

symmetry plane in $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Cr}$ 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*- $[\text{RN}(\text{PF}_2)_2]_2\text{Cr}(\text{CO})_4$ 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*- $\text{L}_2\text{M}(\text{CO})_4$ and *mer*- $\text{L}_3\text{M}(\text{CO})_3$ 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*- $\text{L}_2\text{M}(\text{CO})_4$ 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 $\text{RN}(\text{PF}_2)_2$ ligands is lower than that of the phosphorus atom in PCl_3 but comparable with the phosphorus atom in $\text{C}_2\text{H}_5\text{OPCl}_2$.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 $\nu(\text{CO})$ spectra of $\text{RN}(\text{PF}_2)_2$ 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. $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Cr}(\text{CO})_4$, 73949-36-7; *trans*- $[\text{CH}_3\text{N}(\text{PF}_2)_2]\text{Cr}(\text{CO})_4$, 73949-37-8; $\text{CH}_3\text{N}(\text{PF}_2)_2\text{Mo}(\text{CO})_4$, 79734-75-1; *cis*- $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Mo}(\text{CO})_4$, 79721-42-9; $\text{CH}_3\text{N}(\text{PF}_2)_2\text{W}(\text{CO})_4$, 79734-76-2; *cis*- $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{W}(\text{CO})_4$, 79721-43-0; $\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2\text{Cr}(\text{CO})_4$, 79721-44-1; *trans*- $[\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2]_2\text{Cr}(\text{CO})_4$, 79721-45-2; $\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2\text{Mo}(\text{CO})_4$, 79721-46-3; *cis*- $[\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2]_2\text{Mo}(\text{CO})_4$, 79721-47-4; $\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2\text{W}(\text{CO})_4$, 79721-48-5; *trans*- $[\text{CH}_3\text{N}(\text{PF}_2)_2][\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2]\text{Cr}(\text{CO})_4$, 79721-49-6; *mer*- $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Cr}(\text{CO})_3$, 79721-50-9; *mer*- $[\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2]_2\text{Cr}(\text{CO})_3$, 79734-77-3; $[\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2]_3\text{Cr}_2(\text{CO})_6$, 79721-51-0; $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Cr}_2(\text{CO})_5$, 79721-52-1; $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Mo}_2(\text{CO})_5$, 79721-55-4; $[\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2]_3\text{Mo}_2(\text{CO})_5$, 79721-56-5; $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{W}_2(\text{CO})_5$, 79734-78-4; $[\text{CH}_3\text{N}(\text{PF}_2)_2]_3\text{Mo}_2\text{CO}$, 79746-02-4; $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Mo}_2(\text{CO})_3$, 79721-57-6; $[\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2]_3\text{Mo}_2(\text{CO})_2$, 79734-79-5; $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{W}_2(\text{CO})_3$, 79721-58-7; *mer*- $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{Mo}(\text{CO})_3$, 79721-53-2; *mer*- $[\text{CH}_3\text{N}(\text{PF}_2)_2]_2\text{W}(\text{CO})_3$, 79721-54-3; $[\text{CH}_3\text{N}(\text{PF}_2)_2]_4\text{Cr}_2(\text{CO})_3$, 79734-80-8; $\text{CH}_3\text{N}(\text{PF}_2)_2$, 17648-18-9; $\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2$, 23611-36-1; $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_4$, 12146-36-0; $\text{C}_7\text{H}_8\text{Mo}(\text{CO})_4$, 12146-37-1; $\text{C}_7\text{H}_8\text{W}(\text{CO})_4$, 12129-25-8; $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_3$, 12125-72-3; $\text{Cr}(\text{CO})_6$, 13007-92-6; $\text{W}(\text{CO})_6$, 14040-11-0; $\text{C}_7\text{H}_8\text{Mo}(\text{CO})_3$, 12125-77-8; $\text{Mo}(\text{CO})_6$, 13939-06-5; $[\text{C}_6\text{H}_5\text{N}(\text{PF}_2)_2]_4\text{Mo}_2(\text{CO})_3$, 79721-59-8; $[\text{CH}_3\text{N}(\text{PF}_2)_2]_5\text{W}_2\text{CO}$, 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*- $\text{Ru}(2,2'\text{-bipyridine})_2\text{XY}^{n+}$ have been investigated. The thermal substitution reactions of *trans*- $\text{Ru}(2,2'\text{-bipyridine})_2(\text{OH}_2)_2^{2+}$ 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 $\text{M}(\text{bpy})_2\text{XY}^{n+}$ (where $\text{bpy} = 2,2'\text{-bipyridine}$) 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 $[\text{Pd}(\text{bpy})_2](\text{NO}_3)_2$ was reported,² followed a few years later by the structures^{3,4} of $[\text{Pt}(\text{bpy})_2](\text{TCNQ})_2$ and $\text{Cu}(\text{bpy})_2(\text{ClO}_4)_2$. In recent years two additional examples have appeared. The first was a report, which lacked definitive structural evidence, by Krause⁵ concerning the synthesis of *trans*- $[\text{Ru}(\text{bpy})_2(\text{py})_2](\text{ClO}_4)_2$. The second was the photochemical conversion of *cis*- $\text{Ru}(\text{bpy})_2(\text{OH}_2)_2^{2+}$ to *trans*- $\text{Ru}(\text{bpy})_2(\text{OH}_2)_2^{2+}$ reported by one of the

authors.⁶ In the latter example, the geometry of the oxidized complex *trans*- $[\text{Ru}(\text{bpy})_2(\text{OH})(\text{OH}_2)](\text{ClO}_4)_2$ 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*- $\text{Ru}(\text{bpy})_2\text{XY}^{n+}$. The first of these concerns the stereoretentive substitution reactions of *trans*- $\text{Ru}(\text{bpy})_2(\text{OH}_2)_2^{2+}$. 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)₂Cl₂ and *trans*-[Ru(bpy)₂(OH)₂](ClO₄)₂ were prepared as previously described.^{6,7} In some cases, 4,4'-dimethyl-2,2'-bipyridine⁸ was substituted for 2,2'-bipyridine in these procedures. Acetonitrile (Fisher 488-x) was either dried over 4-Å molecular sieves or distilled over P₂O₅ 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](PF₆)₂.** *trans*-[Ru(bpy)₂(OH)₂](ClO₄)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 RuC₂₆H₂₄N₈F₁₂P₂H₂O: 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](ClO₄)₂.** A mixture of *trans*-[Ru(bpy)₂(H₂O)₂](ClO₄)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 RuC₃₀H₂₆N₆Cl₂O₈: C, 46.76; H, 3.40; N, 10.91. Found: C, 46.56; H, 3.54; N, 10.77.

***trans*-[Ru(bpy)₂(CH₃CN)(H₂O)](ClO₄)₂.** A procedure similar to that used for *trans*-[Ru(bpy)₂(pyz)₂](PF₆)₂ was employed except acetonitrile (0.5 mL/0.150 g of [Ru(bpy)₂(OH)₂](ClO₄)₂) was substituted for pyrazole. No purification beyond an additional wash with water was necessary. Yields averaged 70%. Anal. Calcd for RuC₂₂H₁₉N₅Cl₂O₈H₂O: C, 38.33; H, 3.36; N, 10.15. Found: C, 38.36; H, 3.34; N, 9.89.

***trans*-[Ru(bpy)₂(CH₃CN)₂](ClO₄)₂.** The [Ru(bpy)₂(CH₃CN)(OH₂)](ClO₄)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 RuC₂₄H₂₂N₆Cl₂O₈: C, 41.51; H, 3.19; N, 12.10. Found: C, 41.33; H, 3.22; N, 11.96.

***trans*-Ru(bpy)₂Cl₂.** A procedure similar to that used for *trans*-[Ru(bpy)₂(pyz)₂](PF₆)₂ was used except lithium chloride (0.75 g/0.150 g of [Ru(bpy)₂(OH)₂](ClO₄)₂) was substituted for pyrazole. Alternatively the complex was prepared by irradiating a solution of Ru(bpy)₂CO₃ (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 CH₃CN and filtered out and the washing procedure repeated. Anal. Calcd for RuC₂₀H₁₆N₄Cl₂H₂O: C, 47.82; H, 3.61; N, 11.15. Found: C, 47.85; H, 3.73; N, 10.99.

***trans*-[Ru(Me₂bpy)₂(PPh₃)₂](PF₆)₂.**⁹ This complex was prepared by refluxing Ru(Me₂bpy)₂Cl₂ (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(Me₂bpy)₂(PPh₃)₂](PF₆)₂ from the other major product, *cis*-[Ru(Me₂bpy)₂(PPh₃)₂](Cl)₂PF₆, 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 RuC₆₀H₅₄N₄P₄F₁₂: C, 56.12; H, 4.23; N, 4.36. Found: C, 55.51; H, 4.39; N, 4.26.

***trans*-[Ru(Me₂bpy)₂(PPh₂Me)₂](PF₆)₂.** This complex was prepared in a manner similar to the preceding case but with excess methyl-diphenylphosphine 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 RuC₅₀H₅₀N₄P₄F₁₂: C, 51.77; H, 4.34; N, 4.83. Found: C, 51.74; H, 4.45; N, 4.63.

***trans*-[Ru(Me₂bpy)₂(PPhMe₂)₂](PF₆)₂.** This complex was prepared in a manner similar to that described for [Ru(Me₂bpy)₂(PPh₃)₂](PF₆)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 RuC₄₀H₄₆N₄P₄F₁₂: 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)](PF₆)₂.** *trans*-[Ru(bpy)₂(OH)₂](ClO₄)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 RuC₂₀H₁₇N₅O₃P₂F₁₂: 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 Houston 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)₂XY²⁺ have been isolated from the reactions of *trans*-Ru(bpy)₂(OH)₂²⁺ 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)₂Cl₂ or *cis*-Ru(Me₂bpy)₂Cl₂ 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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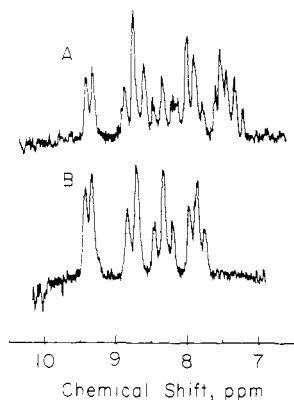


Figure 1. Proton NMR spectra of (A) *cis*-[Ru(bpy)₂(CH₃CN)₂](PF₆)₂ and (B) *trans*-[Ru(bpy)₂(CH₃CN)₂](ClO₄)₂ in Me₂SO-*d*₆.

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 reported⁵ the synthesis of *trans*-[Ru(bpy)₂(py)₂](ClO₄)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(Me₂bpy)₂(py)₂](ClO₄)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 spectroscopy 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(CH₃CN)₂](ClO₄)₂ and *cis*-[Ru(bpy)₂(CH₃CN)₂](PF₆)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* geometry¹³ 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 stereochemical course of the reactions were ex-

pected 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(Me₂bpy)₂(py)₂](PF₆)₂ and *trans*-[Ru(bpy)₂(PPh₃)₂](PF₆)₂, which will appear in a separate report.

The product of the reaction of *trans*-Ru(bpy)₂(OH₂)₂²⁺ 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)₂Cl₂. Elemental analysis of the product is consistent only with Ru(bpy)₂Cl₂·H₂O, [Ru(bpy)₂Cl(H₂O)]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(H₂O)]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)₂Cl₂. 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(Me₂bpy)₂CO₃ under the conditions originally described⁶ for the preparation of *trans*-Ru(bpy)₂(OH₂)₂²⁺ 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(OH₂)₂²⁺ was impossible to separate cleanly. Substitution of hydrochloric acid resulted in the formation and precipitation of *trans*-Ru(bpy)₂Cl₂ 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(Me₂bpy)₂Cl₂ or *trans*-Ru(bpy)₂Cl₂ as a starting material for further synthesis. *trans*-Ru(bpy)₂Cl₂ is not very promising in this regard because it is essentially insoluble in all of the solvents tested. *trans*-Ru(Me₂bpy)₂Cl₂ 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(NO₂)(H₂O)]-NO₂ or Ru(bpy)₂(NO₂)₂, to the nitrosyl complex *trans*-[Ru(bpy)₂(NO)(OH)](PF₆)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) ₂ XY ²⁺ XY	<i>E</i> _{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 ₃ CN) ₂	1.44	1.44	425	440
(CH ₃ CN)(H ₂ O)	<i>c</i>	1.15	445 ^d	465
(P(CH ₃) ₂ (C ₆ H ₅)) ₂	1.45	1.33	396	431
(P(CH ₃)(C ₆ H ₅)) ₂	1.52	1.39	387	427
(H ₂ O) ₂	0.63 ^e	0.46 ^e	480	495

^a *E*_{1/2} vs. SSCE in CH₃CN/0.1 M TBAH. ^b Acetone solution except phosphines which are in acetonitrile and aquo complexes which are in 0.5 M CF₃COOH. ^c Rapid exchange of H₂O for solvent. ^d 1 N H₂SO₄. ^e 1 N aqueous CF₃COOH 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)₂XY²⁺ 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 assigned¹⁶ 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 *d* π levels and a lowering of electron density at the Ru(II) center in the cis isomers relative to those in the trans isomers.¹⁷

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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](PF₆)₂, 79733-75-8; *trans*-[Ru(bpy)₂(py)₂](ClO₄)₂, 63358-69-0; *trans*-[Ru(bpy)₂-(CH₃CN)(H₂O)](ClO₄)₂, 79681-78-0; *trans*-[Ru(bpy)₂-(CH₃CN)₂](ClO₄)₂, 79732-91-5; *trans*-Ru(bpy)₂Cl₂, 34795-02-3; *trans*-[Ru(Me₂bpy)₂(PPh₃)₂](PF₆)₂, 79681-80-4; *trans*-[Ru(Me₂bpy)₂(PPhMe)₂](PF₆)₂, 79681-82-6; *trans*-[Ru(Me₂bpy)₂-(PPhMe)₂](PF₆)₂, 79681-84-8; *trans*-[Ru(bpy)₂(NO)(OH)](PF₆)₂, 79681-86-0; *cis*-[Ru(bpy)₂(CH₃CN)₂](PF₆)₂, 55124-54-4; *cis*-[Ru(Me₂bpy)₂(PPh₃)(Cl)]PF₆, 79681-88-2; *trans*-[Ru(bpy)₂(OH)₂](ClO₄)₂, 72203-26-0; Ru(bpy)₂CO₃, 59460-48-9; *cis*-Ru(Me₂bpy)₂Cl₂, 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*-[AuMe₂Ph(PPh₃)], *cis*-[AuMe₂(4-MeC₆H₄)(PPh₃)], [PtMe(4-MeC₆H₄)(C₈H₁₂)], *cis*-[PtMePh(PMePh₂)₂], and *cis*-[PtMe(4-MeC₆H₄)(PMe₂Ph)₂] have been prepared and characterized. In reactions with electrophilic reagents such as HCl, HgCl₂, and [PtI₂(PMe₂Ph)₂], the complexes undergo selective cleavage of a methyl-metal bond (e.g., *cis*-[PtMePh(PMePh₂)₂]) or an aryl-metal bond (e.g., *cis*-[AuMe₂Ph(PPh₃)], [PtMe(4-MeC₆H₄)(C₈H₁₂)]). 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 elec-

trophile 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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