symmetry plane in $[CH_3N(PF_2)_2]_3Cr$ makes nonequivalent the two fluorine atoms attached to a given phosphorus atom, thereby accounting for the two fluorine doublets of equal relative intensities.

(D) Infrared and Raman Spectra. The approximate CO stretching force constants (Table IV) were calculated by a variation of the Cotton–Kraihanzel method[23,24] as outlined in the Experimental Section. Combination of infrared and Raman data on the *trans*-$[RN(PF_2)_2]_2Cr(CO)_4$ complexes (II) suggested that the trans/cis interaction constant ratio was about 3, a constraint that was used for the force constant calculations for the otherwise underdetermined *cis*-$L_2M(CO)_4$ and *mer*-$L_3M(CO)_3$ derivatives. This contrasts with the trans/cis interaction constant ratio of 2 that was assumed for the original Cotton–Kraihanzel calculations[23,24] as well as in most subsequent treatments. The CO stretching force constants (Table IV) generally fall in the range 15.8–16.0 mdyn/Å except for the mutually trans pair of CO groups in the *cis*-$L_2M(CO)_4$ derivatives of the types I and III, which have appreciably higher stretching force constants (16.4–16.7 mdyn/Å). The magnitudes of these CO stretching force constants suggests that the π-acceptor strength of the donor phosphorus atoms in the $RN(PF_2)_2$ ligands is lower than that of the phosphorus atom in PCl_3 but comparable with the phosphorus atom in $C_2H_5OPCl_2$.[24] The various stretch–stretch interaction constants (t, c, and d in Table IV) appear to be very insensitive toward structural changes. In future analyses of more complicated and highly underdetermined ν(CO) spectra of $RN(PF_2)_2$ metal carbonyls, it probably would not introduce serious errors in the approximate CO stretching constants (corresponding to $k(1)$ and $k(2)$ in Table IV) to use $t = 0.6$ mdyn/Å and $c = d = 0.2$ mdyn/Å as constraints on the calculations provided that such constraints in the stretch–stretch interaction constants were limited to pairs of CO groups on the same metal atom subtending angles of approximately 180 and 90°, respectively.

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Registry No. $CH_3N(PF_2)_2Cr(CO)_4$, 73949-36-7; *trans*-$[CH_3N(PF_2)_2]Cr(CO)_4$, 73949-37-8; $CH_3N(PF_2)_2Mo(CO)_4$, 79734-75-1; *cis*-$[CH_3N(PF_2)_2]_2Mo(CO)_4$, 79721-42-9; $CH_3N(PF_2)_2W(CO)_4$, 79734-76-2; *cis*-$[CH_3N(PF_2)_2]_2W(CO)_4$, 79721-43-0; $C_6H_5N(PF_2)_2Cr(CO)_4$, 79721-44-1; *trans*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_4$, 79721-45-2; $C_6H_5N(PF_2)_2Mo(CO)_4$, 79721-46-3; *cis*-$[C_6H_5N(PF_2)_2]_2Mo(CO)_4$, 79721-47-4; $C_6H_5N(PF_2)_2W(CO)_4$, 79721-48-5; *trans*-$[CH_3N(PF_2)_2][C_6H_5N(PF_2)_2]Cr(CO)_4$, 79721-49-6; *mer*-$[CH_3N(PF_2)_2]_2Cr(CO)_3$, 79721-50-9; *mer*-$[C_6H_5N(PF_2)_2]_2Cr(CO)_3$, 79734-77-3; $[C_6H_5N(PF_2)_2]_3Cr_2(CO)_6$, 79721-51-0; $[CH_3N(PF_2)_2]_3Cr_2(CO)_5$, 79721-52-1; $[CH_3N(PF_2)_2]_3Mo_2(CO)_5$, 79721-55-4; $[C_6H_5N(PF_2)_2]_3Mo_2(CO)_5$, 79721-56-5; $[CH_3N(PF_2)_2]_3W_2(CO)_5$, 79734-78-4; $[CH_3N(PF_2)_2]_5Mo_2CO$, 79746-02-4; $[CH_3N(PF_2)_2]_4Mo_2(CO)_3$, 79721-57-6; $[C_6H_5N(PF_2)_2]_5Mo_2(CO)_2$, 79734-79-5; $[CH_3N(PF_2)_2]_4W_2(CO)_3$, 79721-58-7; *mer*-$[CH_3N(PF_2)_2]_2Mo(CO)_3$, 79721-53-2; *mer*-$[CH_3N(PF_2)_2]_2W(CO)_3$, 79721-54-3; $[CH_3N(PF_2)_2]_4Cr_2(CO)_3$, 79734-80-8; $CH_3N(PF_2)_2$, 17648-18-9; $C_6H_5N(PF_2)_2$, 23611-36-1; $C_7H_8Cr(CO)_4$, 12146-36-0; $C_7H_8Mo(CO)_4$, 12146-37-1; $C_7H_8W(CO)_4$, 12129-25-8; $C_7H_8Cr(CO)_3$, 12125-72-3; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $C_7H_8Mo(CO)_3$, 12125-77-8; $Mo(CO)_6$, 13939-06-5; $[C_6H_5N(PF_2)_2]_4Mo_2(CO)_3$, 79721-59-8; $[CH_3N(PF_2)_2]_5W_2CO$, 79769-50-9.

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Trans Isomers of Ruthenium(II) Complexes Containing Two Bipyridine Ligands

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Three different reactions which lead to the formation of complexes of the type *trans*-Ru(2,2′-bipyridine)$_2XY^{n+}$ have been investigated. The thermal substitution reactions of *trans*-Ru(2,2′-bipyridine)$_2(OH_2)_2^{2+}$ appear to offer the most general and efficient synthetic route to this group of compounds. Species containing pyridine, pyrazole, acetonitrile, substituted phosphines, NO_2^-, NO^+, and Cl^- have been prepared.

Introduction

Transition-metal complexes of the type $M(bpy)_2XY^{n+}$ (where bpy = 2,2′-bipyridine) were thought, for many years, to be unstable in the trans geometry. The instability was attributed to the expected unfavorable interaction of the α hydrogens on the opposing bipyridine ligands. The idea seemed to be well-founded in light of the complete lack of examples and the many incorrect isomeric assignments.[1] In 1972, however, the crystal structure of $[Pd(bpy)_2](NO_3)_2$ was reported,[2] followed a few years later by the structures[3,4] of $[Pt(bpy)_2](TCNQ)_2$ and $Cu(bpy)_2(ClO_4)_2$. In recent years two additional examples have appeared. The first was a report, which lacked definitive structural evidence, by Krause[5] concerning the synthesis of *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$. The second was the photochemical conversion of *cis*-$Ru(bpy)_2(OH_2)_2^{2+}$ to *trans*-$Ru(bpy)_2(OH_2)_2^{2+}$ reported by one of the authors.[6] In the latter example, the geometry of the oxidized complex *trans*-$[Ru(bpy)_2(OH)(OH_2)](ClO_4)_2$ was verified by an X-ray structure determination. The existence of this collection of complexes suggests that complexes in this geometry are not as unstable as suspected. There remains to be found, however, general synthetic procedures which will enable other species to be produced and studied.

To this end we wish to report some observations dealing with reactions which yield complexes of the general type *trans*-$Ru(bpy)_2XY^{n+}$. The first of these concerns the stereoretentive substitution reactions of *trans*-$Ru(bpy)_2(OH_2)_2^{2+}$. The second

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focuses on some reactions which rely on steric bulk of the incoming ligands to force the products into the trans geometry. Lastly, we would like to present evidence which verifies the stereochemical course of the reactions reported by Krause.[5]

Experimental Section

Materials. The complexes *cis*-$Ru(bpy)_2Cl_2$ and *trans*-$[Ru(bpy)_2(OH_2)_2](ClO_4)_2$ were prepared as previously described.[6,7] In some cases, 4,4'-dimethyl-2,2'-bipyridine[8] was substituted for 2,2'-bipyridine in these procedures. Acetonitrile (Fisher 488-x) was either dried over 4-Å molecular sieves or distilled over P_2O_5 for the electrochemical experiments. Tetrabutylammonium hexafluorophosphate was prepared from tetrabutylammonium iodide and ammonium hexafluorophosphate and recrystallized from water/ethanol. Column chromatography was carried out with Fisher A-540 alumina as received in 2.5-cm × 10-cm columns. Other materials were reagent grade and used as received. Elemental analysis was performed by Integral Microanalytical Laboratories, Raleigh, NC, and Galbraith Laboratories, Inc., Knoxville, TN.

***trans*-$[Ru(bpy)_2(pyz)_2](PF_6)_2$.** *trans*-$[Ru(bpy)_2(OH_2)_2](ClO_4)_2$ (0.15 g) was dissolved in 30 mL of water, and an excess of pyrazole (pyz) (0.1 g) was added. The solution was stirred in the dark for 12 h under argon. The deep red product was filtered out, washed with 2-propanol and then ethyl ether, and air-dried; yield 64%. Minor impurities were removed by chromatography on alumina with 10% methanol in acetone as the eluant. The complex was recovered by acidification of the eluate with concentrated hexafluorophosphoric acid followed by precipitation with ethyl ether. The purified product was filtered out and air-dried. Anal. Calcd for $RuC_{26}H_{24}N_8F_{12}P_2{\cdot}H_2O$: C, 36.42; H, 3.05; N, 13.07. Found: C, 36.64; H, 3.06; N, 12.41.

***trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$.** A mixture of *trans*-$[Ru(bpy)_2(H_2O)_2](ClO_4)_2$ (0.15 g) and pyridine (0.5 mL) was refluxed under an argon atmosphere for 1 h. After cooling, the orange-red product was filtered out, washed with water, then 2-propanol, and finally with ethyl ether, and air dried; yield 51%. Anal. Calcd for $RuC_{30}H_{26}N_6Cl_2O_8$: C, 46.76; H, 3.40; N, 10.91. Found: C, 46.56; H, 3.54; N, 10.77.

***trans*-$[Ru(bpy)_2(CH_3CN)(H_2O)](ClO_4)_2$.** A procedure similar to that used for *trans*-$[Ru(bpy)_2(pyz)_2](PF_6)_2$ was employed except acetonitrile (0.5 mL/0.150 g of $[Ru(bpy)_2(OH_2)_2](ClO_4)_2$) was substituted for pyrazole. No purification beyond an additional wash with water was necessary. Yields averaged 70%. Anal. Calcd for $RuC_{22}H_{19}N_5Cl_2O_8{\cdot}H_2O$: C, 38.33; H, 3.36; N, 10.15. Found: C, 38.36; H, 3.34; N, 9.89.

***trans*-$[Ru(bpy)_2(CH_3CN)_2](ClO_4)_2$.** The $[Ru(bpy)_2(CH_3CN)(OH_2)](ClO_4)_2$ from the previous procedure was dissolved in 20 mL of acetonitrile and refluxed under argon for 1 h. After cooling, the bright yellow product was precipitated by adding the reaction mixture slowly to 200 mL of ethyl ether. The precipitate was filtered out, washed with ethyl ether, and air-dried. The solvent was colorless after filtration indicating near quantitative conversion. Anal. Calcd for $RuC_{24}H_{22}N_6Cl_2O_8$: C, 41.51; H, 3.19; N, 12.10. Found: C, 41.33; H, 3.22; N, 11.96.

***trans*-$Ru(bpy)_2Cl_2$.** A procedure similar to that used for *trans*-$[Ru(bpy)_2(pyz)_2](PF_6)_2$ was used except lithium chloride (0.75 g/0.150 g of $[Ru(bpy)_2(OH_2)_2](ClO_4)_2$) was substituted for pyrazole. Alternatively the complex was prepared by irradiating a solution of $Ru(bpy)_2CO_3$ (0.15 g in 100 mL of 0.6 M HCl) for 2 h at 25 °C under argon. A 275-W sunlamp was used as the source. The workup in either case consisted of filtering out the product, washing with water, 2-propanol, and finally ethyl ether, and air-drying. The product was then suspended in CH_3CN and filtered out and the washing procedure repeated. Anal. Calcd for $RuC_{20}H_{16}N_4Cl_2{\cdot}H_2O$: C, 47.82; H, 3.61; N, 11.15. Found: C, 47.85; H, 3.73; N, 10.99.

***trans*-$[Ru(Me_2bpy)_2(PPh_3)_2](PF_6)_2$.**[9] This complex was prepared by refluxing $Ru(Me_2bpy)_2Cl_2$ (0.10 g) with excess triphenylphosphine (0.25 g) in 60 mL of ethanol/water (1:1) for 12 h. The reaction mixture was evaporated under vacuum to half volume, and a mixture of products was precipitated by adding a small amount of aqueous ammonium hexafluorophosphate solution. The precipitate was washed with 2-propanol and then with ethyl ether and air-dried. Separation of *trans*-$[Ru(Me_2bpy)_2(PPh_3)_2](PF_6)_2$ from the other major product, *cis*-$[Ru(Me_2bpy)_2(PPh_3)(Cl)]PF_6$, was accomplished by column chromatography using alumina with dichloromethane/acetone as an eluant. The complexes were recovered by reducing the volumes of the appropriate fractions to 20–30 mL and then precipitating with ethyl ether. The respective yields were 20% and 2%. Anal. Calcd for $RuC_{60}H_{54}N_4P_4F_{12}$: C, 56.12; H, 4.23; N, 4.36. Found: C, 55.51; H, 4.39; N, 4.26.

***trans*-$[Ru(Me_2bpy)_2(PPh_2Me)_2](PF_6)_2$.** This complex was prepared in a manner similar to the preceding case but with excess methyldiphenylphosphine as the ligand. Cyclic voltammetry indicated a 1:1 ratio of cis to trans isomers in the crude products. The trans isomer was separated from the cis isomer by allowing an acetone/ethanol solution to slowly evaporate until the trans isomer crystallized out of solution. The cis isomer remained in solution and was recovered by the addition of ethyl ether. Anal. Calcd for $RuC_{50}H_{50}N_4P_4F_{12}$: C, 51.77; H, 4.34; N, 4.83. Found: C, 51.74; H, 4.45; N, 4.63.

***trans*$[Ru(Me_2bpy)_2(PPhMe_2)_2](PF_6)_2$.** This complex was prepared in a manner similar to that described for $[Ru(Me_2bpy)_2(PPh_3)_2](PF_6)_2$. The trans isomer was purified by allowing a 1,2-dichloroethane solution to evaporate nearly to dryness. The crystals were collected by filtration and washed with 1,2-dichloroethane and finally with ethyl ether. The cis isomer could not be obtained completely free of the trans isomer in this case. Anal. Calcd for $RuC_{40}H_{46}N_4P_4F_{12}$: C, 46.37; H, 4.48; N, 5.41. Found: C, 45.66; H, 4.47; N, 5.09.

***trans*-$[Ru(bpy)_2(NO)(OH)](PF_6)_2$.** *trans*-$[Ru(bpy)_2(OH_2)_2](ClO_4)_2$ (0.18 g) was dissolved in 30 mL of water containing excess sodium nitrite (0.30 g). The solution was stirred for 12 h under argon in the dark. The precipitate was filtered out, washed with 2-propanol and then ethyl ether, and air-dried. The dried material was suspended in 25 mL of methanol, and 0.5 mL of concentrated hexafluorophosphoric acid was added. The solution was stirred until a uniform tan precipitate was formed, about 3 h. The product was filtered out, washed with ethyl ether, and air-dried; yield 68%. Anal. Calcd for $RuC_{20}H_{17}N_5O_2P_2F_{12}$: C, 32.01; H, 2.28; N, 9.33. Found: C, 31.97; H, 2.40; N, 9.28.

Equipment. UV–visible absorption spectra were obtained with a Cary 14 spectrophotometer. Electrochemical measurements were carried out at 22 ± 2 °C in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. A home-built ramp generator,[10] a HI-TEK Instruments potentiostat, and a Housten Model 164 X-Y recorder were used in conjunction with a platinum-bead-working electrode, a platinum-wire auxiliary electrode, and a saturated sodium chloride calomel (SSCE) reference electrode. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. NMR spectra were obtained on a Varian EM 360 NMR spectrometer.

Results and Discussion

A series of ruthenium(II) complexes of the type *trans*-$Ru(bpy)_2XY^{n+}$ have been isolated from the reactions of *trans*-$Ru(bpy)_2(OH_2)_2{}^{2+}$ with pyridine, pyrazole, acetonitrile, nitrite, and chloride. The reactions were carried out for the most part in aqueous solution at room temperature in the presence of excess ligand. In all of the reactions studied, either the monosubstituted or disubstituted product spontaneously precipitated from solution once formed. Since both the starting materials and the cis isomers of the products are soluble under the conditions of the reaction, only a minimal cleanup effort was required to obtain analytically and isomerically pure products. The yields for these reactions were greater than 50% in all cases and in some cases nearly quantitative.

The reactions of *cis*-$Ru(bpy)_2Cl_2$ or *cis*-$Ru(Me_2bpy)_2Cl_2$ with substituted phosphines in aqueous ethanolic solution at refluxing temperatures also gave products in the trans geometry. In these cases it was presumed that the ligands used were sufficiently bulky to make formation of the cis isomers difficult or impossible. The fact that the trans isomers could be prepared in this fashion, which in the past has led exclusively to cis isomers,[11] supports the presumption. These reactions suffer

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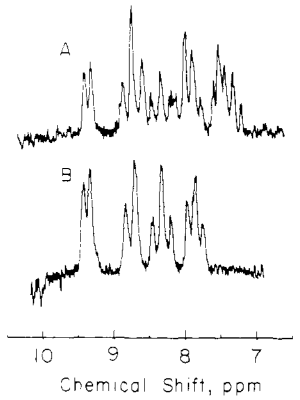

Figure 1. Proton NMR spectra of (A) *cis*-$[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$ and (B) *trans*-$[Ru(bpy)_2(CH_3CN)_2](ClO_4)_2$ in Me_2SO-d_6.

from a synthetic point of view in that they result in a mixture of cis and trans isomers.

It was mentioned in the Introduction that Krause reported[5] the synthesis of *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$ but that the supporting evidence for the assignment of the trans geometry was weak. In order to verify the geometry, we have synthesized *trans*-$[Ru(Me_2bpy)_2(py)_2](ClO_4)_2$ according to the procedure described by Krause.[5] Analysis of the ^1H NMR spectra, which follows, confirms that Krause was indeed correct in his structural assignment.

Proton NMR spectrscopy proved to be the most valuable tool for determining the geometric nature of the products obtained in reactions described above. Figure 1 illustrates the ^1H NMR of *trans*-$[Ru(bpy)_2(CH_3CN)_2](ClO_4)_2$ and *cis*-$[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$ for comparison. The trans isomers are characterized by a relatively simple pattern of resonances from the chelate ring protons. The pattern consists of two doublets and two triplets at slightly higher field than the doublets. The proton spectrum of free 2,2′-bipyridine shows the same major splitting pattern.[12] Some long-range coupling which causes additional, but weak, splitting of the major resonances is also apparent in most cases. The relatively simple spectra are a result of the high symmetry of the bipyridine moieties in the trans complexes. The free ligand, which is planar in solution, is also highly symmetrical. It should be noted that in cases in which other resonances complicate analysis of this region of the spectrum, the doublet corresponding to the 3 and 3′ protons on the bipyridine (8.7 ppm in the case shown) is most diagnostic for isomeric assignments. This resonance appeared as a triplet or more complex pattern in all the cis isomers examined and was only occasionally obscured by other absorptions. Indeed, the ^1H NMR spectra of complexes with the cis geometry[13] show more complex splitting patterns overall than the trans isomers. The complexity arises from the fact that in the cis geometry the individual rings of the bipyridyl ligand are not equivalent. Thus we get the spectra of two slightly dissimilar rings superimposed on one another.

The NMR analysis of the phosphine complexes is obviously not as straight forward because of the additional phenyl resonances. In order to circumvent this problem we prepared the phosphine complexes using 4,4′-dimethyl-2,2′-bipyridine in place of 2,2′-bipyridine. The methyl substituents which should not alter the sterochemical course of the reactions were expected to provide a simple handle for distinguishing between cis and trans isomers. In particular, the trans isomers were expected to exhibit only a single methyl resonance while the cis isomers were expected to exhibit two slightly different methyl resonances. This was indeed observed. The rationale behind this behavior is essentially the same as that for the ring protons of the two isomers. Final verification of the geometry in these cases rests on the X-ray structure determination of *trans*-$[Ru(Me_2bpy)_2(py)_2](PF_6)_2$ and *trans*-$[Ru(bpy)_2(PPh_3)_2](PF_6)_2$, which will appear in a separate report.

The product of the reaction of *trans*-$Ru(bpy)_2(OH_2)_2^{2+}$ with Cl^- is more difficult to unambiguously characterize than the previously described complexes. The difficulty stems from the fact that this species is completely insoluble in all of the usual solvents. The following observations, however, strongly support the identification of this product as *trans*-$Ru(bpy)_2Cl_2$. Elemental analysis of the product is consistent only with $Ru(bpy)_2Cl_2{\cdot}H_2O$, $[Ru(bpy)_2Cl(H_2O)]Cl$, or a mixture of the two. The cis isomers can be eliminated because these are soluble in water. In addition, products which are identical by comparison of IR spectra are obtained whether the reaction is carried out in water or dimethylformamide. Finally, a distinctly blue species, most probably *trans*$[Ru(bpy)_2Cl(H_2O)]Cl$, is apparent in the early stages of the substitution reaction in water, and this species is slowly replaced by the black final product, *trans*-$Ru(bpy)_2Cl_2$. The intermediate is soluble enough to be removed from the final product by washing with various solvents.

As indicated above, it is desirable in some instances to form complexes of 4,4′-dimethyl-2,2′-bipyridine in place of 2,2′-bipyridine. Unfortunately, the photolysis of $Ru(Me_2bpy)_2CO_3$ under the conditions originally described[6] for the preparation of *trans*-$Ru(bpy)_2(OH_2)_2^{2+}$ does not result in the corresponding trans aquo species but instead leads predominantly to ruthenium(III) species. Since the oxidation is known to occur via perchlorate, other acids were tried. Photolysis proceeded as expected in 1 N sulfuric acid, but the *trans*-$Ru(bpy)_2(OH_2)_2^{2+}$ was impossible to separate cleanly. Substitution of hydrochloric acid resulted in the formation and precipitation of *trans*-$Ru(bpy)_2Cl_2$ during photolysis. The photolysis in hydrochloric acid worked equally well with the 4,4′-dimethyl-2,2′-bipyridine-substituted complex. No attempt, however, has been made to utilize the *trans*-$Ru(Me_2bpy)_2Cl_2$ or *trans*-$Ru(bpy)_2Cl_2$ as a starting material for further synthesis. *trans*-$Ru(bpy)_2Cl_2$ is not very promising in this regard because it is essentially insoluble in all of the solvents tested. *trans*-$Ru(Me_2bpy)_2Cl_2$ on the other hand is soluble in methanol, dimethyl sulfoxide, or dimethylformamide but undergoes further reactions which are currently under investigation.

Thermal substitution reactions involving nitrite ion indicate a similar course of reaction to that observed with chloride. Again the products were completely insoluble in all of the solvents tested and were difficult to analyze unambiguously. We have, however, been able to convert the rather intractable nitrite complex, presumably *trans*-$[Ru(bpy)_2(NO_2)(H_2O)]NO_2$ or $Ru(bpy)_2(NO_2)_2$, to the nitrosyl complex *trans*-$[Ru(bpy)_2(NO)(OH)](PF_6)_2$ using a procedure similar to that reported by Meyer.[14] The nitrosyl complex is sufficiently soluble to permit NMR analysis, and the observed resonances clearly indicate the trans geometry. The fact that the isolated product contained coordinated hydroxide rather than water is consistent with the pK_a's measured for the corresponding cis isomers.[15] A sharp absorbance observed at 3600 cm^{-1} in the IR spectrum also supports the presence of hydroxide.

Neither visible nor infrared spectroscopy nor cyclic voltammetry are suitable for making an isomeric distinction where

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Table I. Visible Absorption and Cyclic Voltammetric Data for Various Cis and Trans Complexes

$Ru(bpy)_2XY^{2+}$ XY	$E_{1/2}$,[a] V		λ_{max},[b] nm	
	cis	trans	cis	trans
$(py)_2$	1.30	1.28	455	475
$(pyz)_2$	1.18	1.11	473	480
$(CH_3CN)_2$	1.44	1.44	425	440
$(CH_3CN)(H_2O)$	*c*	1.15	445[d]	465
$(P(CH_3)_2(C_6H_5))_2$	1.45	1.33	396	431
$(P(CH_3)(C_6H_5)_2)_2$	1.52	1.39	387	427
$(H_2O)_2$	0.63[e]	0.46[e]	480	495

[a] $E_{1/2}$ vs. SSCE in CH_3CN/0.1 M TBAH. [b] Acetone solution except phosphines which are in acetonitrile and aquo complexes which are in 0.5 M CF_3COOH. [c] Rapid exchange of H_2O for solvent. [d] 1 N H_2SO_4. [e] 1 N aqueous CF_3COOH vs. SCE reference.

only one isomer is available, but some interesting trends are nevertheless apparent. The visible absorption maxima and $E_{1/2}$'s for all known cis–trans isomer pairs of ruthenium(II) complexes of the type $Ru(bpy)_2XY^{n+}$ are listed in Table I. The most obvious trend concerns the charge-transfer maxima. In every case the trans isomers absorb at lower energies than the corresponding cis isomers. These transitions have been assigned[16] as charge-transfer to ligand transitions, presumably to a π^* level of the bipyridine ligand. The Ru(III)/Ru(II) reduction potentials as reflected by the reversible $E_{1/2}$'s also show a consistent trend in that the trans isomers are oxidized at similar or less positive potentials than the corresponding cis isomers. Both of these observations suggest a stabilization of the dπ levels and a lowering of electron density at the Ru(II) center in the cis isomers relative to those in the trans isomers.[17] Preliminary analysis of the infrared spectra of these complexes did not show any reliable differences which might be used to make a distinction between the two isomers.

A final word concerning the stability of the trans isomers is perhaps in order. Simply stated, they are remarkably stable and show little or no tendency to isomerize. Several attempts were made to quantify this aspect of the chemistry by measuring either kinetic or equilibrium parameters, but thermal isomerization could not be obtained in any of the complexes studied. The most extreme conditions employed consisted of heating acetone solutions of the complexes to 60 °C in sealed tubes for 12 h with 0.1 M ligand. No isomerization was observed with the trans complexes of pyridine, pyrazole, acetonitrile, or the substituted phosphines. The problem is under current consideration, and we are pursuing the possibility that the high ligand concentration is inhibiting the reaction, perhaps, by capturing one of the reaction intermediates before rearrangement can occur.

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Registry No. *trans*-$[Ru(bpy)_2(pyz)_2](PF_6)_2$, 79733-75-8; *trans*-$[Ru(bpy)_2(py)_2](ClO_4)_2$, 63358-69-0; *trans*-$[Ru(bpy)_2(CH_3CN)(H_2O)](ClO_4)_2$, 79681-78-0; *trans*-$[Ru(bpy)_2(CH_3CN)_2](ClO_4)_2$, 79732-91-5; *trans*-$Ru(bpy)_2Cl_2$, 34795-02-3; *trans*-$[Ru(Me_2bpy)_2(PPh_3)_2](PF_6)_2$, 79681-80-4; *trans*-$[Ru(Me_2bpy)_2(PPh_2Me)_2](PF_6)_2$, 79681-82-6; *trans*-$[Ru(Me_2bpy)_2(PPhMe_2)_2](PF_6)_2$, 79681-84-8; *trans*-$[Ru(bpy)_2(NO)(OH)](PF_6)_2$, 79681-86-0; *cis*-$[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$, 55124-54-4; *cis*-$[Ru(Me_2bpy)_2(PPh_3)(Cl)]PF_6$, 79681-88-2; *trans*-$[Ru(bpy)_2(OH_2)_2](ClO_4)_2$, 72203-26-0; $Ru(bpy)_2CO_3$, 59460-48-9; *cis*-$Ru(Me_2bpy)_2Cl_2$, 68510-55-4.

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Selectivity in Reactions of Alkyl–Aryl–Transition-Metal Complexes with Electrophiles

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The new methylarylmetal complexes *cis*-$[AuMe_2Ph(PPh_3)]$, *cis*-$[AuMe_2(4\text{-}MeC_6H_4)(PPh_3)]$, $[PtMe(4\text{-}MeC_6H_4)(C_8H_{12})]$, *cis*-$[PtMePh(PMePh_2)_2]$, and *cis*-$[PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2]$ have been prepared and characterized. In reactions with electrophilic reagents such as HCl, $HgCl_2$, and $[PtI_2(PMe_2Ph)_2]$, the complexes undergo selective cleavage of a methyl–metal bond (e.g., *cis*-$[PtMePh(PMePh_2)_2]$) or an aryl–metal bond (e.g., *cis*-$[AuMe_2Ph(PPh_3)]$, $[PtMe(4\text{-}MeC_6H_4)(C_8H_{12})]$). From the selectivity observed and from studies of relative rates of reaction, it is argued that the S_E2 mechanism leads to selective aryl–metal bond cleavage and that a different mechanism, probably involving an oxidative-addition–reductive-elimination sequence, leads to selective methyl–metal bond cleavage.

Introduction

There has been considerable interest in the mechanisms of reactions of electrophiles with alkyl and aryl derivatives of transition metals.[1] In such complexes there are typically high-energy occupied orbitals having M–C σ-bonding character and also nonbonding d orbitals.[1-4] Attack of the electrophile at a metal–carbon bond gives cleavage of this bond by the classical S_E2 mechanism,[5,6] but attack at the metal (oxidative addition) followed by reductive elimination can yield the same product.[1-4,7,8] This mechanism has been termed

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