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Photochemistry of *cis*- and *trans*-Ru(dmpe)$_2$Cl$_2$. Stereochemical Consequences of Aqueous and Nonaqueous Photosubstitution Processes[1]

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Ligand field excitation of *cis*- or *trans*-Ru(dmpe)$_2$Cl$_2$ in a variety of solvents results in the formation of trans photolysis products regardless of the geometry of the starting complex. In ethanol or methanol the product is *trans*-Ru(dmpe)$_2$Cl$_2$. In water/alcohol mixtures or water, the photolysis product is always *trans*-Ru(dmpe)$_2$(H$_2$O)Cl$^+$, and *trans*-Ru(dmpe)$_2$(Me$_2$SO)Cl$^+$ is always observed in Me$_2$SO. The quantum yields vary with solvent, but the nature of the ligand loss and product geometry is always the same. The results are consistent with the formation of a five-coordinate excited-state fragment as the primary photochemical process and the thermodynamic preference for [Ru(dmpe)$_2$Cl$^+$]* to rearrange to the isomer with the chloro ligand in the apical position.

Introduction

Models have been proposed[2-4] for the stereochemical rearrangements often observed during the ligand field photosubstitution reactions of d^6 transition-metal complexes. These models have been supported by a number of experimental studies using complexes of Rh(III)[5-10] and Co(III)[3] in aqueous solution. The model can be briefly described for an [MA$_4$XY] system as follows: (1) Photodissociation of Y occurs from the lowest, triplet, ligand field excited state in [MA$_4$XY]. (2) With use of apical and basal to denote the position of Y, it is found that apical and basal forms of [MA$_4$X] are separated by an often low activation barrier at the trigonal-bipyramidal structure, when the triplet electronic configuration is maintained during loss of Y. (3) For the triplet [MA$_4$X] fragment, the apical X position is favored when $e_\sigma{}^A > e_\sigma{}^X$,[2,3] while the basal X position is favored when $e_\sigma{}^X > e_\sigma{}^A$.[3] Thus, specific product geometries are expected and usually observed when rearrangement is faster than triplet → singlet deactivation of the [MA$_4$X] fragment.

The geometric product obtained from ligand field photosubstitution reactions of *cis*- and *trans*-[MA$_4$XY] depends on the relative values of four rate constants.[4,11] Two of these rate constants involve the interconversion of the triplet apical and basal forms of [MA$_4$X]. The other two rate constants involve electronic relaxation of the triplet square-pyramidal [MA$_4$X] fragments to the lower energy, singlet fragments. The magnitude of the four rate constants depends on the relative and absolute values of $e_\sigma{}^X$ and $e_\sigma{}^A$ as well as all parameters that affect the intersystem crossing rate (e.g., spin-orbit coupling constant of the metal) from the triplet to the singlet state in the [MA$_4$X] fragment. Qualitatively, one might expect that the heavier metals would have larger e_σ values (retard apical $\rightleftarrows$ basal conversion) and larger spin-orbit coupling constants (enhance intersystem crossing) and thus be less likely to undergo rearrangement and more likely to give geometric retention in photosubstitution reactions than lighter metals.

Previous experimental work[3-11] involving photorearrangements has involved mainly irradiation in aqueous solution. In terms of the model described above,[2,3] there is no consideration of solvent other than to obtain e_σ and e_π values from electronic absorption spectra. This lack of consideration of solvent has created some problems with the theory[12] predicting the nature of the labilized ligand, as some experimental reports[13] show that the nature of the leaving group changes with solvent. We were concerned about the effect of solvent on the rearrangement of the excited-state [MA$_4$X] fragment but felt this angular motion would be much less susceptible to solvent changes than the radial, and highly dipolar, effects of metal-ligand bond cleavage. To test this hypothesis concerning solvent and to enlarge the number of metal and ligand systems treated by the photostereochemical model,[2,3] we decided to study the ligand field photochemistry of *cis*- and *trans*-Ru(dmpe)$_2$Cl$_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) in aqueous and nonaqueous solvents. A recent study of Sullivan and Meyer[14] has shown that the analogous *cis*-Ru(dppm)$_2$Cl$_2$ (dppm = bis(diphenylphosphino)methane) undergoes cis to trans conversion photochemically.

Experimental Section

Materials. All reagents used in compound preparation were analytical reagent grade and used without further purification. The 1,2-bis(dimethylphosphino)ethane (dmpe) was obtained from Strem Chemical Co. and stored in an inert-atmosphere glovebox.

Synthesis of Metal Compounds. *trans*-Dichlorobis[1,2-bis(dimethylphosphino)ethane]ruthenium(II). This complex was prepared by the method of Chatt and Hayter.[15] A solution was prepared by the addition of 1.00 g of 1,2-bis(dimethylphosphino)ethane to 120 mL of ethanol, which had been degassed by two freeze-pump-thaw cycles in liquid nitrogen in a nitrogen glovebox. (Note: The phosphine ligands involved in these procedures are air sensitive, unpleasant smelling, and harmful.) This solution was placed on a Schlenk line, and 0.60 g of RuCl$_3$ in 25 mL of nitrogen-purged water was added. The mixture was heated at reflux under an overpressure of nitrogen for ~2 h. At this point, 100 mL of water was added to the solution to precipitate the product. After complex formation, the materials were no longer air sensitive and were handled on the bench top for further manipulation. The product was recrystallized from ethanol, collected, and dried under vacuum; yield 0.66 g, (48%).

Tris(μ-chloro)hexakis(diethylphenylphosphine)diruthenium(II) Chloride. This bimetallic species was prepared according to the procedure of Chatt and Hayter.[15] RuCl$_3$·3H$_2$O (1.61 g) was placed

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in 50 mL of water, and 6.5 mL of diethylphenylphosphine in 150 mL of methanol was added. The mixture was heated vigorously at reflux under an overpressure of nitrogen for a period of about 24 h. During this time, the solution slowly changed color from black to green to yellow, and the yellow product slowly precipitated out of solution. The precipitate was collected, washed with water and ether, and air-dried; yield 4.45 g (82%).

***cis*-Dichlorobis[1,2-bis(dimethylphosphino)ethane]ruthenium(II).** The cis complex was prepared from tris(μ-chloro)hexakis(diethylphenylphosphine)diruthenium(II) chloride by the method of Chatt and Hayter.[15] A 1.74-g quantity of the above bimetallic complex and 0.74 g of dmpe were heated without solvent under nitrogen. When the reaction temperature reached 145 °C, reaction occurred with effervescence. The temperature was raised to 200 °C to complete the reaction and vaporize any excess phosphine ligands. Upon cooling, the material was washed with petroleum ether to remove any displaced diethylphenylphosphine. The complex was recrystallized from benzene and ethanol and was then collected and dried under vacuum; yield 0.60 g (55%).

Nuclear Magnetic Resonance Spectroscopy. Proton-decoupled phosphorus-31 NMR spectra were obtained with a Varian XL-100-15 spectrometer operating at a frequency of 40.5 MHz and equipped with a Nicolet FT-100 Data System with quadrature phase detection and 20K of memory, allowing 16K data points, 8K points in the frequency domain for 3012-Hz spectral width. Phosphorus-31 spectra were measured in pure ethanol with an insert containing phosphoric acid for reference and hydrochloric acid to ensure complete protonation of the phosphoric acid, and this was diluted with a 1:1 (v/v) mixture of water and deuterium oxide for signal-lock purposes.

Proton-decoupled carbon-13 NMR spectra were obtained in methanol with a JEOL FX90-Q operating at 22.50 MHz. A capillary containing 1 drop of dioxane in deuterium oxide was used as an external reference and for signal lock.

The number of pulses required to obtain a good signal-to-noise ratio was concentration dependent and varied from 512 to 30000. The deuterium resonance of D$_2$O was used as the lock signal. Carbon-13 chemical shifts were measured relative to external dioxane (Fisher Scientific Co.) but are reported relative to Me$_4$Si. The conversion to external Me$_4$Si was calculated with the relationship

$$\delta(\text{ext Me}_4\text{Si}) = \delta(\text{ext dioxane}) + 67.40 \text{ ppm}$$

The spectral reproducibility was ±0.05 ppm.

Photolysis Apparatus. Quantum yields were measured with use of a 200-W high-pressure mercury arc lamp and optics described elsewhere.[16] Usable intensities at irradiation wavelengths of 405 and 366 nm were determined by using ferrioxalate actinometry[17] and approximated 1×10^{18} and 2×10^{18} quanta/min, respectively.

Photolysis Procedures. All photolyses were carried out at 25 °C in 2-cm or 5-cm quartz cylindrical cells. Quantum yields were calculated from changes in the electronic spectra as a function of irradiation time, plotted vs. percent reaction, and extrapolated to 0% reaction to correct for inner-filter effects. Photolysis products were identified by ^{13}C NMR and electronic absorption spectroscopy from samples photolyzed to ~100% reaction.

Results and Discussion

The electronic spectra for the three isolated ruthenium complexes in a variety of solvents are listed at the top of Table I. The ethanol/water mixtures are 70:30 (v/v) while the methanol/water mixtures are 80:20 (v/v). The *trans*-Ru(dmpe)$_2$Cl$_2$ complex shows only one peak in the visible region of the spectrum around 420 nm. The low extinction coefficient and relative insensitivity of the band maxima to solvent changes indicate that this is a ligand field transition, most likely a reduced-symmetry component of the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition in octahedral symmetry.

Table I. Electronic Spectral Data

complex	solvent[a]	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}
Ru$_2$(Cl)$_3$(PEt$_2$Ph)$_6$	ethanol	352	2750
		290	5470
trans-Ru(dmpe)$_2$Cl$_2$	ethanol	419	56
	EtOH/H$_2$O	422	54
	MeOH/H$_2$O	424	55
	Me$_2$SO	416	58
cis-Ru(dmpe)$_2$Cl$_2$	ethanol	355	840
		314	1130
		290	1060
	methanol	350	880
		312	1320
		296	1210
	EtOH/H$_2$O	346	750
	MeOH/H$_2$O	341	905
	Me$_2$SO	322	1060
	H$_2$O	338	988
trans-Ru(dmpe)$_2$(Me$_2$SO)Cl$^+$ [b]	Me$_2$SO	425 (sh)	~14
trans-Ru(dmpe)$_2$(H$_2$O)Cl$^+$ [b]	H$_2$O	400	~74
	EtOH/H$_2$O	405	~200
	MeOH/H$_2$O	418	~100

[a] The solvents EtOH/H$_2$O and MeOH/H$_2$O represent 70:30 and 80:20 (v/v), respectively. [b] Absorption spectra are obtained by irradiation of *cis*- and *trans*-Ru(dmpe)$_2$Cl$_2$ to completion (see text).

Table II. ^{13}C and ^{31}P NMR Spectral Data

complex	$\delta(^{13}\text{C})$[a]	$J_{^{13}\text{C}-^{31}\text{P}}$[b]	$\delta(^{31}\text{P})$[c]	$^3J_{\text{PP}}$[b]
Ru$_2$(PEt$_2$Ph)$_6$Cl$_3$			34.94	
trans-Ru(dmpe)$_2$Cl$_2$	12.15	7.2	37.44	
	29.22	12.8		
cis-Ru(dmpe)$_2$Cl$_2$	10.49	*d*	37.71	22.8
	15.37		49.93	22.8
	16.41			
	18.51			
	22.58			
	33.18			
trans-Ru(dmpe)$_2$(H$_2$O)Cl$^+$	12.5[e]	*f*		
	29.3[e]	*f*		

[a] ^{13}C chemical shift in ppm vs. external Me$_4$Si in methanol. [b] ^{13}C–^{31}P coupling in Hz. [c] ^{31}P chemical shift in ppm vs. external H$_3$PO$_4$. [d] Multiple splitting by nonequivalent ^{31}P nuclei and possibly ^{99}Ru ($I = 5/2$, 12.8%) and ^{101}Ru ($I = 5/2$, 17%). [e] EtOH/H$_2$O (70:30) as solvent. [f] Coupling constant not resolved.

The electronic spectrum (Table I) of the *cis*-Ru(dmpe)$_2$Cl$_2$ complex in a variety of solvents shows numerous peaks extending into the ultraviolet spectral region. The longest wavelength peak is centered around 340 nm and, like the trans counterpart, has a peak position that is relatively solvent insensitive. We choose to assign this peak as a ligand field transition (a component of $^1T_{1g} \leftarrow {}^1A_{1g}$ in octahedral symmetry) although the larger extinction coefficients may be due to either contributions from other excited states or larger transition moment probability due to lower symmetry in the cis vs. trans complex. All photolysis studies involved irradiation into the long-wavelength (LF) bands associated with *trans*- and *cis*-Ru(dmpe)$_2$Cl$_2$. These spectral assignments are consistent with emission studies[18] of Ru(dppm)$_2$Cl$_2$.

The electronic spectra listed as *trans*-Ru(dmpe)$_2$(H$_2$O)Cl$^+$ and *trans*-Ru(dmpe)$_2$(Me$_2$SO)Cl$^+$ in Table I are the result of extensive photolysis of either dichloro complex in alcohol/water mixtures or Me$_2$SO, respectively. The peak position observed in the Ru(dmpe)SCl$^+$ (S = solvent) complex (400–425 nm) and the relatively low molar extinction coefficient (10–200 M^{-1} cm^{-1}) are consistent with the trans geometric assignment. It should be noted that the identical spectrum of *trans*-Ru(dmpe)$_2$SCl$^+$ is observed from extensively photolyzed samples of *cis*- or *trans*-Ru(dmpe)$_2$Cl$_2$ in the appropriate solvent. Also, heating the photolyte solution in the presence of excess chloride quantitatively generates *trans*-Ru(dmpe)$_2$Cl$_2$. The ^{13}C and ^{31}P NMR spectra of the ruthe-

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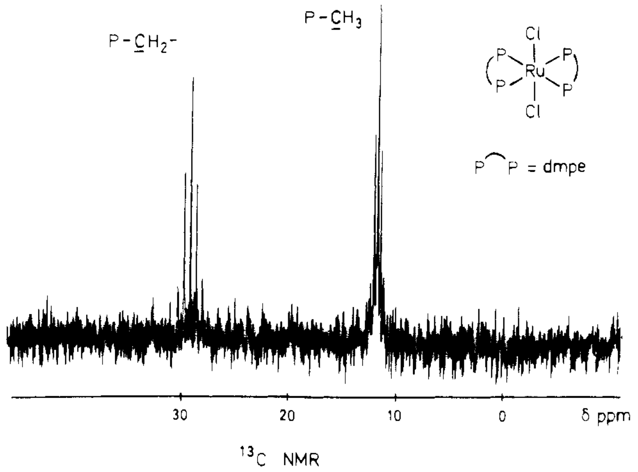

Figure 1. Proton-decoupled ^{13}C NMR spectrum of *trans*-Ru$(dmpe)_2Cl_2$ in methanol (vs. Me_4Si).

nium complexes are given in Table II. The ^{31}P spectra are very straightforward. The trans complex shows one peak at 37.44 ppm vs. H_3PO_4 while the cis complex exhibits two triplets, centered at 49.93 and 37.71 ppm and coupled with $^3J_{PP}$ of 22.8 Hz, due to the two sets of two equivalent phosphorus atoms (each virtually coupled[19] to the other set). The similarity in chemical shift between one of the set of ^{31}P peaks in the cis complex and the single peak in the trans complex would suggest that the 37.71-ppm resonance in the cis complex is due to the P atoms trans to each other and the 49.93-ppm resonance is due to the P atoms trans to the Cl ligand.

The ^{13}C spectra of *cis*- and *trans*-Ru$(dmpe)Cl_2$ are more complex than the ^{31}P spectra, especially for the cis complex. In Figure 1, the proton-decoupled ^{13}C spectrum of the trans complex shows two triplets, one assigned to the eight equivalent methyl groups bound to the four phosphorus atoms (12.15 ppm) and one due to the four equivalent methylene groups in the chelate backbone (29.22 ppm). In each case, the ^{13}C peak is split into a triplet by the adjacent phosphorus atom and the virtually coupled[19] trans phosphorus atom. The coupling constants, $J_{^{13}CP}$, for the methylene peak and the methyl peak are 12.8 and 7.2 Hz, respectively.

The proton-decoupled ^{13}C NMR spectrum of the *cis*-Ru$(dmpe)_2Cl_2$ complex (Figure 2) is more complicated than that of the trans complex. An expanded spectrum of the cis complex shows multiplets (mostly triplets due to virtual coupling, $^2J_{PP}$[19b]) for all six different carbon environments. The chemical shift values for the center of each multiplet are reported in Table II. In Figure 2, we have divided the spectral region into two areas, methyl and methylene. A major difference in the ^{13}C NMR spectra of the trans and cis complexes is that the methylene resonance in the trans complex appears between the two methylene multiplets found in this cis complex. This difference allows geometric identification of photolysis products as illustrated later in this report.

Two sets of peaks are observed in the proton-decoupled ^{13}C NMR spectrum of extensively photolyzed *cis*- or *trans*-Ru$(dmpe)_2Cl_2$ in ethanol/water solvent. These multiplets are centered at 12.5 and 29.3 ppm (Table II). The number of peaks and the peak positions are consistent with the assignment of trans geometry (*trans*-Ru$(dmpe)_2(H_2O)Cl^+$) made from the electronic spectrum of this complex. The ^{13}C NMR spectrum of extensively photolyzed *cis*- or *trans*-Ru$(dmpe)_2Cl_2$ in Me_2SO resulted in a high noise level. However, a signal was observed in the 28–29-ppm region consistent with formation of trans product. There is also a small peak at 43 ppm, adjacent to a large Me_2SO peak at 41.48 ppm, which we assign as bound Me_2SO. The conclusion drawn from the ^{13}C NMR spectra in conjunction with the electronic spectra of extensively photolyzed samples is that the photolysis products are *trans*-Ru$(dmpe)_2SCl^+$ complexes.

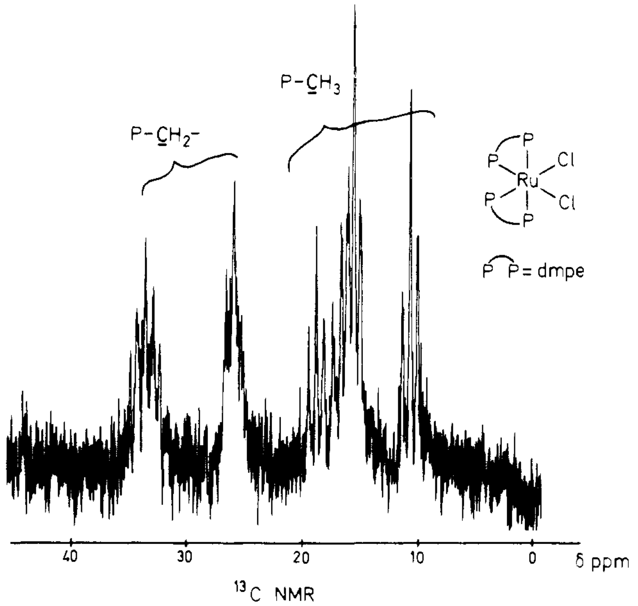

Figure 2. Proton-decoupled ^{13}C NMR spectrum of *cis*-Ru$(dmpe)_2Cl_2$ in methanol (vs. Me_4Si).

Table III. Photochemical Data

complex	solvent	Φ, mol/einstein[a]
trans-Ru$(dmpe)_2Cl_2$[b]	ethanol	no change
	methanol	no change
	$EtOH/H_2O$ (70:30)	0.12
	$MeOH/H_2O$ (80:30)	0.60
	Me_2SO	0.18
cis-Ru$(dmpe)_2Cl_2$[c]	ethanol	0.28[d]
	methanol	0.34[d]
	$EtOH/H_2O$ (70:30)	0.42
	$MeOH/H_2O$ (80:20)	0.33
	Me_2SO	0.18
	H_2O	0.38

[a] Quantum yield for formation of *trans*-Ru$(dmpe)_2ClS^+$, except where noted. [b] Irradiation wavelength of 405 nm. [c] Irradiation wavelength of 366 nm. [d] Quantum yield for formation of *trans*-Ru$(dmpe)_2Cl_2$.

The results of photolysis studies of *cis*- and *trans*-Ru$(dmpe)_2Cl_2$ are reported in Table III for a variety of solvents. From previous discussion of the electronic spectra, irradiations of the trans and cis complexes at 405 and 366 nm, respectively, were designed to populate the lowest, singlet, ligand field excited state. Reactions leading to two types of products were observed. In pure ethanol or pure methanol, there was no net photosubsitution observed, with *trans*-Ru$(dmpe)_2Cl_2$ being the only detectable product, regardless of which isomer was irradiated. The other type of reaction observed was loss of chloro ligand and coordination of solvent. In water, alcohol/water mixtures, or Me_2SO, irradiation of either *cis*- or *trans*-Ru$(dmpe)_2Cl_2$ results in formation of *trans*-Ru$(dmpe)_2ClS^+$ (S = H_2O for water or alcohol/water solvent, and S = Me_2SO for Me_2SO solvent).

The quantum yields in Table III show a solvent dependence, which is not surprising given that the rate constants for Ru–Cl bond breaking and nonradiative deactivation should be solvent dependent. What is surprising is the relatively insensitive solvent effects on the quantum yield of *cis*-Ru$(dmpe)_2Cl_2$.[13] However, the stereochemical fate of the photochemical reac-

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tions is the same for all solvent systems and is consistent with a single explanation. Irradiation of *cis*- or *trans*-Ru(dmpe)$_2$Cl$_2$ results in loss of chloro ligand from the lowest ligand field excited state[20] as the primary photochemical event. The five-coordinate fragment [Ru(dmpe)$_2$Cl$^+$]*, in a ligand field excited state, shows a thermodynamic preference for Cl to appear in the apical position of the square pyramid ($e_\sigma^{P} > e_\sigma^{Cl}$[2-4]). Apparently, the excited-state, five-coordinate fragment is long-lived enough that the basal isomer, formed by Ru–Cl dissociation in the cis starting material, undergoes the thermodynamically preferred basal → apical isomerization. The trans starting complex generates the apical isomer directly upon Ru–Cl bond breaking, and the apical isomer, in both cases, undergoes electronic relaxation and ligand addition to form the observed photolysis products.[21] It should be noted that, under conditions where Ru(dmpe)$_2$Cl$_2$ and Ru(dppe)$_2$Cl$_2$[11] undergo cis to trans photoisomerization, Os(dppe)$_2$Cl$_2$ does not.[14] This is due, presumably, to a combination of a larger barrier for basal → apical isomerization and more rapid electronic relaxation (spin–orbit coupling) for the third-row congener.

In the weakly coordinating alcohol solvents, ligand addition is just recoordination of the previously dissociated chloro ligand. In aqueous solution or water/alcohol mixtures, aquo ligand is added to [Ru(dmpe)$_2$Cl$^+$]* to form *trans*-Ru(dmpe)$_2$(H$_2$O)Cl$^+$ as the sole photolysis product. In Me$_2$SO, irradiation of the *cis*- or *trans*-Ru(dmpe)$_2$Cl$_2$ gives a complex with electronic spectrum, a ^{13}C NMR spectrum with a methylene peak in roughly the same place as the trans isomer in Figure 1, and a peak due to coordinated Me$_2$SO as well as solvent Me$_2$SO. All indications are that irradiation of either isomer leads to *trans*-Ru(dmpe)$_2$(Me$_2$SO)Cl$^+$ via [Ru(dmpe)$_2$Cl$^+$]* as the photolysis product.

Conclusion

The stereochemical model[2-4] correctly predicts the product geometry when *cis*- or *trans*-Ru(dmpe)$_2$Cl$_2$ is irradiated in the ligand field spectral region in a variety of solvents. In the case of Ru(dmpe)$_2$Cl$_2$, the solvents used in this study did have some effect on the quantum yield but did not alter the nature of the leaving group or the stereochemistry of the photolysis product. Although there is still no direct evidence for the existence of a five-coordinate, excited-state fragment along the reaction coordinate for photosubstitution reactions, a continued amount of experimental data[3,5-11] strongly suggests that this type of mechanism is correct and that it may be operable for systems other than d^6 complexes.[4]

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Registry No. *trans*-Ru(dmpe)$_2$Cl$_2$, 19206-05-4; *cis*-Ru(dmpe)$_2$Cl$_2$, 84172-85-0; *trans*-Ru(dmpe)$_2$(H$_2$O)Cl$^+$, 84130-50-7; *trans*-Ru(dmpe)$_2$(Me$_2$SO)Cl$^+$, 84130-51-8; [Ru$_2$(Cl)$_3$(PEt$_2$Ph)$_6$]Cl, 84130-52-9.

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[20] The use of the given model[2-4] to describe the photochemistry does not require the assumption of either a spin-singlet or spin-triplet excited state for the five-coordinate fragment. However, it is far more likely that the triplet state is the reactive excited state since the longer lifetime of this state may be necessary for the isomerization reaction to occur.

[21] An alternate explanation for the photochemical formation of *trans*-Ru(dmpe)$_2$Cl$_2$ from *cis*-Ru(dmpe)$_2$Cl$_2$ in pure alcohol would be a nondissociatve twist mechanism. Although this mechanism cannot be ruled out, the exclusive formation of *trans*-Ru(dmpe)$_2$SCl$^+$ in the other solvent systems make this possibility unlikely.

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Pressure Effects on the Photochemical and Photophysical Properties of the Rhodium(III) Complexes RhA$_5$X^{2+} (A = NH$_3$, ND$_3$; X = Cl, Br) in Aqueous Solution

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The effect of pressure up to 200 MPa was studied for ligand labilizations resulting from the ligand field photoexcitation of Rh(NH$_3$)$_5$X^{2+} (X = Cl, Br) and of the perdeuterio analogues Rh(ND$_3$)$_5$X^{2+} in H$_2$O or D$_2$O solutions, respectively. Quantum yields for halide photoaquation displayed negative volumes of activation (ΔV^*) ranging from −10.3 cm^3 mol^{-1} for Br$^-$ aquation from Rh(NH$_3$)$_5$Br^{2+} in H$_2$O to −4.2 cm^3 mol^{-1} for Cl$^-$ loss from Rh(ND$_3$)$_5$Cl^{2+} in D$_2$O. In contrast, ammonia photolabilization quantum yields gave positive ΔV^* values ranging from +3.4 cm^3 mol^{-1} for ND$_3$ loss from Rh(ND$_3$)$_5$Br^{2+} in D$_2$O to +12.7 cm^3 mol^{-1} for NH$_3$ loss from Rh(NH$_3$)$_5$Cl^{2+} in H$_2$O. In addition, the pressure dependence of the luminescence lifetimes τ was studied under conditions comparable to those of the photochemical investigations for the perdeuterio complexes Rh(ND$_3$)$_5$Cl^{2+} and Rh(ND$_3$)$_5$Br^{2+} in D$_2$O. The volumes of activation for the total deactivation rates τ^{-1} were calculated as −3.5 and +4.1 cm^3 mol^{-1} for X = Cl and Br, respectively. Combination of lifetime and quantum yield pressure effects allows the estimation of ΔV^* values for rates of the individual excited-state deactivation processes, ligand aquation, and nonradiative deactivation. Comparison of these data with calculated reaction volume profiles supports the view that the key ligand labilization pathways from the ligand field excited states are dissociative in character.

Introduction

The photosubstitution reactions resulting from the ligand field (LF), i.e. d to d, excitations of d^3 and d^6 Werner-type transition-metal complexes have been the subject of considerable experimental and theoretical investigation. However, despite these efforts, information regarding the intimate mechanisms of the excited-state reactions leading to substitution products has not been fully elucidated. In the interest of providing such mechanistic information, the effects of pressure on the photoaquation and photoisomerization reactions of some Cr(III) and Rh(III) amine complexes were investigated in several recent studies.[3-6] In general, quantum

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