Table I. Product Yields Resulting from the Ligand Field Photolysis of $Rh^{III}(NH_3)_5X$ Complexes

X	T, °C	Wavelength irradiated,[a] nm	Assignment[b]	Direct photolysis product yields[c] ϕ_X	ϕ_{NH_3}	Biacetyl sensitized product yields[d] ϕ_X	ϕ_{NH_3}
Cl	25	350	$^1A_1 \rightarrow {}^1T_1$	0.16 ± 0.01[e]	$<10^{-3}$	0.16	$<10^{-3}$
	75			0.18 ± 0.01	$<10^{-3}$		
Br	25	360	$^1A_1 \rightarrow {}^1A_2$	0.019 ± 0.001	0.18 ± 0.02	0.02	0.20
	75			0.021 ± 0.001	0.34 ± 0.03		
I	25	385	$^1A_1 \rightarrow {}^1A_2$	0.01	0.82 ± 0.08	<0.01	0.90
	75			0.01	0.83 ± 0.04		

[a] Bandwidth ± 20 nm. [b] T. R. Thomas and G. A. Crosby, *J. Mol. Spectrosc.*, **38**, 118 (1971); C. K. Jorgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962. [c] Based on 3–30 determinations with varying periods of irradiation. [d] Precision 10–20%. [e] Moggi[4] reported $\phi_{Cl} = 0.14$ on irradiating this band at 380 nm.

plexes we obtain the same products and product yields from the sensitized and direct (ligand field) photolysis. This indicates that in each case the intersystem crossing yield (ligand field singlet → triplet), ϕ_{isc}, is 1.0 and that all the products arise from a "ligand field" excited state with triplet spin multiplicity. Thus the different product yields cannot be attributed to different intersystem crossing yields or different populations of singlet and triplet excited states. The single simplest inference is that there are two photochemically active excited states of triplet spin multiplicity which differ little in (vibrationally equilibrated) energy, but which are very different in geometry; one state must involve a greatly lengthened Rh(III)–halide bond, the other a greatly lengthened Rh(III)–ammonia bond (note that all excited states are considered to have electron density in antibonding orbitals). In Figure 1 we have designated these states as ^3Y and ^3X, respectively. The state leading to ammonia aquation, ^3X, appears to have an intrinsically high yield for product formation (*i.e.*, to be nearly dissociative at room temperature). In fact, the product yields for $Rh(NH_3)_5Br^{2+}$ depend on temperature in a manner which suggests that ^3X is higher in energy than ^3Y (energy difference of about 300 cm^{-1}, assuming that the intrinsic product yield from ^3X is about 1)[8] for this complex. In the case of $Rh(NH_3)_5Cl^{2+}$, the energy gap appears to be sufficiently large ($\geq 10^3$ cm^{-1}) that there is not significant thermal activation of the corresponding ^3X state while in $Rh(NH_3)_5I^{2+}$ it would appear that ^3X must have the same or lower energy than ^3Y.

Our inference that there are two distinct photochemically active rhodium(III) excited states of similar energy but differing in geometry and in chemical reactivity, suggests that any simple, limiting strong field description is inappropriate for the excited states of coordination complexes. For example, since *trans*-ammonia and halide aquation appear as uncoupled processes in the ligand field photochemistry of these complexes, the photochemically important excited states are not usefully described in terms of electron density in orbitals of either "d_{z^2}" or "$d_{x^2-y^2}$" symmetry.

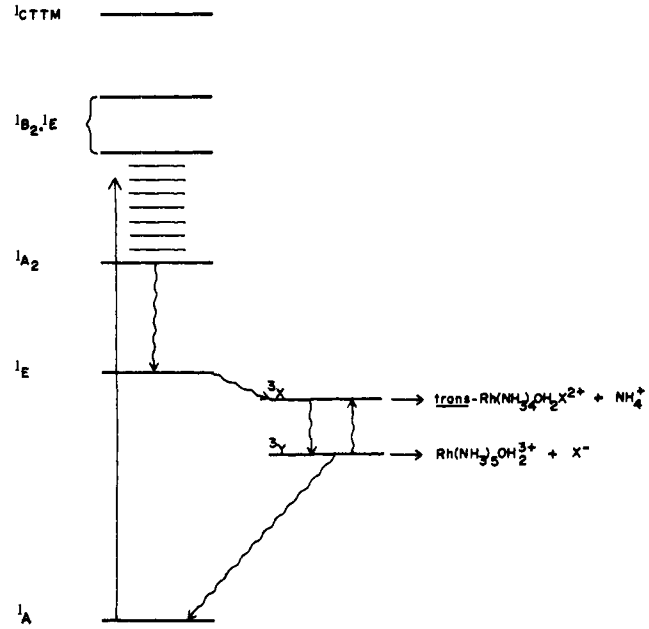

Figure 1. Relative energy level scheme for $Rh^{III}(NH_3)_5X$. Nonradiative activation and deactivation processes are indicated by wavy lines. The higher energy ligand field transitions (B_2, E^1) are obscured by the CTTM transition when X = Br or I. For illustrative purposes the ordering of the photochemically active states, ^3X and ^3Y, is that inferred for X = Br or Cl. Assignments based on T. R. Thomas and G. A. Crosby, *J. Mol. Spectrosc.*, **38**, 118 (1971).

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(8) Actually if the intrinsic product yield from ^3X is about 1, then the energy gap would be greater than 300 cm^{-1} since the population of ^3X and ^3Y could not then be in equilibrium. The actual product yields according to our proposed model must depend on the intrinsic rate constants of the competitive processes

$$^3X \longrightarrow {}^3Y$$

$$^3X \longrightarrow \text{products}$$

$$^3Y \longrightarrow {}^3X$$

$$^3Y \longrightarrow \text{products}$$

$$^3Y \longrightarrow \text{nonradiative deactivation}$$

This kinetic argument will be developed in detail elsewhere.

An Organic Transition State[1]

Sir:

The geometrical isomerization of cyclopropane is one of the simplest organic reactions. Since its discovery in 1958[2] many attempts have been made to elucidate its mechanism[3-8] as well as that of related

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(1) The material on which this communication is based was presented in a plenary lecture at the 23rd IUPAC Congress, Boston, Mass., July 1971. The proceedings of this congress appear in: Y. Jean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, *Pure Appl. Chem., Suppl.* (*23rd Congr.*), **1**, 197 (1971).

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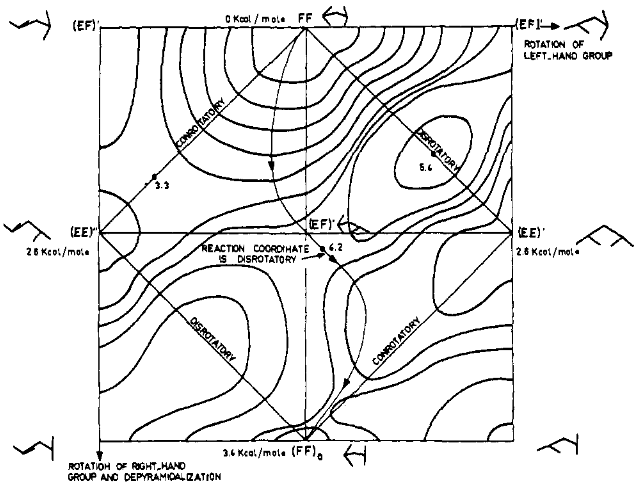

Figure 1. Reaction path in two-dimensional energy plot. Energies are relative to structure FF. The notations FF and $(FF)_0$ represent conformations of the face-to-face diradical, (EE)' and (EE)'' conformations of the edge-to-edge diradical, and (EF)' conformations of the edge-to-face diradical. Energy contours are separated by intervals of 0.6 kcal/mol. The energy contours in certain regions, particularly in the lower half, are approximate.

reactions.[9] Thermochemical calculations have led to the suggestion[4] that the reaction proceeds *via* a trimethylene diradical intermediate that would appear as a secondary minimum for the energy along the reaction coordinate.

We have totally resolved the structure of the transition state for geometrical isomerization of cyclopropane within the full 21-dimensional hypersurface. The detailed procedure of our search and its successive stages are exposed elsewhere.[10a-g] The energies were calculated by the self-consistent field (SCF) molecular orbital method, using a minimal basis set of Slater orbitals. The computational program was developed by one of us and its essential features and original characteristics are given elsewhere.[11] An open-shell program is incorporated in the main program; it uses the restricted Hartree-Fock formalism suggested by Nesbet together with a single Hamiltonian for all the electrons.[12] This Hamiltonian includes an arbitrary factor, $-x$, multiplying those exchange integrals which involve the two odd electrons. We considered x as an additional variation parameter and used the optimum value $x = 0.42$. In the region of the trimethylene diradical we performed a 3×3 configuration interaction between the ground, doubly excited, and singly excited configurations. This is equivalent to the search of the best "valence-bond" plus "ionic" type wave function.[10f]

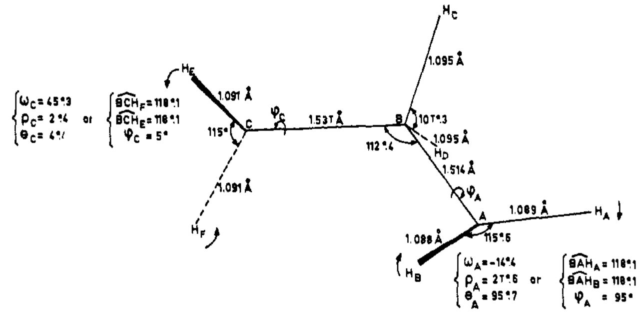

Figure 2. Internal coordinates of the transition state for geometrical isomerization of cyclopropane. On each methylene group three independent orthogonal coordinates (ω, ρ, θ) describe, respectively, the wagging, rocking, and twisting motions of the methylene group. An alternative set of coordinates is the rotation angle ϕ relative to the neighboring carbon–carbon axis and the two carbon–carbon–hydrogen bond angles. The internal atom H_B has already crossed the ABC plane. The arrows indicating motion of the methylene groups are all reversed in the reverse pathway, in which the external atom crosses the ABC plane first.

Figure 1 is a contour map showing the nondynamic reaction pathway with least activation energy. The vertical and horizontal axes represent, respectively, the rotations of the principal and secondary methylene groups. For the principal group, the lower half of the diagram involves rotation *plus* depyramidalization, while the upper half involves pure rotation. With these axes, optical isomerization corresponds to either of the diagonal directions, with the edge-to-edge configurations (EE)' and (EE)'' as half-way points, while geometrical isomerization corresponds to the vertical axis direction. The optimum path involves initial conrotatory motion of both groups; then, at ~60° rotation, the principal group continues to rotate while the other secondary group rotates *backward.* At 90–100°, in the transition-state region, the concerted motion is *disrotatory.* In the final period of rotation of the main group, the secondary group again changes its direction of rotation, so that the final process is conrotatory. The overall rotational motion of the secondary group remarkably consists of an alternating forward–backward–forward balancing motion. The reason for the initial and final conrotatory motions is the obvious tendency to follow the allowed concerted pathways.[6,13] The disrotatory motion in the transition-state region is required to link the initial and final conrotatory processes. Another salient feature is that the entire route proceeds *without any secondary minimum;* indeed, the energy decreases monotonically from the col to the open face-to-face diradical FF, which in turn can reclose to cyclopropane without any energy barrier.[10b] The minute secondary maximum observed at 160° disappears unambiguously if the CCC bond angle is allowed to reclose slightly, from 113 to 108°.

The geometry of the transition state (Figure 2) is defined in terms of a set of 21 internal coordinates. The

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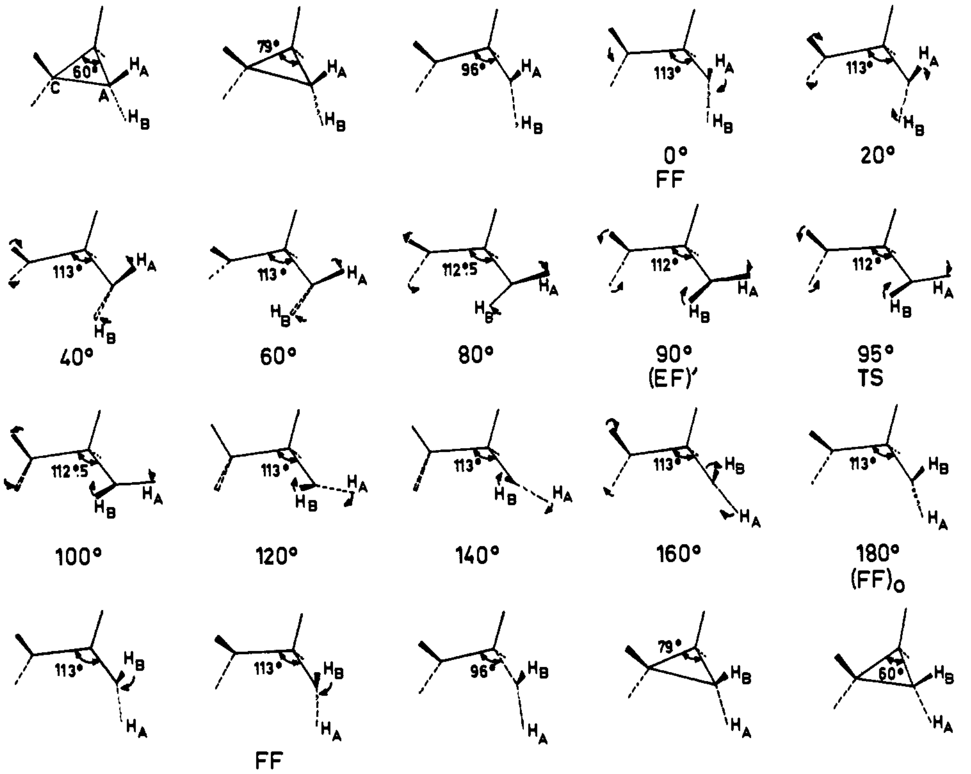

Figure 3. A nondynamic pathway passing through the transition state. The rotation angle ϕ_A of the principal methylene group is shown below the molecule. Central CCC angles have been rounded off. The notations FF, $(FF)_0$, (EF)′, and TS represent, respectively, a face-to-face trimethylene in its stable pyramidalized form, the same with one methylene group trigonal, an edge-to-face diradical in its stable pyramidalized form, and the transition state.

calculated energy of the transition state structure is 52.6 kcal/mol relative to cyclopropane, whereas the experimental activation energy[1] is 64.2 kcal/mol. (The calculated activation energy for optical isomerization is 52 kcal/mol.) Improvement of the basis set—for instance by including d functions for polarization[14]—will affect differently the tighter cyclic system (cyclopropane) and the open chain (trimethylene) system. Also, there should be a large negative correlation energy correction for cyclopropane,[15] for which no configuration interaction has been performed, whereas in the transition state region the 3 × 3 configuration interaction has already accounted for the greater part of the correlation of *one* electron pair.[16] To prove that the structure shown in Figure 2 is indeed the transition state *on the calculated surface*, we verified[10g] that the energy around the transition state increases by at least 0.0001 au (0.06 kcal/mol) along all 20 internal coordinates other than the reaction coordinate.[17]

Figure 3 shows a typical pathway which could be followed by the molecule in the geometrical isomerization process. Part of this path is shown in Figure 1. It is a "nonminimum" energy pathway (since the system has been forced to proceed *via* FF) and "nondynamic" (since we have no information on the vibrational energy distribution).

The reliability of our proposed structure is hard to assess, since the conditions under which minimal basis set calculations are faithful to experiment have not yet been fully explored. It is well known that there are situations where such calculations give extremely poor results (for instance, geometries of O_2F_2 and N_2F_2).[18] However, they are extremely successful for hydrocarbon geometries.[19] It is also very encouraging that other nonempirical explorations[20] of the potential energy surface of cyclopropane share similar features with ours. In particular, a recent calculation by the GVB method[20c-d] also yields nearly equal activation energies for geometrical and optical isomerization and no secondary minimum.

Our results are in agreement with the main experimental observations[8b-d] that, at least in 1,2-disubstituted cyclopropanes, the overall rate constants for geometrical isomerization and optical isomerization are comparable. They also indicate that the kinetic analysis of the overall rate constants could be done better by comparing direct one-step processes from reactant to geometrical or optical product than by invoking two-step schemes with intermediate diradicals.

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[14] H. Marsmann, J.-B. Robert, and J. R. Van Wazer, *Tetrahedron*, 27, 4377 (1971).

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[16] If the same 3 × 3 configuration interaction is performed for cyclopropane, its energy is lowered by 4.6 kcal/mol and the calculated activation energy is raised to 57.2 kcal/mol. Indeed, such a limited configuration interaction is relatively ineffective for producing the correlation energy of a closed-shell system.[15]

[17] Rigorously, the force constants along all 21 normal coordinates are required. (It would therefore be necessary to calculate the 210 interaction constants between all internal coordinates.) We assume that the internal coordinates are a good approximation to the normal coordinates.

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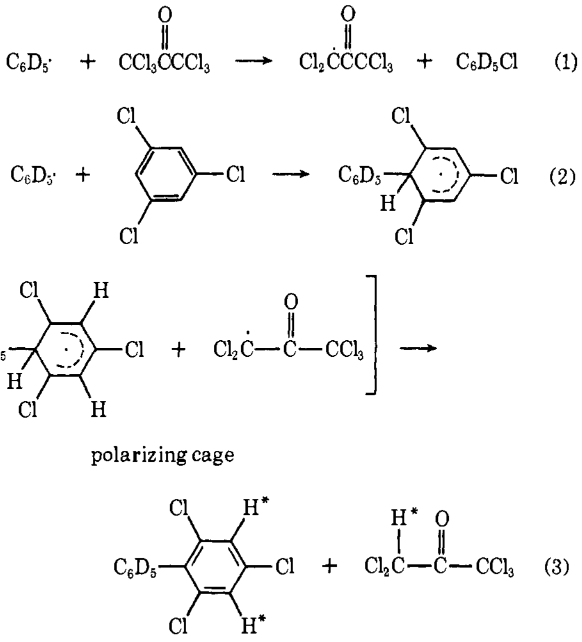
Chemically Induced Dynamic Nuclear Polarization Techniques in the Study of the Arylation Reaction. A Novel Demonstration of the Intermediacy of the Aryl Cyclohexadienyl Radical[1]

Sir:

The phenylcyclohexadienyl radical (PCD·) has been assumed to be the key intermediate in the extensively studied free-radical arylation of aromatic compounds.[2] While the presence of this radical had been inferred from chemical evidence we have been able to obtain physical evidence for it by the use of CIDNP techniques.[3] The CIDNP effect detects electron–nuclear spin interactions between unsymmetric radical pairs by a net polarization in the nmr spectrum of the resulting products.[4]

Phenyl radicals are most conveniently produced by the thermal or photochemical decomposition of benzoyl peroxide (BPO). Whatever the source, phenyl radicals will react with aromatic substrates by a complicated mechanism leading to arylated products.[2] In fact, it has been calculated that there are 100 significant steps in the decomposition of BPO in benzene.[5] In order to simplify the nmr spectra, perdeuterated BPO was used as the source of phenyl radicals, and 1,3,5-trisubstituted benzenes were used as the aromatic substrate. Thus, the reaction produced a single biphenyl containing only one kind of hydrogen. Furthermore, perchlorinated radicals were used as acceptors for any abstractable hydrogens which thereby appeared in a one-line spectrum. The perchlorinated radicals are formed by chlorine abstraction of excess radicals during the BPO decomposition. For example, see eq 1–3, where an asterisk denotes polarization.



$$C_6D_5\cdot + CCl_3\overset{\overset{O}{\|}}{C}CCl_3 \longrightarrow Cl_2\dot{C}\overset{\overset{O}{\|}}{C}CCl_3 + C_6D_5Cl \quad (1)$$

polarizing cage

The perchlorinated radicals also served the purpose of providing a radical with a different *g* value from that of the PCD·, a condition which must be met for net polarization.[4c,6] (Normally the predominant reactions are the coupling and disproportionation of two PCD· radicals.[2f])

We observed polarized nmr spectra from both products of reaction 3, the biphenyl and the pentachloroacetone, the polarized hydrogens being those of the PCD·. Similarly, an emission spectrum of pentachloroethane or chloroform was observed when hexachloroethane or carbon tetrachloride[7] was the chloro substrate. Among the aromatic compounds which were used successfully as hydrogen sources to produce these one-line nmr spectra were benzene, toluene, xylene, mesitylene, chlorobenzene, 1,3,5-trichlorobenzene, diphenylmethane, and naphthalene. The corresponding biphenyl polarization, however, an enhanced absorption, is easily obscured by the solvent spectrum and was only observed in the substrates mesitylene and 1,3,5-trichlorobenzene. These 1,3,5-substituted benzenes also provide more favorable conditions for biphenyl formation since coupling of their PCD radicals is sterically inhibited. For a typical run see Figure 1. The observed polarization may be analyzed on the basis of a simple formulation used to predict the sign of nmr enhancement.[8] Then the emission spectrum of the pentachloroacetone (chloroform or pentachloroethane) is consistent with hydrogen abstracted from the PCD· within the polarizing cage. The perchlorinated radicals are expected to have a higher *g* value than any

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[1] Presented in part at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, Abstract No. ORGN-42. For Part I, see S. R. Fahrenholtz and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **93**, 251 (1971).

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