78) *a*	293 (4.87) *a*		
$\{(bpy)_2Ru[(CH_3(CH_2)_3)_3P]Cl\}(PF_6)$	485 (3.85) (7.48×10^{-2})	347 (3.81) (11.96×10^{-2})	295 (4.63) (2.62×10^{-1})	244 (4.25) *a*	>200 (>4) *a*
$[(bpy)_2Ru(Ph_2PC{\equiv}CPPh_2)Cl](ClO_4)$	441 (3.84) (1.2×10^{-1})	~325 (3.85) *a*	292 (4.67) (4.30×10^{-1})	231 (4.79) *a*	>209 (>4) *a*
$\{(bpy)_2Ru[Ph_2P(CH_2)_3PPh_2]Cl\}(PF_6)$	462 (3.78) (8.14×10^{-2})	326 (3.90) *a*	294 (4.60) (3.41×10^{-1})	228 (4.63) *a*	>207 (>4) *a*
$[(bpy)_2Ru(Ph_3As)Cl](PF_6)$	468 (3.81) (8.51×10^{-2})	337 (3.80) *a*	294 (4.61) (3.44×10^{-1})	232 (4.47) *a*	>204 (>4) *a*
$[(bpy)_2Ru(Ph_3Sb)Cl](PF_6)$	470 (3.85) (8.57×10^{-2})	340 (3.86) (3.58×10^{-2})	294 (4.72) (3.47×10^{-1})	245 (4.51) *a*	>210 (>4) *a*
$[(bpy)_2Ru(Ph_2AsCH_2AsPh_2)Cl](PF_6)$	472 (3.80) (8.31×10^{-2})	341 (3.75) (3.62×10^{-2})	294 (4.69) (3.53×10^{-1})	244 (4.48) *a*	>210 (>4) *a*

[a] Not well enough resolved for accurate measurement.

The coulometric results in Table II show that oxidation of the Ru(II) complexes gives Ru(III) complexes which in most cases are stable in acetonitrile as shown by *n* values on re-reduction. One notable exception is the oxidized form of $\{(bpy)_2Ru[Sb(C_6H_5)_3]Cl\}^+$, which is also photosensitive. A second is the oxidized form of $\{(bpy)_2Ru[P(p\text{-tol})_3]_2\}^{2+}$ where steric crowding may cause phosphine dissociation and oxidation of the liberated phosphine. Phosphine dissociation would explain the high *n* value obtained during coulometry (Table II).

The reduction potentials for the Ru(III)–Ru(II) couples are expected to respond to both σ-donor and π-acceptor properties of the group 5 ligands. Donor properties of ligands probably lead to a differential stabilization of Ru(III) over Ru(II), while acceptor properties are important in terms of stabilization of Ru(II).[25] The basicity of ligands toward the proton is one measure of their σ-donor strength. A trialkylphosphine like $(n\text{-Bu})_3P$ has a greater basicity toward the proton than does pyridine.[26] With the assumption of no metal to ligand π-back-bonding, it might be expected that $\{(bpy)_2Ru(Cl)[(n\text{-Bu})_3P]\}^+$ would be more easily oxidized than its pyridine analogue, but just the opposite is observed. Given the comparative reduction potential values, the ability of the phosphine ligands to accept π-electron density from Ru(II) must be at least equal to that of pyridine. The same observations apply to the chelating di(tertiary phosphine) ligands compared to fused pyridine heterocycles such as 2,2′-bipyridine and 1,10-phenanthroline. For the complex $[(bpy)_2Ru((C_6H_5)_2CH_3P)_2]^{2+}$, the free ligand has a proton basicity similar to that of pyridine, yet the $E_{1/2}$ for the 3+/2+ couple is 200 mV more anodic than $E_{1/2}$ for the $Ru(bpy)_3{}^{3+/2+}$ couple.

The increase in reduction potential for the Ru(III)–Ru(II) couples follows the expected increase in π-acceptor ability of the phosphine ligands: $[CH_3(CH_2)_3]_3P < [p\text{-}CH_3C_6H_4]_3P \approx CH_3(C_6H_5)_2P < (C_6H_5)_3P \approx$ *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2 < (C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$. It is interesting to note that the lowest energy CT transition increases in energy in the same order. The linear correlations between CT band energies and Ru(III)–Ru(II) reduction potentials have been observed for other ruthenium(II) complexes.[24,27]

Electronic Absorption Spectra. An absorption spectrum which is more or less characteristic of the spectra for the complexes $[(bpy)_2Ru(L)Cl]^+$ is shown in Figure 4A. Five major absorption bands are observed. For purposes of discussion the bands are labeled from Ia to Va in order of increasing energy. Bands Ia and IIIa are sufficiently well resolved that oscillator strengths could be calculated.[30] Table III shows that band IIIa maintains both a constant position (±5 nm) and a constant oscillator strength throughout the series of compounds. Essentially identical absorption bands have been observed in related complexes where they have been assigned to bpy-localized $\pi^* \leftarrow \pi$ transitions.[31,32] The same transition is found in free 2,2′-bipyridine at 280 nm so that coordination of the ligand results in a red shift in the transition energy of approximately 1300 cm^{-1}.

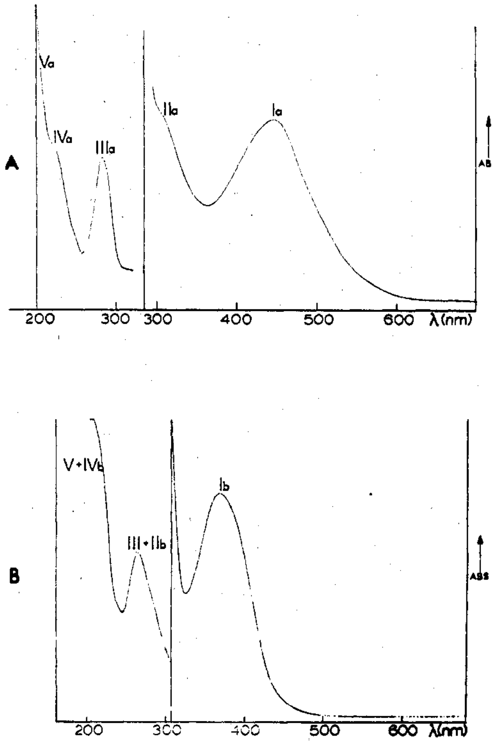


Figure 4. Electronic absorption spectra of the complexes in CH_3CN solution: (A) $[(bpy)_2Ru(PPh_3)Cl](PF_6)$, (B) $[(bpy)_2Ru(Ph_2PCH_2PPh_2)](PF_6)_2$.

Band Ia has a relatively high oscillator strength and its assignment to a $\pi^*(bpy) \leftarrow d\pi(Ru)$ transition is consistent with previous assignments in related bpy–Ru(II) complexes.[31] No evidence was found for Ru(II) to group 5 ligand charge-transfer (CT) bands probably because they are obscured by high-energy $\pi^* \leftarrow \pi$ transitions localized on the bpy ligands.

As the λ_{max} values for band Ia move to higher energies, the

Table IV. Electronic Spectra for the Complexes $(bpy)_2Ru(P\text{-}P)_2^{2+}$ in CH_3CN Solution

complex	λ_{max}, nm (log ϵ_{max}) (f) Ib	IIb	IIIb	IVb	Vb	VIb	VIIb
$\{(bpy)_2Ru[MePh_2P]_2\}(PF_6)_2$	427 (3.84) (5.63×10^{-2})			282 (4.70)	275 (4.69)	233 (4.8)	>215 (>4)
$\{(bpy)_2Ru[(p\text{-}MeC_6H_4)_3P]_2\}(PF_6)_2$	439 (3.80) (5.71×10^{-2})		289 (4.62)	277 sh (4.59)	255 (4.75)	230 (4.79)	>215 (>4)
$[(bpy)_2Ru(Ph_2PCH_2PPh_2)](PF_6)_2$	384 (3.76) (8.07×10^{-1})	319 sh (3.97)		280 (4.43)	271 sh (4.38)	277 (4.70)	>215 (>4)
$[(bpy)_2Ru(cis\text{-}Ph_2PCH{=}CHPPh_2)](PF_6)_2$	373 (3.94) (1.13×10^{-1})	317 sh (4.21)	293 sh (4.26)	276 (4.55)	268 sh (4.52)	223 (4.88)	>202 (>4)
$\{(bpy)_2Ru[Ph_2P(CH_2)_3PPh_2]\}(PF_6)_2$	394 (3.73) (5.88×10^{-2})	321 sh (3.91)		289 (4.36)	277 sh (4.33)	232 (4.61)	>210 (>4)

Table V. Electronic Absorption Spectra for Complexes in Ru(III) Generated by Electrochemical Oxidation

complex	potential,[a] V	solution color	λ_{max}, nm (log ϵ_{max}) Ic	IIc	IIIc	IVc	Vc	VIc
$[(bpy)_2Ru(Ph_3P)Cl]^{2+}$	1.2	green	602 (2.60)	412 (3.74)	313 (4.25)	297 (4.11)		>225
$\{(bpy)_2Ru[CH_3(CH_2)_3P]Cl\}^{2+}$	1.2	purple	564 (2.93)	415 (3.55)	315 (4.55)	301 (4.09)	246	>220
$[(bpy)_2Ru(Ph_3As)Cl]^{2+}$	1.2	yellow-green	625 (2.56)	432 (3.65)	315 (4.39)	295 (4.20)	247	>225
$[(bpy)_2Ru(Ph_3Sb)Cl]^{2+}$	1.2	yellow	646 (2.54)	432 (3.32)	312 (4.50)	294 (4.13)	240	>225
$[(bpy)_2Ru(cis\text{-}Ph_2PCH{=}CHPPh_2)]^{3+}$	2.0	forest green	840 (2.10)	~385	~305 (4.66)	275 (4.17)		>220
$\{(bpy)_2Ru[Ph_2P(CH_2)_3PPh_2]\}^{3+}$	1.8	light green	779 (2.00)	~385	~305 (4.71)	275 (4.15)		>220

[a] Potential at which electrolysis was performed (CH_3CN solution with 0.1 *M* tetrabutylammonium hexafluorophosphate as supporting electrolyte).

oscillator strength (f) of the transition increases.[18] Table III shows that ϵ_{max} for the bands is relatively constant and f increases because of increases in the bandwidths at half-heights. The increase in bandwidth suggests an increase in excited-state distortion compared to the ground state. Broader bands are expected if there are large differences between ground- and excited-state nuclear configurations since the number of vibronic components in the electronic transition are greater. As the CT transition moves to higher energy, the extent of charge transfer probably increases because of less π^*(bpy) character in the dπ levels in the ground state. An increase in the extent of charge transfer could lead to greater distortions in the excited state. The absorption bands are not purely Gaussian in shape but rather are skewed noticeably to higher energy. The amount of skew also increases as the band energy, a fact that also suggests increasing distortion in the excited state.[34]

Band IIa is partially obscured because of its overlap with the first $\pi^*(bpy) \leftarrow \pi(bpy)$ transition (band IIIa). The extinction coefficient data (Table III) support its assignment as a charge-transfer process, probably $\pi_2^*(bpy) \leftarrow d\pi(Ru)$. In complexes which contain phosphines which are stronger π acids, both bands Ia and IIa move to higher energies. This behavior is expected if the d orbitals are increasingly stabilized because of increased Ru → group 5 ligand back-bonding. In this context, the $\pi^*(bpy) \leftarrow Ru$ transitions act as spectator transitions for the ruthenium–phosphine interaction.

The bands IVa appear as shoulders on band Va and from their ϵ_{max} and λ_{max} values can be assigned to intraligand $\pi^* \leftarrow \pi(bpy)$ transitions[28,31] or where aromatic phosphines are present to a mixture of $\pi(bpy)$–$\pi^*(bpy)$ and $\pi(phenyl)$–$\pi^*(phenyl)$ transitions. Band Va is most likely a mixture of $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow \pi$ localized on the phenyl groups. Because of its high energy, >215 nm, no attempt was made to resolve this transition.

In spectral features, the dications are similar to the monocations although as many as seven absorption bands are found (Table IV) and they will be referred to as Ib through VIIb. In general, the bands are shifted to higher energies compared to the monocations. The simplest explanation for the effect is that there is increased formal charge on the metal ion, resulting in a net stabilization of the dπ orbitals largely Ru in character. Since at least two of the bands are most reasonably assigned to MLCT transitions (see below) and the other bands to predominantly ligand-localized transitions with some MLCT character, the entire absorption spectrum exhibits a hypsochromic shift.

Band Ib can be assigned to a MLCT transition based on oscillator strengths (Table IV) and previous assignments in related complexes. It is generally Gaussian in shape and broad ($\Delta\nu_{1/2} \approx 2500$ cm^{-1}) but does have a slight skew to higher energy. It shows the same phenomenon of increasing oscillator strength, with increasing transition energy which was noted earlier.

Band IIb occurs as a low-energy shoulder on band IIIb and is probably also MLCT in nature. Bands IIIb–VIIb most probably arise from $\pi^* \leftarrow \pi$ transitions localized on either the bipyridine ligands or the phenyl groups. Bands Vb (~275 nm) and VIb (~225 nm) can reasonably be assigned to bipyridine-localized transitions. Figure 4B shows one of the least complicated examples, that of $[(bpy)_2Ru(Ph_2PCH_2PPh_2)]^{2+}$.

Representative examples of the Ru(III) forms of both the singly and disubstituted group 5b complexes were generated by controlled-potential electrolysis. They were not isolated as solids but the electronic spectra were obtained. In all cases re-reduction to Ru(II) gave the starting complex quantitatively (as judged by the electronic spectra of the reduced form). Table V summarizes the electronic spectra of the Ru(III) ions. In general their color in solution is determined by a relatively low-energy transition of low intensity ($\epsilon \sim 500$). The position of the band (Ic) is highly dependent on the charge on the complex and on the group 5 ligand. Such bands have been assigned to LMCT transitions in related complexes.[35,36]

For the $[(bpy)_2Ru(L)Cl]^{2+}$ complexes, both ϵ_{max} and λ_{max} for the low-energy transition increase as the ligand varies in the series L = Ph_3Sb, Ph_3As, Ph_3P, $(n\text{-}Bu)_3P$, and pyridine. The origin of the transitions can be reasonably assigned to a $d\pi(Ru) \leftarrow p\pi(Cl)$ LMCT transition designated as Ic. A $d\pi(Ru) \leftarrow p\pi(Cl)$ transition should be at lower energies than a $d\pi(Ru) \leftarrow \pi_b$(pyridine ligand) transition given the relative optical electronegativies of Cl vs. pyridine-type ligands.[37] LMCT processes involving $d\pi \leftarrow \sigma$ transitions from Cl, bipyridine, or group 5 σ-based levels are symmetry-forbidden processes and should also occur at relatively high energies.[38,39]

The effect of the group 5 ligand on the energy and intensity of the low-energy band can be understood in terms of the σ-donor strength of the ligand. Increased electron donation to $d\pi(Ru(III))$ causes an increase in the energy of the $d\pi$ levels decreasing $d\pi(Ru)-p\pi(Cl)$ mixing and increasing the energy of the $d\pi \leftarrow Cl$ CT band.

A second band occurs at ~400 nm depending somewhat on the group 5 ligand and the charge type. The ϵ_{max} values ($\sim 5 \times 10^3$) support the assignment of the band as a charge-transfer process, either LMCT ($d\pi(Ru) \leftarrow \pi_b(bpy)$) or MLCT ($\pi^*(bpy) \leftarrow d\pi(Ru)$). The remainder of the electronic spectrum (bands IIIc–Vc) is dominated by $\pi^* \leftarrow \pi$ transitions based on the bipyridine ligands. The bands are shifted to lower energy compared to those of the corresponding Ru(II) complexes as expected for coordination to a more acidic metal center.[40]

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Registry No. $[(bpy)_2Ru(Ph_3P)Cl](PF_6)$, 67710-99-0; $\{(bpy)_2Ru[(p\text{-}MeC_6H_4)_3P]Cl\}(PF_6)$, 67673-80-7; $\{(bpy)_2Ru(MePh_2P)Cl\}(PF_6)$, 67673-82-9; $\{(bpy)_2Ru[(CH_3(CH_2)_3)_3P]Cl\}(PF_6)$, 67673-84-1; $[(bpy)_2Ru(Ph_2PC\equiv CPPh_2)Cl](ClO_4)$, 67673-86-3; $\{(bpy)_2Ru[Ph_2P(CH_2)_3PPh_2]Cl\}(PF_6)$, 67673-88-5; $[(bpy)_2Ru(Ph_3As)Cl](PF_6)$, 67711-01-7; $[(bpy)_2Ru(Ph_3Sb)Cl](PF_6)$, 67673-90-9; $[(bpy)_2Ru(Ph_2AsCH_2AsPh_2)Cl](PF_6)$, 67673-92-1; $\{(bpy)_2Ru[(p\text{-}MeC_6H_4)_3P]_2\}(PF_6)_2$, 67673-94-3; $[(bpy)_2Ru(Ph_2PCH_2PPh_2)](PF_6)_2$, 67673-96-5; $[(bpy)_2Ru(cis\text{-}Ph_2PCH{=}CHPPh_2)](PF_6)_2$, 67673-98-7; $[(bpy)_2Ru(Ph_2P(CH_2)_3PPh_2)](PF_6)_2$, 67674-00-4; $\{(bpy)_2Ru(MePh_2P)_2\}(PF_6)_2$, 67674-02-6; $[(bpy)_2Ru(Ph_3P)Cl]^{2+}$, 67674-03-7; $\{(bpy)_2Ru[(p\text{-}MeC_6H_4)_3P]Cl\}^{2+}$, 67673-64-7; $\{(bpy)_2Ru(MePh_2P)Cl\}^{2+}$, 67673-65-8; $\{(bpy)_2Ru[\{CH_3(CH_2)_3\}_3P]Cl\}^{2+}$, 67673-66-9; $[(bpy)_2Ru(Ph_2PC\equiv CPPh_2)Cl]^{2+}$, 67673-67-0; $\{(bpy)_2Ru[Ph_2P(CH_2)_3PPh_2]Cl\}^{2+}$, 67673-68-1; $[(bpy)_2Ru(Ph_3As)Cl]^{2+}$, 67673-69-2; $[(bpy)_2Ru(Ph_3Sb)Cl]^{2+}$, 67673-70-5; $[(bpy)_2Ru(Ph_2AsCH_2AsPh_2)Cl]^{2+}$, 67673-71-6; $\{(bpy)_2Ru(MePh_2P)_2\}^{3+}$, 67673-72-7; $[(bpy)_2Ru(Ph_2P(CH_2)_3PPh_2)]^{3+}$, 67673-73-8; $[(bpy)_2Ru(cis\text{-}Ph_2PCH{=}CHPPh_2)]^{3+}$, 67673-74-9; $[(bpy)_2Ru(Ph_2PCH_2PPh_2)]^{3+}$, 67673-75-0; $\{(bpy)_2Ru[(p\text{-}MeC_6H_4)_3P]_2\}^{3+}$, 67673-76-1; $[(bpy)_2Ru(CH_3COCH_3)_2](PF_6)_3$, 67673-78-3; $[(bpy)_2Ru(CH_3COCH_3)Cl](PF_6)$, 67710-97-8; *cis*-$Ru(bpy)_2Cl_2$, 19542-80-4.

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