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Photostereochemistry and Electronic Selection Rules in Strong-Field d^6 Transition-Metal Complexes

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The photostereochemistry of hexacoordinated transition-metal complexes has been studied in the case of ligand field irradiation. A general connection has been proposed between the labilization mode of the complexes (axial or equatorial) and their stereochemistry (stereomobile or stereoretentive). While d^3 systems have been treated in detail in a previous paper, the present work centers on d^6 complexes. A ligand field analysis of strong-field d^6 systems shows that the stereochemical behavior can be rationalized in terms of the properties of the relevant wave functions and correlation diagrams. An electronic selection rule is shown to be operative in the stereochemistry of the reactions.

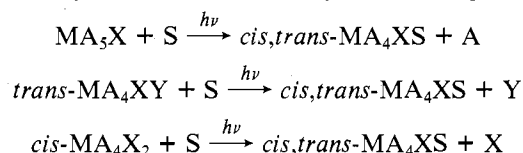
Introduction

In a recent communication,¹ Strauss and Ford reported some photochemical reactions of a few *cis*-diacidorhodium(III) tetraamines. We believe that their results might be of considerable help in elucidating the photostereochemistry of d^6 transition-metal complexes.

It is the purpose of this paper (i) to situate the Strauss-Ford experiments into a larger context, (ii) to discuss the general trends emerging from the stereochemical data of d^3 and d^6 ligand field photochemistry, and (iii) to analyze the d^6 reaction mechanism by means of an appropriate ligand field model.

Labilization Mode and Stereochemistry

Complexes of Cr(III) (d^3) and Co(III), Rh(III), and Ir(III) (strong field d^6) exhibit a remarkable and often quite effective photoactivity upon irradiation in the ligand field part of their spectrum.^{2,3} From a stereochemical point of view, this photoactivity can be summarized⁴ by the following reactions:



X and Y stand for acido groups, S stands for a solvent molecule and A stands for amine (Cr, Co, Rh, Ir) or cyanide (Co).

The mono- and disubstituted complexes under consideration are characterized by an effective D_{4h} -holohedron symmetry. Therefore, using Adamson's "labilized axis" terminology,⁵ one might classify each complex as being either axially or equatorially labilized.⁶ Table I shows the correlation between the labilization mode and the stereochemistry of the reactions, as inferred from an increasing number of experimental data; these data will be examined in detail in the next section.

In a previous paper,⁷ the axial labilization of the d^3 systems has been related to the corresponding stereomobility of the Cr(III) complexes.

The equatorial labilization of d^3 systems is not very well documented from a stereochemical point of view. In almost all cases, including *trans*-Cr(NCS)₄(NH₃)₂⁻ and *trans*-Cr(en)₂F₂⁺, as well as a number of *cis* disubstituted complexes, the product of the photoreaction is known or expected to be CrA₃X₂S.⁶ This product has three isomers and its stereochemistry is not always easily determined; this fact explains the scarcity of unambiguous experimental data in this area.

For the d^6 systems on the other hand, the leaving ligand is usually the heteroligand,⁶ and the photoproduct MA₄XS is readily characterized as *cis* or *trans*. In what follows, attention will be focused on the reactions of low-spin d^6 complexes.

Labilization of Strong-Field d^6 Complexes: Review of the Experimental Data

(a) **Axial Labilization.** By now, it appears well established that axial labilization is characterized by a strongly dominant

Table I. Empirical Correlation between Labilization Mode and the Experimental Stereochemistry of the Photosubstitution in d^3 and d^6 Strong-Field Systems^a

	d^3	d^6
axial labilization MA ₅ X trans-MA ₄ XY	stereomobility in all cases cis-MA ₄ XS	stereoretention in all cases trans-MA ₄ XS
equatorial labilization cis-MA ₄ X ₂	MA ₃ X ₂ S	stereomobility in most cases trans-MA ₄ XS

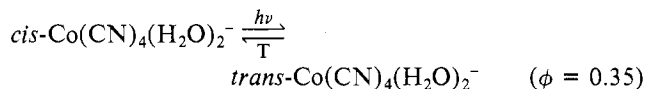
^a Both Reinecke salt, *trans*-Cr(NCS)₄(NH₃)₂⁻, and *trans*-Cr(en)₂F₂⁺ are not incorporated in the table and will be commented upon separately.

stereoretention; this fact has been verified for a number of complexes:^{2,3,8-11} *trans*-Co(en)₂(NH₃)Cl₂⁺, *trans*-Co(en)₂Cl₂⁺, *trans*-Co(CN)₄X₂ⁿ⁻ (X = SO₃²⁻, H₂O), *trans*-Rh(NH₃)₄X₂⁺ (X = Cl, Br, I), *trans*-Rh(en)₂X₂⁺ (X = Cl, Br, I), *trans*-Rh(cyclam)Cl₂⁺, and *trans*-Ir(en)₂X₂⁺ (X = Cl, Br, I).

It is generally accepted that the first step in the photoreaction consists of a simple dissociative loss of the X ligand, without any significant concerted rearrangement of the five-coordinated fragment. Indeed, increasing the degree of chelation or ring stricture in the equatorial plane has no major effect on the quantum yield of X-release (as opposed to the Cr(III) complexes).¹²

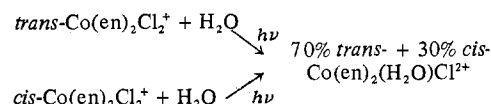
(b) **Equatorial Labilization.** The experimental basis linking labilization mode and stereochemistry does not appear equally compelling in this case. Yet, critical examination of the relevant data strongly suggests the validity of Table I, associating stereomobility with equatorial labilization.

(i) The photoreaction in



has been interpreted^{10,13} as an *intramolecular* Bailar twist over a trigonal-prismatic transition state. We propose, on the other hand, that the *cis* → *trans* photoreaction rather be viewed as a dissociative process, characterized by equatorial labilization, and we intend to show in the next sections that the observed phenomena can be explained quite satisfactorily by postulating a five-coordinated excited Co(CN)₄(H₂O)⁻ fragment.

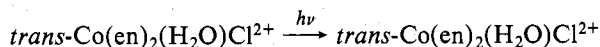
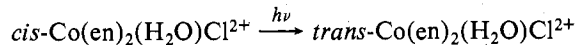
(ii) The two reactions



are both characterized by low quantum yields¹¹ and by the same product mixture.^{2,14} The first reaction was mentioned already as an example of the stereoretention, accompanying

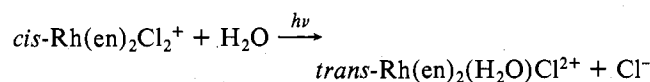
axial labilization. Here, it is well to stress that the equal product composition of the two reactions suggests a common intermediate fragment, obtained from the trans complex by axial labilization but from the cis complex by equatorial labilization.

In fact, also the photochemical behavior of *cis*- and



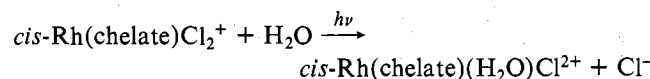
trans-Co(en) $_2$ (H $_2$ O)Cl $^{2+}$ might readily be understood if H $_2$ O is the leaving ligand. Indeed, if the same Co(en) $_2$ Cl $^{2+}$ fragment is the reaction intermediate, the trans complex will be effectively photoinert in aqueous solution and the cis complex will tend to isomerize, controlled by the same factors that govern the course of the substitution reactions of the dichloro complexes.

(iii) There is experimental evidence^{15,16} for a stereomobile reaction:



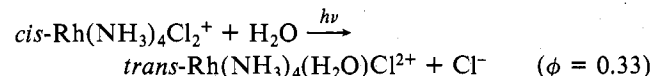
The earlier proposal of an "edge-displacement" mechanism¹⁶ must be considered unlikely in view of a recent study of the Rh(en) $_3$ $^{3+}$ photolysis by Petersen and Jakse.²⁸

(iv) The obvious exception to Table I is the reaction

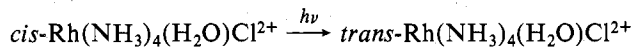
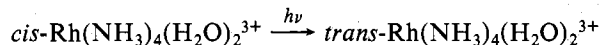


where chelate stands for the tetradentate cyclam¹⁷ and for two phenanthroline or bipyridyl bidentate ligands.^{12,15,16} The stereoretention of these reactions is not surprising, since the five-coordinated intermediate will be expected to be immobilized for steric reasons, certainly in a tetradentate ligand, and also quite probably for bulky bidentates. From a comparison of quantum yields it has been shown^{12,18} that for d^6 —as opposed to d^3 systems—stereomobility is not a *conditio sine qua non* to realize photoaquation.

(v) The most clearcut and conclusive evidence in favor of stereomobility is provided by the Strauss-Ford experiments:¹



In this case, the complications due to chelate effects are avoided, and an intramolecular *cis* \rightarrow *trans* twist is precluded since isomerization and photoaquation are concomitant. A five-coordinated fragment, characterized by a trans preference for solvent addition, would also explain the observed¹ isomerization reactions



This interpretation is of course quite similar to the reaction mechanism we proposed for the disubstituted tetracyano-cobalt(III) complexes, sub (i).

Theoretical Analysis of the Substitution Reactions

A. The Reaction Paths. As opposed to the Cr(III) photochemistry, the experimental evidence pertaining to d^6 systems^{2,3,12,15,16} points to a simple dissociative initial step, i.e., a photolysis *without* a significant concerted rearrangement of the five-coordinated fragment. This leaves a square-pyramid (SP) MA_4X with the heteroligand X either in apical or in equatorial position. The rigidity or else the flexibility of this fragment will determine the stereochemistry of the substitution reaction. The most obvious structure, whose accessibility from

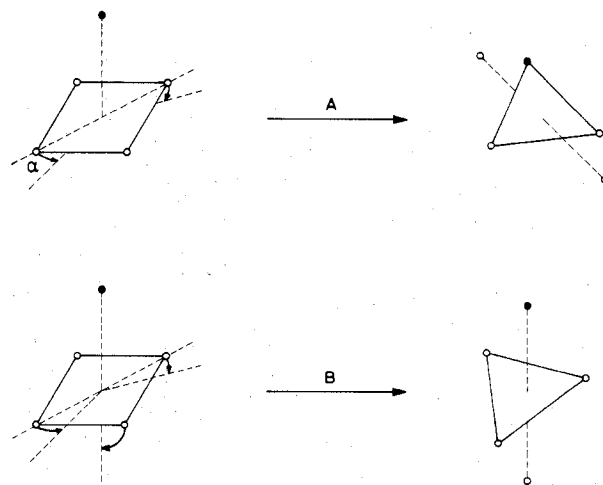


Figure 1. Two different reaction paths connecting a square pyramid and a trigonal bipyramid: (A) the axial ligand of the SP (black circle) becomes an equatorial ligand in the TBP (α runs from 0 to 30°); (B) the axial ligand of the SP remains axial in the TBP.

the excited square pyramid has to be examined, is a trigonal bipyramid (TBP); here again, X can be either apical or equatorial.

In principle, two distinct reaction paths might be considered to carry a square pyramid into a trigonal bipyramid. Figure 1 shows how the apical ligand of the square pyramid can become either an equatorial or an axial ligand in the trigonal bipyramid. The latter possibility was shown to be unfavorable in the Cr(III) photochemistry.⁷ It is not difficult to show that the same conclusion holds true here as well. In what follows, only the reaction path of Figure 1A will be considered.

In summary, the possible initial reaction steps might be represented as follows:

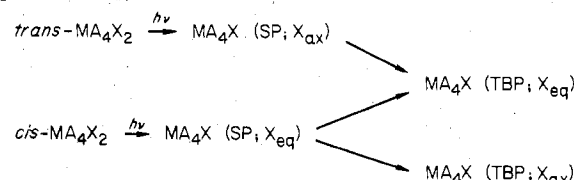


Figure 1A does not allow (TBP; X $_{ax}$) to be connected directly with (SP; X $_{ax}$). Several authors¹⁹⁻²¹ also consider square pyramids where the ligand-metal-ligand angles are different from 90°. From ligand field considerations alone, the orthogonal structure constitutes the most stable square pyramid (this point will be made more explicit when discussing the results). But a slightly distorted SP might indeed be more favorable when considering ligand-ligand repulsions. However, the conclusions to be drawn from the present treatment are independent of small angle variations.

B. Method of Calculation. Use was made of the same additive point ligand model (APLM) that provided an adequate method to describe the Cr(III) photochemistry.⁷ To each metal-ligand interaction are associated two semiempirical parameters, σ and π . The most striking experimental examples were provided by the *cis*-diacidorhodium(III) tetramines. Therefore, Rh(NH $_3$) $_4$ Cl $^{2+}$ is taken to be the representative pentacoordinated entity, whose internal reactive motions will be studied.

The spectrochemical parameters are based on the values taken from Jorgensen:²² for Rh(NH $_3$) $_6$ $^{3+}$, $10Dq = 3\sigma - 4\pi = 3.410 \mu\text{m}^{-1}$, $B = 0.043 \mu\text{m}^{-1}$; for Rh(Cl) $_6$ $^{3-}$, $10Dq = 2.030 \mu\text{m}^{-1}$, $B = 0.035 \mu\text{m}^{-1}$; in both cases $C = 4B$ (where B and C are the in situ Racah parameters). The ratio π/σ is unknown for the Rh(III) complexes; if the same values are assumed as for Cr(III), one obtains for Rh-NH $_3$, $\sigma = 1.136$

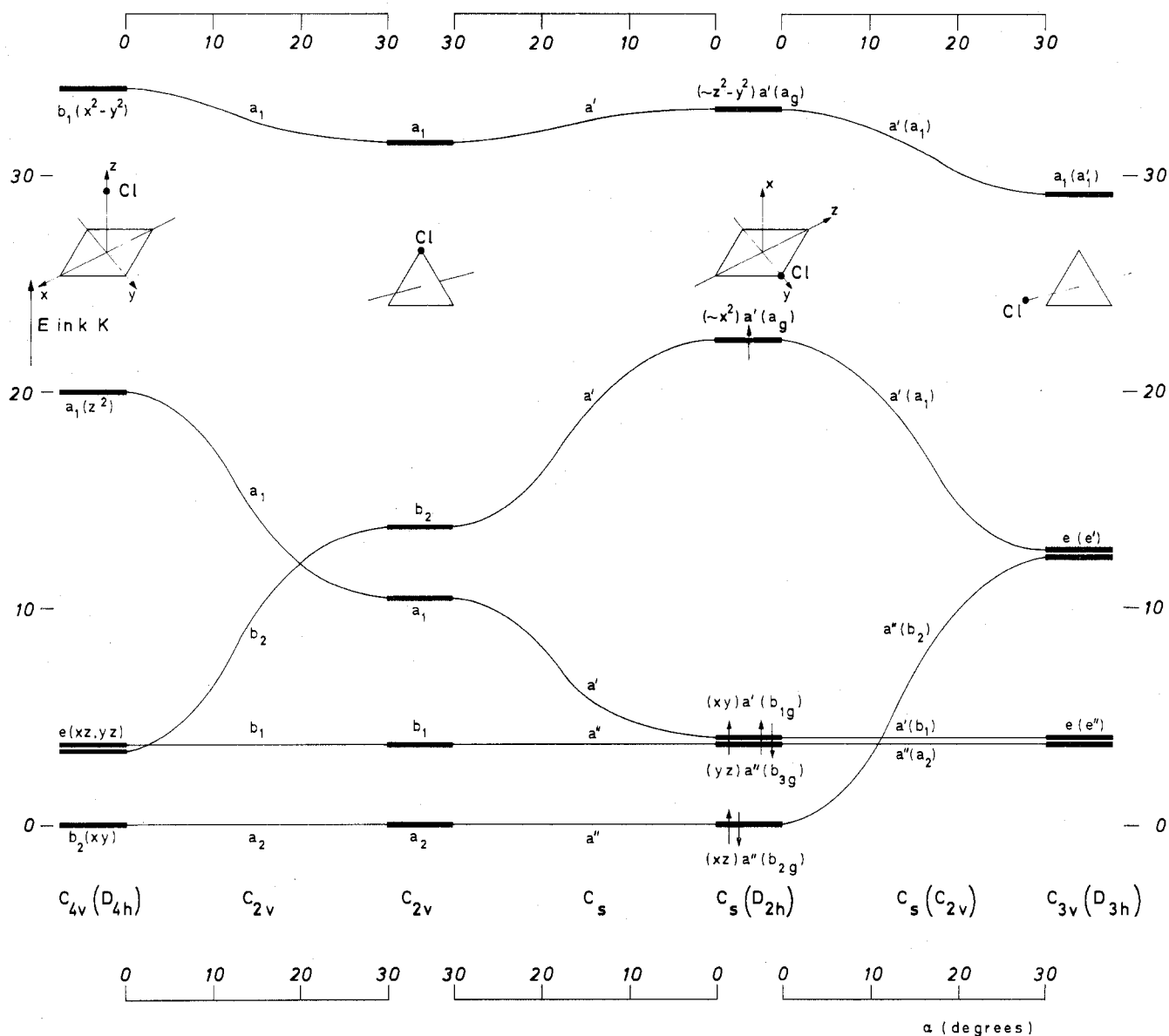


Figure 2. Orbital energy correlation diagram connecting the four $\text{Rh}(\text{NH}_3)_4\text{Cl}_2^{2+}$ species, in the sequence $\text{SP}(\text{Cl}_{\text{ax}})\text{-TBP}(\text{Cl}_{\text{eq}})\text{-SP}(\text{Cl}_{\text{eq}})\text{-TBP}(\text{Cl}_{\text{ax}})$. The reaction coordinate between any two adjacent species is the angle α defined in Figure 1A.

μm^{-1} , $\pi = 0$ and for Rh-Cl , $\sigma = 0.862 \mu\text{m}^{-1}$, $\pi = 0.140 \mu\text{m}^{-1}$. If the Racah parameters are taken to be the weighted average from the values quoted above, one finds $B = 0.041 \mu\text{m}^{-1}$ and $C = 0.166 \mu\text{m}^{-1}$.

These parameter values also satisfy the leaving ligand conditions, in that they account correctly⁶ for the fact that Cl^- is the leaving ligand in irradiated *cis*- $\text{Rh}(\text{NH}_3)_4\text{Cl}_2^+$. It should be noted, however, that the specific value of the σ and π parameters is not of prime importance. Indeed, the photochemical behavior will be rationalized by using only the qualitative features of the diagrams and calculations. In that sense, one might replace Cl^- by some average π donor, characterized by roughly the same sort of parameters.

Results and Comparison with Experiment

In Figures 2 and 3, the energy correlation diagrams are shown for the four relevant $\text{Rh}(\text{NH}_3)_4\text{Cl}_2^{2+}$ species, interconnected according to the reaction path of Figure 1A. The distortion angle α varies from 0° in the square pyramids to 30° in the trigonal bipyramids. Figure 3 is an enlargement with respect to Figure 2 and shows only the lowest excited states. The ground state of square pyramids is at approximately $-1.250 \mu\text{m}^{-1}$ and falls outside the energy range of

Figure 3; its correlation line enters the figure in the neighborhood of $18\text{-}20^\circ$.

The symmetry of the reacting species is designated at each point along the reaction coordinate; if the holohedron symmetry is different, it is added in parentheses.²³ The representation labels of the orbitals and states are also given in holohedron symmetry wherever necessary. If the holohedron representations of two energy levels are different, level crossing along the reaction path is allowed, even when the corresponding representations in the actual symmetry group are identical.⁷

In Figure 2 an orbital description for the tetragonal pyramids is given in terms of the appropriate real d orbitals. This description requires the specification of the coordinate systems shown in Figure 2. The reflection operators for C_{2v} are denoted as in Figure 4; accordingly the symmetry designations are completely unambiguous.

In order to interpret the correlation diagrams, one additional element is needed in the elaboration of the model: how does the five-coordinated fragment associate with a solvent molecule, so as to complete the substitution reaction? In this respect, d^6 systems are strikingly different from d^3 systems: none of the four considered fragments has favorable association possibilities. Indeed, it is difficult to distribute six d electrons

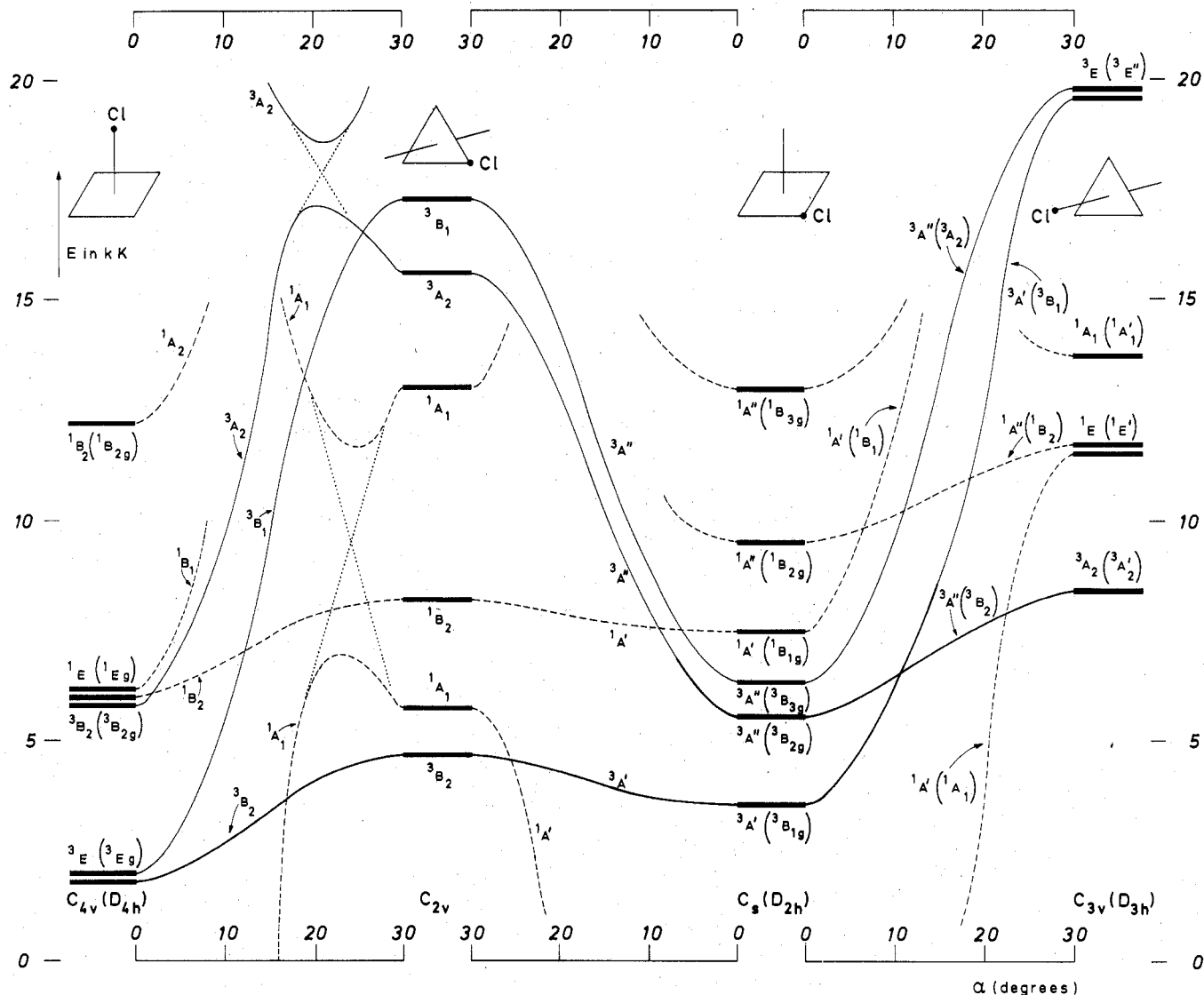


Figure 3. State energy correlation diagram connecting the four $\text{Rh}(\text{NH}_3)_4\text{Cl}_2^{2+}$ species, in the sequence $\text{SP}(\text{Cl}_{\text{ax}})$ – $\text{TBP}(\text{Cl}_{\text{eq}})$ – $\text{SP}(\text{Cl}_{\text{eq}})$ – $\text{TBP}(\text{Cl}_{\text{ax}})$. The reaction coordinate between any two adjacent species in this sequence is the distortion angle α , defined in Figure 1A. Triplet states are shown in full lines and singlet states in dotted lines. The heavy lines represent the correlations that are particularly important in the photochemistry.

in space and still keep one vacant site: the solvent molecule will always find a σ^* electron on its line of approach. In fact, the only favorable distribution is the square-pyramidal *ground state*, with access direction in trans of the axial ligand.¹⁹

The association reactions might of course be analyzed in more detail by constructing correlation diagrams for approach of a solvent molecule to each of the relevant fragments. The results of such an analysis only confirm the previous qualitative considerations; therefore, it does not seem worthwhile to pursue this line any further at this point.

The important conclusion to be drawn from the above is this: even if the excited five-coordinated fragment develops a certain nonrigidity along the reaction coordinate of Figure 3, it will eventually be carried into one of the SP ground states by intersystem crossing. *Therefrom* hexacoordination will be restored by association of a solvent molecule in trans of the axial ligand.

Consider now the correlation line in Figure 3, corresponding to the lowest excited state of the square pyramids, and labeled ${}^3\text{E}({}^3\text{E}_g)$ in $\text{C}_{4v}(\text{D}_{4h})$, or ${}^3\text{A}'({}^3\text{B}_{1g})$ in $\text{C}_s(\text{D}_{2h})$. In the photo-substitution of *trans*- $\text{Rh}(\text{NH}_3)_4\text{Cl}_2^{2+}$, the C_{4v} square pyramid is generated by dissociation of a Cl^- ligand. The ${}^3\text{E}({}^3\text{E}_g)$ state is seen to be situated in a minimum of the potential energy curve (the barrier being of the order of $0.280 \mu\text{m}^{-1}$).

Therefore, the system is prevented rather effectively from moving along the reaction coordinate of Figure 3. Since it cannot react by association with a solvent molecule either, the only possibility is simply relaxing back to the ground state of the original square pyramid, followed by trans association of a solvent molecule. The stereoretention of this reaction is thus easily rationalized from the figure.

The situation is different for *cis*- $\text{Rh}(\text{NH}_3)_4\text{Cl}_2^{2+}$; the $\text{C}_s(\text{D}_{2h})$ square pyramid is obtained in its ${}^3\text{A}'({}^3\text{B}_{1g})$ excited state. A very steeply increasing potential energy curve prevents the system from moving toward the $\text{TBP}(\text{Cl}_{\text{ax}})$. On the other hand, the TBP with Cl in equatorial position is at a very small potential barrier. Crossing this barrier moves the system into the $\text{SP}(\text{Cl}_{\text{ax}})$ minimum. This potential well can then act as a trap, wherefrom the trans product is generated. It is proposed that the existence of the energy trap at $\text{SP}(\text{X}_{\text{ax}})$ is at the basis of the stereomobility of the cis complexes and more generally at the basis of the cis \rightarrow trans preference observed in the d^6 photochemistry.

A number of other experimental details are also in agreement with this proposal:

(i) The stereoretention of the trans complexes is more pronounced for the rhodium(III) amines than for the cobalt(III) amines. Indeed, the energy difference between the

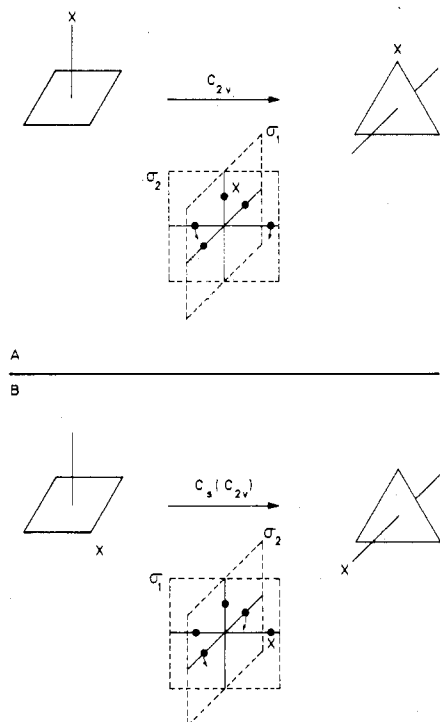


Figure 4. Symmetry planes in the (holohedron) C_{2v} group. (A) $SP(X_{ax}) \rightarrow TBP(X_{eq})$; the ligand motion is situated in σ_2 . (B) $SP(X_{eq}) \rightarrow TBP(X_{ax})$; σ_1 corresponds to the only symmetry plane of the actual symmetry group C_s ; the ligand motion is in σ_2 , which is a symmetry plane in the holohedron only.

two SP triplet states drops significantly in going from the Rh(III) to the Co(III) complexes.

(ii) The qualitative picture of two local minima separated by a potential barrier which is definitely smaller on the one side than on the other naturally leads to the idea of a thermal equilibrium in the excited states; this appears to be quite compatible with the photochemistry of *cis*- and *trans*-Co(en)₂Cl₂⁺ where the same product mixture was obtained.

(iii) Since the square pyramids are both at local minima, no energy is released when the system reacts to generate the TBP. Therefore, this deformation can not possibly assist in the photolytic splitting of the leaving ligand. The situation is quite different for the Cr(III) complexes,⁷ where the TBP is at much lower energy than the SP; therefore, in the Cr(III) photoreactions, the concerted rearrangement of the five-coordinated fragment *does* contribute to the ease of ligand release.

With these points in mind, the differences in the cyclam photochemistry of d³ and d⁶ systems can be rationalized in a very simple way.

Discussion of the Results

A. Analysis of the Wave Functions and the Labilization Modes. It is useful to supplement Figures 2 and 3 in two different ways, first by connecting the triplets in the five-coordinated fragments to the photoactive state in the original complexes and second by writing out the wave functions, corresponding to some of the energy levels shown in the figures.

The lowest triplet state of the Rh(III) complexes has been identified as the precursor of the photochemical reaction.²⁴ Taking the ligand removal along the z axis as the reaction coordinate in the primary step of axial labilization, the precursor level is directly correlated to the ³E(³E_g) level of Figure 3. The corresponding configuration is approximately⁶ given by $(xy)^2(xz, yz)^3(z^2)^1$.

In the case of planar labilization, the situation is less trivial, and the correlation is shown in Figure 5. One Cl⁻ ligand is

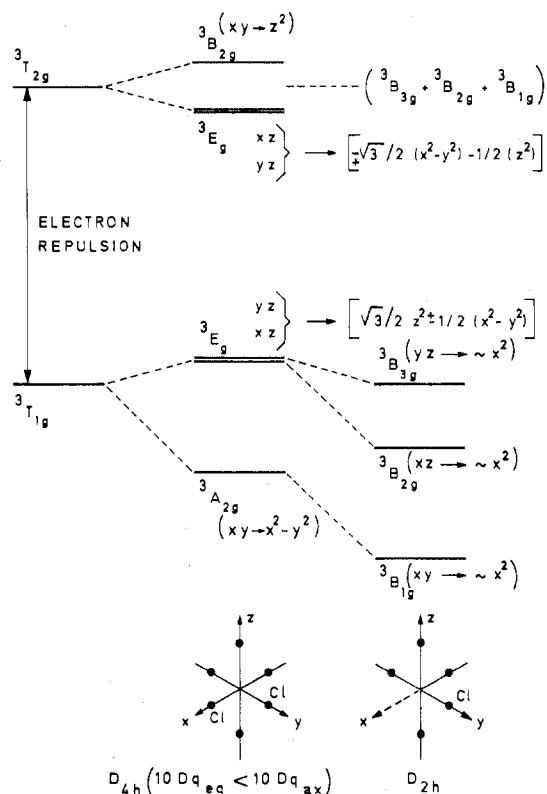


Figure 5. State correlation between a *cis* disubstituted tetraamine d⁶ complex, the octahedral parent complex, and the five-coordinated TP(X_{eq}) obtained from equatorial labilization.

removed along the x axis, reducing the holohedron symmetry from D_{4h} to D_{2h} . Some zero-order orbital descriptions are added to the state labels. The photochemically active level of the *cis* complex ³A₂(D_{4h}) is directly correlated to the lowest triplet level in SP(Cl_{eq}) D_{2h}, i.e., the ³B_{1g} state which has been considered in the previous section. While the x²-y² population is responsible for the equatorial labilization mode, an additional factor comes in during the course of the dissociation reaction. Indeed, the removal of Cl⁻ along the x axis induces an orbital mixing from (z², x²-y²) into a set of linear combinations closer to (x², z²-y²). The lowest a_g orbital in D_{2h}, represented by (\sim x²), is given by

$$a_g(\sim x^2) = (\sin p)d_{x^2-y^2} - (\cos p)d_{z^2}; \quad p \approx 67^\circ$$

The pure d_{x²} orbital is obtained for p = 60°; the (small) deviation from this value causes the electron density to increase slightly around the y axis at the expense of the z axis. However, the d_{x²} character is essentially preserved, as is obvious from the alternative expression

$$a_g(\sim x^2) = (\sin p)d_{x^2} + (\cos p)d_{z^2-y^2}; \quad p \approx 83^\circ$$

The energies of the three lowest orbitals in C_s(D_{2h}) are given by

$$E(yz) = \pi_{Cl} + 3\pi_N$$

$$E(xy) = \pi_{Cl} + 2\pi_N$$

$$E(xz) = 3\pi_N$$

Since $\pi_{Cl} > \pi_N$, the orbital sequence of the SP(Cl_{eq}) is readily verified.

From the energy diagram in Figure 2, one would expect the lowest excited state to correspond to a degenerate (xy, yz) → \sim x² excitation. From Figures 3 and 5, however, the yz →

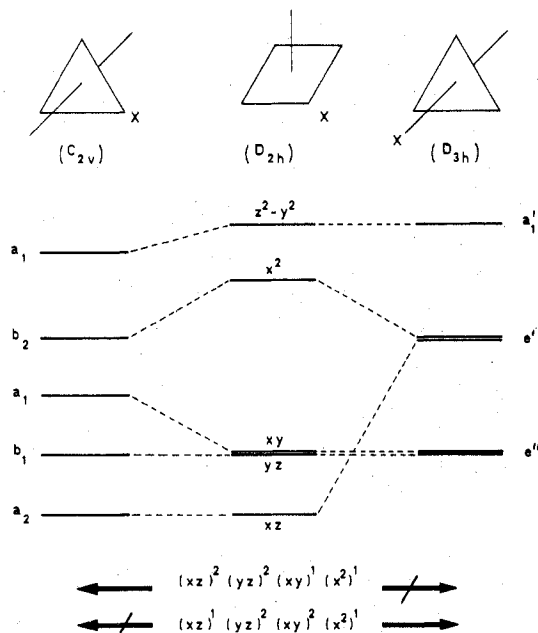


Figure 6. Schematic d orbital correlation diagram for the SP(X_{eq}) and the two connected TBP (holohedron point groups).

$\sim x^2$ excitation, giving rise to the ${}^3A''({}^3B_{3g})$ state, is at much higher energy. This is due to electron repulsion effects: the zero-order description of the $yz \rightarrow \sim x^2$, ${}^3B_{3g}$ state in D_{2h} is equivalent to $xy \rightarrow z^2$, ${}^3B_{2g}$ in D_{4h} (see Figure 5). The latter state corresponds to ${}^3T_{2g}$ in O_h symmetry and is therefore characterized by a much larger interelectronic repulsion than the ${}^3T_{1g}$ -related states $xz \rightarrow \sim x^2$ and $xy \rightarrow \sim x^2$. Therefore the lowest excited triplet has to be ${}^3A'({}^3B_{1g})$ as shown in Figure 3.

B. Electronic Selection Rule for the Square Pyramid (X_{sq}). Part of Figure 2 is resumed schematically in Figure 6. The configuration of the photoactive ${}^3A'({}^3B_{1g})$ state is given by $(xz)^2(yz)^2(xy)^1(x^2)^1$. Clearly this particular orbital occupation will be unfavorable for ligand motion in the xz plane (leading to TBP(X_{ax})) and favorable for ligand motion in the xy plane (leading to TBP(X_{eq})). Indeed in the first case, *two* electrons will be forced into a high-energy orbital, vs. *one* in the second case.

The same fact can be expressed by the simple rule that ligand motions tend to avoid occupied orbitals and are directed toward (partially) vacant orbitals.^{7,25} Depopulation of d_{xy} induces a reactive motion in the xy plane, while the complete occupation of d_{xz} holds the ligand of the xz plane in place.

Figure 6 illustrates a clearcut selection rule, comparable to the rule obtained for solvent association in Cr(III) complexes.⁷ In the present case, however, the reaction path leading to the SP(X_{eq}) is more nearly on an equipotential energy surface, because no completely vacant orbital is available. In d^3 systems on the other hand, where a vacant orbital *is* available, the allowed reaction is exoenergetic.⁷

The next excited triplet ${}^3A''({}^3B_{2g})$, with configuration $(xz)^1(yz)^2(xy)^2(x^2)^1$ exhibits exactly the opposite behavior. It has the d_{xz} orbital partly depopulated, and, therefore, the motion of the ligands in the xz plane is favored over the motion in the xy plane.

The first and second excited triplets are characterized by a different symmetry: they are not subject to a noncrossing rule, and each state preserves its own specific properties along the entire reaction path.

It should be noted here that the simultaneous movement of the four equatorial ligands is unfavorable. Indeed, this motion, taking the metal ion into the inside of the pyramid, increases the energy of both d_{xz} and d_{xy} (occupation number 3); the

energy stabilization of the singly occupied d_{xz} orbital will not be able to compensate for this effect.

C. Relative Position of ${}^3A'({}^3B_{1g})$ and ${}^3E({}^3E_g)$. The lower energy of 3E was essential in explaining the trans preference of the substitution reactions. The energies shown in Figure 3 are the result of a "complete" calculation on the d^6 system, allowing for all possible interactions due to the ligand field and to interelectronic repulsion. Therefore, an exact analytical expression for the state energies is difficult to obtain. In zero order, however, the following simple relations hold true:

$$\begin{aligned} {}^3A'({}^3B_{1g}) - {}^3E({}^3E_g) &= E[(d_{xz}); SP(X_{eq})] - E[(d_{xz}); SP(X_{ax})] \\ &= \frac{3}{4}(\sigma_N - \sigma_X) \end{aligned}$$

In other words, in order to favor the trans structure, the heteroligand has to be the weaker σ donor; this condition is satisfied in all the cases considered so far.

D. Nature of the d⁶ Metal Ion. In Rh^{3+} , spin-orbit coupling is obviously more important than in Co^{3+} . More specifically, the crossover between the lowest singlet and triplet states (approximately halfway between SP and TBP) might be affected by increasing the value of the spin-orbit coupling constant. It should be noted, however, that the triplet level has always at least *one* component which is not totally symmetric and where crossing remains allowed. In this sense, one does not expect the introduction of spin-orbit coupling to give rise to a significant increase of the energy barrier between the two square pyramids.

The Racah parameters increase from rhodium to cobalt; qualitatively, the resulting energy pattern remains more or less unaffected. The increased energy splitting between the lowest singlet states and the lowest triplet state in TBP is of no consequence from the present point of view.

In the final analysis, the validity of our considerations for a MA_4X_2 complex depends on the relative values of the APLM parameters $\pi_X > \pi_A$, from (A), and $\sigma_X < \sigma_A$, from (C). These relations are probably always satisfied, both for Co(III) and for Rh(III), when A is NH_3 or CN^- and X is an acido group with moderate σ and π characteristics.

E. Possibility of an Intramolecular Mechanism. It is obvious that the photochemical cis \rightarrow trans isomerization of the tetracyano-cobalt(III) complexes¹⁰ can be rationalized as a dissociative process on the basis of Figure 3. The interpretation is not affected by the fact that the cis complex is thermally the most stable isomer. Indeed, the *same* reaction path can have opposite preferential directions on *different* potential surfaces. The dissociative mechanism is also compatible with the observation¹⁰ that the photochemical isomerization has a much lower quantum yield for the dihydroxo than for the diaquo complex. Indeed, the Co-OH bond is considerably stronger than the Co-H₂O bond.^{6,26}

Apart from the experimental evidence reported by Strauss and Ford,¹ two additional points contribute to the invalidation of an intramolecular mechanism:

(a) The energy barrier corresponding to a trigonal prism or a bicapped tetrahedron transition state is calculated to be at roughly $1.6 \mu m^{-1}$. Any process with an activation energy of this order of magnitude is definitely too slow to be effective during the lifetime of the excited state.

(b) There are several distinct but statistically equivalent intramolecular twists in both cis and trans complexes. In order to explain the high quantum yield observed for the cis \rightarrow trans photoreaction, one needs to show that a number of cis \rightarrow cis reactions are effectively impossible. A careful and detailed study of the different possibilities shows that no selection rule of any kind is operative in this respect. Therefore, one must conclude that an intramolecular twist mechanism does not explain the observations.

Conclusion

The empirical generalizations of Table I are based on the existing experimental evidence. This evidence is neither abundant nor entirely compelling; additional facts would certainly be useful in order to substantiate the present proposal. As a matter of fact, Table I might be of some help in carrying out future experiments.

From a more theoretical point of view, the connection between labilization modes and stereochemistry has been shown to be compatible with a detailed ligand field analysis. The formulation of electronic selection rules is an interesting feature apparently underlying the photochemistry of both the d^3 and d^6 complexes.

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Nature of the Lowest Excited States and Dynamic Behavior of Group 6B (Diazeno)pentacarbonylmetal Complexes

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Electronic absorption and emission data are reported for (diazeno) $M(CO)_5$ ($M = Cr, Mo, W$; diazeno = *trans*-dicyclohexyldiazeno, 2,3-diazanorbornene, 4-R-3,3-bis(methoxycarbonyl)-1-pyrazoline ($R = isopropyl, phenyl$), pyridazine, *cis*-azobenzene, benzo[*c*]cinnoline). The lowest absorption band is assigned to a metal \rightarrow diazeno charge-transfer transition (CTML) on the basis of solvent, ligand, and temperature effects and the next higher band is assigned to a metal-centered transition (LF). Dynamic vis-UV spectroscopy at -100 to $-185^\circ C$ gives evidence for small differences in the contribution of π bonding to the M-N bond and for restricted rotation around this bond. In addition to this fast process, a slow 1,2-shift of the $M(CO)_5$ group along the N=N linkage occurs at higher temperatures as demonstrated by dynamic ^{13}C and 1H NMR spectra.

Preparatively and structurally, transition-metal complexes of diazenes have been increasingly investigated during the last decade.¹ The electronic spectroscopy of these compounds has not been explored in a comparable fashion. Recently the lowest absorption band in the spectra of the π complexes bis(triethylphosphine)(*trans*-azobenzene)nickel have been assigned to an $n \rightarrow \pi^*$ transition on the basis of its variation upon introduction of substituents in the para position of azobenzene.² Tentative assignments of the two low-energy bands of the σ complexes $Cr(CO)_5$ (*cis*-azobenzene)³ and $M(CO)_5$ (benzo[*c*]cinnoline)⁴ ($M = Cr, Mo, W$) as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ of the coordinated diazeno ligand have appeared while this work was in progress. Comparison with the well-investigated spectra of $W(CO)_5(L)$, where L is an oxygen or nitrogen σ donor like acetone or an amine,⁵ points to the

more likely assignment of these transitions as ligand field (LF) and charge transfer $M \rightarrow$ diazeno (CTML). In this paper this latter assignment is experimentally supported by examining the influence of the metal, the diazeno ligand, the solvent, and the temperature on the low-energy bands of a series of pentacarbonylmetal σ -diazeno complexes. Some of the tungsten compounds exhibit emission at low temperature. With regard to the current interest⁶ in low-lying CTML states of transition-metal compounds we note that these diazeno complexes constitute the fifth class of substituted mononuclear metal carbonyls having CTML lowest excited states. The other examples known are $(L)W(CO)_4$ ($L = 1,10$ -phenanthroline, 2,2'-bipyridine,⁷ 1,4-diazabutadienes⁸), $(L)W(CO)_5$ ($L = 4$ -R-pyridine (R is an electron-withdrawing group like CN, CH_3CO , etc.)^{9a}), $(C_5H_5)Mn(CO)_2(NCAr)$ ($Ar = C_6H_5$