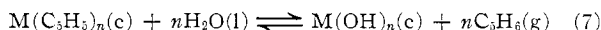


Discussion

With the data now available, summarized in Table II, the free energy change of the general "hydrolysis" reaction may be considered



where M = metal and n = metal valence. The free energy of formation of C_5H_6 ideal gas (1 atm pressure) is taken to be 42.2 kcal/mole¹¹ and that of water is -56.69 kcal/mole.¹⁰

TABLE II
STANDARD FREE ENERGIES OF FORMATION AT 25°,
 $\Delta G_f^\circ_{298}$, KCAL/MOLE

$TiC_5H_5(c)$	42.3 ± 0.5	$TiOH(c)$	-46.8 ± 0.1^b
$Fe(C_5H_5)_2(c)$	70.9 ± 1.5^a	$Fe(OH)_2(c)$	-115.6 ± 1^c
$Mg(C_5H_5)_2(c)$	53.1 ± 2^a	$Mg(OH)_2(c)$	-199.3 ± 0.5^c

^a See ref 4. ^b See ref 10. ^c F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, U. S. National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

For $M = Ti$, $\Delta G^\circ_{298}(7) = 9.8$ kcal, in agreement with the observation that TiC_5H_5 is only very slightly hydrolyzed by water and may be made from $TiOH$ and

C_5H_6 . Similarly for $M = Fe$, $\Delta G^\circ_{298}(7) = 11.3$ kcal, so that $Fe(C_5H_5)_2$ is also resistant to hydrolysis as observed in practice.³ The reaction between $Fe(OH)_2(c)$ and C_5H_6 , though possible in principle, is not observed in practice, probably owing to the extremely low solubilities of $Fe(OH)_2$ and $Fe(C_5H_5)_2$ in water.

For $M = Mg$, however, $\Delta G^\circ_{298}(7) = 54.6$ kcal, in agreement with the observation⁴ that $Mg(C_5H_5)_2$ undergoes rapid and quantitative hydrolysis. Consideration of Table II shows clearly that it is the relative free energies of the hydroxides which determine whether or not hydrolysis will occur. This effect overrides the smaller variations of free energy of the cyclopentadienyl-metal compounds. Previous workers³ have proposed the hydrolysis reaction to distinguish between "ionic" and "covalent" cyclopentadienyl compounds. The present work shows that such a test reveals little about the type or strength of the cyclopentadienyl-metal bond. The hydrolysis of $Mg(C_5H_5)_2$ depends on the high affinity of Mg for oxygen, whereas the preparation of TiC_5H_5 in aqueous solution depends on the low affinity of Ti for oxygen and the solubility of $TiOH$ in water.

CONTRIBUTION FROM THE AEROSPACE RESEARCH LABORATORIES, ARC, WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433,
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Determination of Rates of Optical Inversion of Aluminum β -Diketonate Complexes by Nuclear Magnetic Resonance Studies of Racemic Mixtures^{1a}

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Compounds of the form $Al(AA)_2(BB)$ and $Al(AA)(BB)_2$ can be prepared from $Al(AA)_3$ and $Al(BB)_3$, where AA and BB represent symmetrical bidentate ligands such as 2,2,6,6-tetramethyl-3,5-heptanedione [$H(thd)$], 2,4-pentanedione [$H(acac)$], and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione [$H(hfa)$]. Chlorobenzene solutions of these compounds in equilibrium with the parent tris species have been studied by nmr, and the equilibrium constants for the ligand exchange reactions measured at 25° are: $Al(acac)_3$ with $Al(thd)_3$, $K = 1.5$; $Al(hfa)_3$ with $Al(acac)_3$, $K = 3.34 \times 10^4$; and $Al(hfa)_3$ with $Al(thd)_3$, $K = 3.68 \times 10^4$. Large deviations from the statistical distribution of ligands ($K = 9$) were found. The mixed-ligand complexes are favored in both systems in which hfa is present while in the other equilibria the parent tris complexes are favored. The terminal groups of AA in complexes of the form $Al(AA)_2(BB)$ exhibit different resonances due to their structural nonequivalence; the two peaks coalesce as the temperature is raised. The coalescence is attributed to the optical inversion of the complex. The coalescence temperatures and rate constants of environmental averaging are: $Al(acac)_2(thd)$, 105°, 12.6 sec⁻¹; $Al(acac)(thd)_2$, 105°, 8.5 sec⁻¹; $Al(hfa)(thd)_2$, -8°, 6.9 sec⁻¹; and $Al(hfa)(acac)_2$, -18°, 5.3 sec⁻¹. Rates are determined for other temperatures, allowing the calculation of frequency factors and energies and entropies of activation. The rates were found to be independent of complex concentration and the presence of uncomplexed ligand, indicating an intramolecular racemization process. The relationship of the determined rates of environmental averaging to the rates of optical inversion are shown to be dependent on the mechanism of the process, and these relationships are discussed in detail for both bond rupture and nonbond rupture mechanisms. This technique permits the estimation of rates of racemization of complexes of the type $M(AA)_2(BB)$ without prior resolution of optical isomers.

Introduction

The great importance of nmr in structural studies of octahedral complexes of mixed bidentate ligand chelates was first demonstrated by Collman and co-workers² in

1962. Fay and Piper³ have well established the value of nmr in estimating rates of geometrical isomerization of octahedral complexes with unsymmetrical bidentate ligands. Other systems have been examined in which

(1) (a) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967; (b) Wright State University; supported as a Visiting Research Associate, Ohio State Research Foundation; (c) Aerospace Research Laboratories.

(2) J. P. Collman, R. L. Marshall, and W. L. Young, III, *Chem. Ind. (London)*, 1380 (1962).

(3) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964), and references cited therein.

the complexes may undergo either geometrical isomerization, racemization, or both, to produce coalescence of nmr resonances.⁴⁻⁸ More recent work has extended such procedures to complexes which may only racemize.^{5,9} The present work points out how nmr may be used to measure rates of environmental averaging of nonequivalent protons in octahedral complexes and to relate these to rates of optical inversion by examination of complexes of the appropriate symmetry.

The general form of compounds which seem so well suited for these studies is $M(AA)(BB)_2$, where AA and BB represent different symmetrical bidentate ligands and M is a metal. The systems reported herein are aluminum complexes of mixed symmetric β -diketones. Complexes of this type exist as optical isomers but not geometrical isomers, thus eliminating the difficulty of distinguishing geometrical isomerization phenomena from optical inversion. Also, this absence of geometrical isomers makes it easier to consider the relationship of rates of environmental averaging determined by nmr to the rates of loss of optical activity. This relationship depends on which mechanism of inversion might be assumed.

The method presented has the distinct advantage that it may be used with racemic mixtures, thus eliminating the necessity for prior resolution of optical isomers. It should be particularly useful for studies of complexes which racemize too rapidly to allow resolution and examination by classical methods.

Finally it should be noted that, if racemization of the types of complexes herein presented can be studied by both nmr and independent methods, it could well allow the determination of the most probable mechanism of optical inversion of these complexes.

Experimental Section

Preparation of Tris(2,4-pentanedionato)aluminum(III).— $Al(acac)_3$ was prepared by the method of Young.¹⁰ The product was recrystallized from benzene by the addition of hexane.

Preparation of Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum(III).— $Al(hfa)_3$ was prepared by the reaction of anhydrous aluminum chloride with $H(hfa)$ ¹¹ and recrystallized from carbon tetrachloride.

Preparation of Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)aluminum(III).— $Al(thd)_3$ was prepared by the method of Hammond, *et al.*,¹² and purified by sublimation *in vacuo*.

Characterization of Parent Complexes.—The complexes were characterized by melting point determinations and elemental analyses. All complexes were found to be anhydrous.

Preparation of Mixed-Ligand Complexes.—Samples of the two parent tris complexes to undergo ligand exchange were weighed into nmr tubes in 2:1 or 1:2 mole ratios. Sufficient chlorobenzene dried over molecular sieves (some systems were also pre-

pared with dry carbon tetrachloride as solvent) was added to dissolve the samples. Karl Fischer analyses showed the chlorobenzene to contain less than 0.05 mg of water/ml. Independently prepared samples gave the same kinetic and thermodynamic results within experimental errors. The nine solutions had initial molar concentrations as follows: $Al(acac)_3:Al(thd)_3$ equal to 0.010:0.020, 0.030:0.015, and 0.0019:0.0009 in chlorobenzene, 0.012:0.023 and 0.032:0.016 in carbon tetrachloride; $Al(hfa)_3:Al(acac)_3$ equal to 0.013:0.006 and 0.008:0.016 in chlorobenzene; and $Al(hfa)_3:Al(thd)_3$ equal to 0.015:0.030 and 0.014:0.007 in chlorobenzene. Tetramethylsilane was added as an internal standard; the tubes were sealed *in vacuo*, heated to 120° in an oven for at least 15 hr, and then allowed to stand at 25° for several days until the spectra showed no further variations in concentrations of the four species in equilibrium. The samples showed no further variations even after standing several months at room temperature.

Instrumentation.—The spectra were recorded on a Varian A-60 spectrometer equipped with a V-6057 variable-temperature system. The values of the chemical shifts are believed accurate to ± 0.5 cps and the separations between coalescing resonances were reproducible within ± 0.1 cps. The temperatures were believed to be valid to within $\pm 2^\circ$ or better. High temperatures were measured using the splittings of ethylene glycol and low temperatures using methanol spectra. Integral presentations are estimated to be accurate to within 2%.

Results

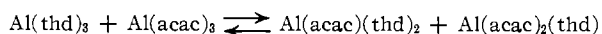
Ligand-Interchange Equilibria.—The assignments of the chemical shifts of the resonance peaks for the solution of $Al(acac)_3$, $Al(acac)(thd)_2$, $Al(acac)_2(thd)$, and $Al(thd)_3$ in chlorobenzene are shown in Table I. From

TABLE I
CHEMICAL SHIFTS IN CHLOROBENZENE
SOLUTIONS AT ROOM TEMPERATURE^a

Complex	<i>t</i> -Butyl protons	Methyl protons	Methylene protons of		
			acac	thd	hfa
$Al(acac)_3$		1.78	5.36		
$Al(thd)_3$	1.16			5.85	
$Al(acac)_2(thd)$	1.15	1.72, 1.83	5.37	5.90	
$Al(acac)(thd)_2$	1.14, 1.20	1.78	5.38	5.88	
$Al(hfa)_2(acac)$		1.71	5.35		6.35
$Al(hfa)(acac)_2$		1.74	5.35		6.30
$Al(hfa)_2(thd)$	1.05			5.98	6.38
$Al(hfa)(thd)_2$	1.11			5.90	6.32

^a In ppm (δ) relative to internal TMS.

the integrated areas of these peaks the equilibrium constant for the process



was calculated as follows. The areas of the resonances due to $Al(acac)(thd)_2$ and $Al(thd)_3$ in the *t*-butyl region were normalized by dividing by the appropriate number of protons per molecule. For $Al(acac)_2(thd)$ the average of the normalized areas found for its peaks in the *t*-butyl and methyl regions was used. Since the remaining peak in the methyl region was due to both $Al(acac)_3$ and $Al(acac)(thd)_2$, the area due to the methyl groups of the acac ligand of $Al(acac)(thd)_2$ (determined by comparison with the *t*-butyl resonance) had to be subtracted from the total area in order to get the area due to $Al(acac)_3$. The best determinations of areas were obtained for the system which started with a 2:1 $Al(acac)_3:Al(thd)_3$ ratio in chlorobenzene. The average value of K thus obtained is 1.5 at 25°.

(4) R. A. Palmer, R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 875 (1964).

(5) D. C. Bradley and C. E. Holloway, *Chem. Commun.*, 284 (1965); "Proceedings of the 9th International Conference on Coordination Chemistry," W. Schneider, Ed., Verlag Helvetica Chimica Acta, Basle, Switzerland, 1966, p 483.

(6) R. C. Fay, T. J. Pinnavaia, N. Serpone, and R. N. Lowry, ref 5, p 486.

(7) J. W. Faller and A. Davidson, *Inorg. Chem.*, **6**, 182 (1967).

(8) R. C. Fay and R. N. Lowry, *Inorg. Nucl. Chem. Letters*, **3**, 117 (1967); *Inorg. Chem.*, **6**, 1512 (1967).

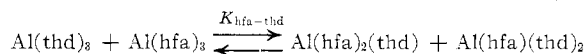
(9) R. G. Linck and R. E. Sievers, *ibid.*, **5**, 806 (1966).

(10) R. C. Young, *Inorg. Syn.*, **2**, 25 (1946).

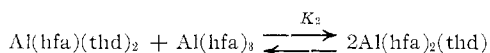
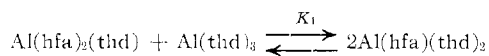
(11) M. L. Morris, R. W. Moshier, and R. E. Sievers, *ibid.*, **9**, 28 (1967).

(12) G. S. Hammond, D. C. Nonhebel, and C. S. Wu, *Inorg. Chem.*, **2**, 73 (1963).

Assignments of the proton resonance peaks observed from the mixture of $\text{Al}(\text{thd})_3$, $\text{Al}(\text{hfa})_3$, $\text{Al}(\text{hfa})(\text{thd})_2$, and $\text{Al}(\text{hfa})_2(\text{thd})$ are also given in Table I. In this system the mixed-ligand complexes are greatly favored and the particular parent tris complex initially less abundant is not detectable in the equilibrium mixture. Therefore, the equilibrium constant of the over-all equilibrium



was calculated from the equilibrium constants of the two observed equilibria



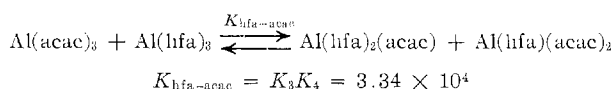
obtained for the 2:1 $\text{Al}(\text{thd})_3:\text{Al}(\text{hfa})_3$ and the 2:1 $\text{Al}(\text{hfa})_3:\text{Al}(\text{thd})_3$ samples, respectively. From the integrated, normalized areas, a value of 100 is obtained for K_1 , and 368 for K_2 . In the second equilibrium $\text{Al}(\text{thd})_3$ is not seen in the spectra at equilibrium, and since the starting mole ratio of $\text{thd}:\text{hfa}$ was 0.50, it is assumed that the concentration of $\text{Al}(\text{hfa})_3$ must equal the concentration of $\text{Al}(\text{hfa})(\text{thd})_2$. By combining these results, it is possible to obtain the over-all equilibrium constant for $K_{\text{hfa-thd}} = K_1K_2 = 3.68 \times 10^4$ (in chlorobenzene).

For systems of $\text{Al}(\text{hfa})_3$ with $\text{Al}(\text{acac})_3$ instead of $\text{Al}(\text{thd})_3$ similar arguments yield

$$K_3 = \frac{[\text{Al}(\text{hfa})(\text{acac})_2]^2}{[\text{Al}(\text{acac})_3][\text{Al}(\text{hfa})_2(\text{acac})]} = 46$$

$$K_4 = \frac{[\text{Al}(\text{hfa})_2(\text{acac})]^2}{[\text{Al}(\text{hfa})_3][\text{Al}(\text{hfa})(\text{acac})_2]} = 725$$

and for



All values of K given are calculated from the average of at least five integrations and are summarized in Table II.

TABLE II

EQUILIBRIUM CONSTANTS FOR LIGAND-EXCHANGE REACTIONS

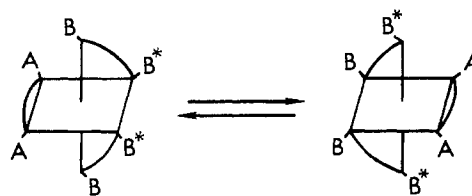
Ligands AA-BB	Equilibrium constants ^a		
	$\frac{[\text{Al}(\text{AA})(\text{BB})_2]^2}{[\text{Al}(\text{AA})_2(\text{BB})_2][\text{Al}(\text{AA})(\text{BB})_2]}$	$\frac{[\text{Al}(\text{AA})_2(\text{BB})_2]^2}{[\text{Al}(\text{AA})_3][\text{Al}(\text{AA})(\text{BB})_2]}$	$\frac{[\text{Al}(\text{AA})(\text{BB})_2]^2}{[\text{Al}(\text{AA})_3][\text{Al}(\text{BB})_3]}$
acac-thd	1.1	1.4	1.5
hfa-thd	100	368	3.68×10^4
hfa-acac	46	725	3.34×10^4

^a In chlorobenzene solutions. The relative standard deviation is $\pm 25\%$ for the acac-thd constants and $\pm 10\%$ for the hfa-thd and hfa-acac constants.

Coalescence Temperatures and Rates of Environmental Averaging.—Of particular interest are the complexes with the ligands in a 2:1 or 1:2 ratio, since the terminal groups of the BB ligand in a complex of form $\text{Al}(\text{AA})(\text{BB})_2$ exhibit different nmr resonance frequencies due to their structural nonequivalence. One of the

terminal groups of each of the BB ligands is opposite a terminal group of the other BB ligand, while the remaining group of each BB is opposite a terminal group of the AA ligand. A detailed study of the spectra of the complexes $\text{Al}(\text{acac})_2(\text{thd})$, $\text{Al}(\text{acac})(\text{thd})_2$, $\text{Al}(\text{hfa})(\text{acac})_2$, and $\text{Al}(\text{hfa})(\text{thd})_2$ as a function of temperature showed that the two proton resonances of the terminal groups of the bis ligands coalesce as the temperature is raised. Spectra of the *t*-butyl and methyl regions of the mixture of $\text{Al}(\text{acac})_3$, $\text{Al}(\text{acac})_2(\text{thd})$, $\text{Al}(\text{acac})(\text{thd})_2$, and $\text{Al}(\text{thd})_3$ at various temperatures are shown in Figure 1. Note that the two outer resonances in the *t*-butyl region due to $\text{Al}(\text{acac})(\text{thd})_2$ coalesce under the *t*-butyl resonances of the $\text{Al}(\text{thd})_3$ and $\text{Al}(\text{acac})_2(\text{thd})$ species. The two outer peaks in the methyl region due to $\text{Al}(\text{acac})_2(\text{thd})$ also coalesce under the methyl peak due to the $\text{Al}(\text{acac})_3$ and $\text{Al}(\text{acac})(\text{thd})_2$ complexes. In chlorobenzene $\text{Al}(\text{acac})_2(\text{thd})$ and $\text{Al}(\text{acac})(\text{thd})_2$ both exhibit coalescence at 105° while $\text{Al}(\text{hfa})(\text{acac})_2$ and $\text{Al}(\text{hfa})(\text{thd})_2$ show coalescence at -18 and -9° , respectively. Owing to the unfortunate fact that coalescence occurs under peaks due to other species, these coalescence temperatures could possibly vary by as much as $\pm 3^\circ$.

The coalescence is attributed to the averaging of the environments of the terminal groups of the bis ligands such as would accompany optical inversion¹³



Because of the symmetry of the $\text{Al}(\text{AA})(\text{BB})_2$ complexes, each bidentate BB ligand has one terminal group in each magnetic environment; therefore, the two sites are equally populated. Consequently, the rate of environmental averaging can be calculated at various temperatures up to coalescence from the expression

$$k = (1/2\sqrt{2})[\delta\nu_{\text{max}}^2 - \delta\nu_T^2]^{1/2}$$

as given by Gutowsky and Holm,¹⁴ where $\delta\nu_{\text{max}}$ is the maximum frequency separation in the limit of slow environmental exchange and $\delta\nu_T$ is the frequency separation at temperature T , both expressed in radians. The measured frequency separations and the rates calculated from them at various temperatures are given in Tables III and IV. Rates obtained in this fashion are, of course, more approximate than the rates obtained from a curve-fitting approach utilizing line shapes and transverse relaxation times, but it should be noted that such a simple approach when applied to the data of Fay and Lowry⁸ in most cases gave fairly good agreement with their more rigorously calculated rates. Unfortunately, the presence of other complexes in the

(13) As will be discussed later environmental averaging in certain idealized cases can be caused by processes other than optical inversion.

(14) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

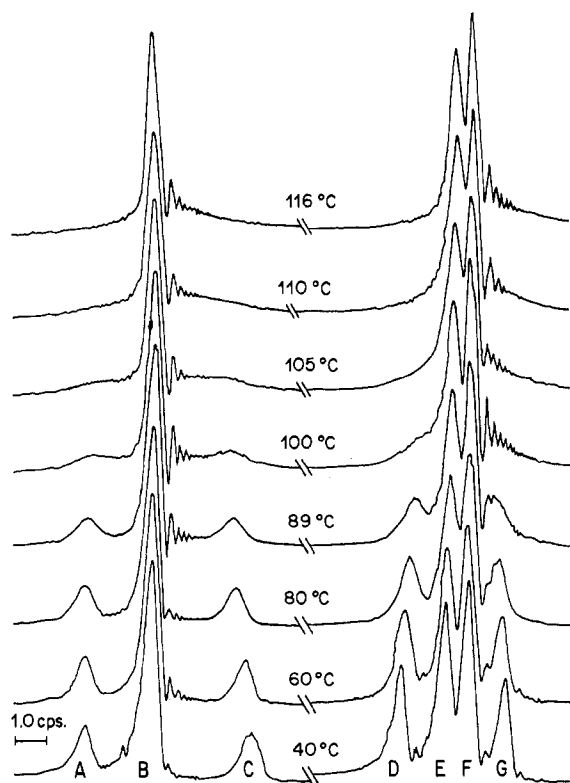


Figure 1.—The nmr spectra of the *t*-butyl (right) and methyl (left) regions of a mixture of $\text{Al}(\text{acac})_3$, $\text{Al}(\text{acac})_2(\text{thd})$, $\text{Al}(\text{acac})(\text{thd})_2$, and $\text{Al}(\text{thd})_3$, in chlorobenzene solution at various temperatures. Initial solution was 0.030 *M* in $\text{Al}(\text{acac})_3$ and 0.015 *M* in $\text{Al}(\text{thd})_3$. The peaks are assigned as follows: A and C, acac in $\text{Al}(\text{acac})_2(\text{thd})$; B, acac in both $\text{Al}(\text{acac})(\text{thd})_2$ and $\text{Al}(\text{acac})_3$; D and G, thd in $\text{Al}(\text{acac})(\text{thd})_2$; E, thd in $\text{Al}(\text{thd})_3$; and F, thd in $\text{Al}(\text{acac})_2(\text{thd})$.

TABLE III
SPLITTING AND RATE CONSTANTS FOR ENVIRONMENTAL AVERAGING OF TERMINAL GROUPS OF THE BIS LIGANDS IN CHLOROBENZENE SOLUTION

Temp, °C	$\text{Al}(\text{acac})_2(\text{thd})$		$\text{Al}(\text{acac})(\text{thd})_2$	
	$\delta\nu$, cps	k , sec ⁻¹	$\delta\nu$, cps	k , sec ⁻¹
105	Coalescence	12.6	Coalescence	8.5
103	3.2	10.4	1.5	7.3
102	4.3	8.3	1.7	7.0
100	4.6	7.5	2.0	6.6
89	5.0	6.1	2.7	5.3
80	5.2	5.2	3.0	4.4
60	5.6	2.4	3.4	2.6
50	5.7		3.6	

mixtures discussed herein makes the more rigorous fitting exceedingly difficult, if not impossible. Furthermore, if it were necessary to separate the $\text{M}(\text{AA})_2(\text{BB})$ species from the other complexes, this would greatly reduce the usefulness of the general method. Even if the separations could easily be achieved, there is considerable doubt that the other complexes could be removed and the measurements made before ligand-interchange reactions would begin to generate more of the interfering species. For comparison with the rate data for the complexes in chlorobenzene the rates of environmental averaging for $\text{Al}(\text{acac})(\text{thd})_2$ and $\text{Al}(\text{acac})_2(\text{thd})$ in carbon tetrachloride were calculated¹⁵ to be 7.5 and

(15) Rates were calculated from the maximum frequency separations of 3.4 and 3.5 cps, respectively.

TABLE IV
SPLITTINGS AND RATES CONSTANTS FOR ENVIRONMENTAL AVERAGING OF TERMINAL GROUPS OF THE BIS LIGANDS IN CHLOROBENZENE SOLUTION

$\text{Al}(\text{hfa})(\text{thd})_2$			$\text{Al}(\text{hfa})(\text{acac})_2$		
Temp, °C	$\delta\nu$, cps	k , sec ⁻¹	Temp, °C	$\delta\nu$, cps	k , sec ⁻¹
-8	Coalescence	6.9	-18	Coalescence	5.3
-9	1.2	6.3	-19	0.6	5.2
-10	1.4	6.1	-21	0.8	5.0
-19	2.8	3.0	-22	1.0	4.8
-27	2.8	3.0	-24	1.1	4.7
-39	3.1		-31	1.5	4.2
			-35	1.7	3.8
			-39	1.9	3.3
			-47	2.4	

7.8 sec⁻¹, respectively, at their fortuitously identical coalescence temperature of 105°.

Total intermolecular ligand interchange can be eliminated as the cause of the coalescence as the individual $\text{Al}(\text{acac})_2(\text{thd})$ and $\text{Al}(\text{thd})_3$ resonances in the *t*-butyl region are still distinct at the coalescence temperature (see Figure 1). The methylene resonances observed are also still separate at the temperature of coalescence. Furthermore, in all three cases studied the rate at which intermolecular ligand interchange occurs is very slow compared to the rate of inversion, as the samples must be heated at temperatures above 100° for several hours before equilibrium is established.

The coalescence temperatures and rates of environmental exchanges for $\text{Al}(\text{acac})(\text{thd})_2$ and $\text{Al}(\text{acac})_2(\text{thd})$ complexes in chlorobenzene were found to be independent of complex concentration, thus indicating that the rates are first order.

A free-ligand dissociation mechanism of the type proposed by Thomas,¹⁶ whereby a ligand would dissociate completely from the complex, has also been eliminated, as samples with uncomplexed ligand added to them exhibited separate resonances at the coalescence temperatures due to the uncomplexed ligand, while the remainder of the spectra were unchanged. The above observations all suggest an intramolecular inversion process.

Discussion

Equilibrium Constants and Intermolecular Ligand Interchange.—The great variation of the values of the equilibrium constants for the various ligand-interchange reactions is indeed surprising. For the reaction of $\text{Al}(\text{hfa})_3$ with $\text{Al}(\text{acac})_3$ the equilibrium constant indicates $\Delta F^\circ = -6.1$ kcal at 25° and for the reaction of $\text{Al}(\text{hfa})_3$ with $\text{Al}(\text{thd})_3$ a ΔF° of -6.2 kcal is obtained. The reaction of $\text{Al}(\text{acac})_3$ with $\text{Al}(\text{thd})_3$ gives a ΔF° of only -0.24 kcal. The large free energy changes for those systems involving hfa is difficult to explain.

A random distribution of the ligands would yield a 1:3:3:1 ratio of $\text{Al}(\text{AA})_3:\text{Al}(\text{AA})_2(\text{BB}):\text{Al}(\text{AA})(\text{BB})_2:\text{Al}(\text{BB})_3$. Such a statistical distribution would require a K of 9, giving a ΔS° of +4.4 eu. At 25° this would contribute only -1.3 kcal to ΔF° . The same results are

(16) W. Thomas, *J. Chem. Soc.*, **119**, 1140 (1921).

obtained considering the change from reactants of D_3 symmetry to products of C_2 symmetry by the method of Benson.¹⁷

Using the theoretical value of ΔS° , a ΔH° of -4.9 and -4.8 kcal would be necessary for the hfa-thd and hfa-acac systems, respectively, and a ΔH° of $+1.1$ kcal is required for the equilibrium involving thd and acac. A partial explanation for the large enthalpy terms in the fluorinated systems might be obtained from a consideration of the electron-withdrawing power of the fluorines in hfa as opposed to the more electron-releasing methyl and *t*-butyl groups in acac and thd. It might be argued that in $Al(hfa)_3$ the six CF_3 groups are all competing for the electrons participating in bond formation with the metal. In the mixed complexes the aluminum might be more electron rich due to the thd or acac ligands, thus stabilizing the hfa linkage to the metal ion. The net result would be stabilization of the mixed-ligand complexes relative to $Al(hfa)_3$. In contrast, because thd and acac chelate ring systems have more similar electron densities, the thd-acac mixed complexes would gain little if any stability over the pure $Al(thd)_3$ or $Al(acac)_3$ parents, and this is experimentally reflected in the more nearly statistical distribution of ligands in the system involving thd and acac. This argument receives some support from the metal-oxygen force constants calculated by Nakamoto, *et al.*,¹⁸ for the hexafluoroacetylacetonate complexes of Cu(II) and Ni(II) as opposed to the acetylacetonate complexes. In each case the hfa complex has an appreciably smaller force constant than the acac complex. The relative instability of $Al(hfa)_3$ is further indicated by a consideration of the equilibrium constants of the reactions of the tris complexes with the mixed-ligand complexes. In both cases the equilibrium constants involving reaction of $Al(hfa)_3$ are larger than those that do not; K_2 is better than 3 times as large as K_1 , and K_4 more than 15 times larger than K_3 .

Rates of Environmental Averaging.—The rates listed in Tables III and IV may be used to estimate the thermodynamic functions of activation and the rates of environmental averaging at room temperature. Plots of $\log k$ vs. $1/T$ give straight lines for $Al(acac)(thd)_2$, $Al(hfa)(acac)_2$, and $Al(hfa)(thd)_2$ in chlorobenzene solutions, from which Arrhenius activation energies (E_a) and frequency factors (A) can be obtained. These are tabulated¹⁹ in Table V along with rates extrapolated to 25° obtained from this information. The entropies of activation (ΔS^\ddagger) were calculated assuming that the Eyring equation is valid.

Inversion Rates and Mechanisms.—Nmr measurements of the rates of racemization are based on the premise that the rate of optical inversion is directly related to the rate of environmental averaging of the terminal groups of the bis ligands. As was earlier

TABLE V
THERMODYNAMIC FUNCTIONS FOR ENVIRONMENT AVERAGING
OF TERMINAL GROUPS OF THE BIS LIGANDS^a

	$Al(acac)(thd)_2$	$Al(hfa)(acac)_2$	$Al(hfa)(thd)_2$
E_a , kcal/mole	6.4	2.7	7.0
Log A	4.61	3.05	6.62
ΔS^\ddagger , eu	-16	-19	-12
k_{25} sec ⁻¹	0.79	11.6	29.4

^a In chlorobenzene solutions. Error limits estimated at $\pm 20\%$.

stated, these rates need not necessarily be equal to each other and the exact relationship will depend upon the mechanism by which the intramolecular rearrangements occur. It is, therefore, useful to consider the possible mechanisms by which optical inversion can occur and compare the rates of environmental averaging of the methyl groups with the rates of optical inversion.²⁰ The two principal types of intramolecular mechanisms proposed for inversion may be classed either as those that involve bond rupture or as those that do not.

The Bailar twist^{21,22} can occur about any one of the four axes extending through the centers of the octahedral faces as can be seen in Figure 2. In complexes with two different symmetrical bidentate ligands three distinct manifestations of the Bailar twist can be depicted. (In Figure 2c and d there are identical transition states.) In these mechanisms the intra-ring oxygen-metal-oxygen bond angles contract, causing distortion of the ring structures. The Rây and Dutt²³ twist involves the translation of two of the chelate rings with respect to the third without distortion of any of the three rings. For the systems considered, there are two manifestations of this mechanism proceeding through intermediates similar to those in Figures 2b and c or d. Another mechanism²¹ involves the rotation of two rings with respect to the third without distortion of any of the rings and has an intermediate similar to that of Figure 2a. It is very difficult, however, to show *a priori* that there would be a very great energetic preference for any particular one of these six possibilities. For simplicity in the following discussion only the possible contributions of the Bailar twist about the four axes will be discussed in detail. Twist mechanisms about any of the four octahedral face axes would not be expected to require greatly differing energies. A combination of the mechanism proposed most recently²¹ and the Rây and Dutt twist²³ about all of the possible axes would give the same overall relationship. The two mechanisms are also considered separately by relating them to the respective Bailar twists to which they may be considered as the fixed ring limits.

If a bond-rupture mechanism is proposed, various intermediates might be considered, but only the two most probable will be treated herein. One of these

(17) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

(18) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Phys. Chem.*, **66**, 346 (1962).

(19) The plot for $Al(acac)_2(thd)$ showed considerable scatter of points and thus no information is tabulated for this complex. Taking an approximate median slope would yield $E_a = 9.0$ kcal/mole, $\log A = 6.26$, and $k = 0.43$ sec⁻¹ at 25° for this complex.

(20) This is the rate of interconversion of optical isomers and half the rate of racemization (loss of optical activity).

(21) C. S. Springer, Jr., and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967).

(22) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

(23) P. C. Rây and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

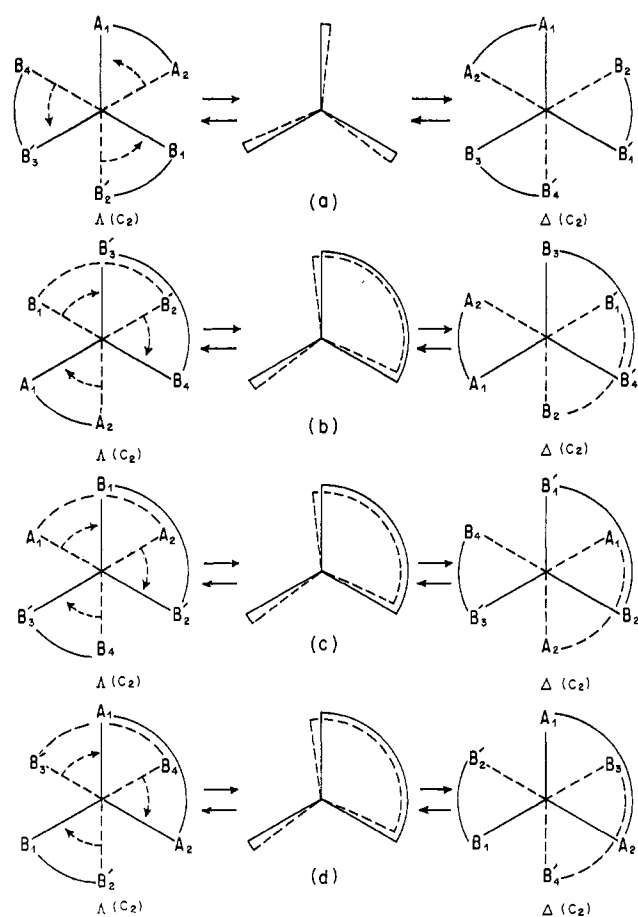


Figure 2.—The Bailar twist depicted about the four axes extending through the centers of the octahedral faces of a complex of the form $M(AA)(BB)_2$.

would be pictured as a trigonal bipyramid and the other as a square-based pyramid. The case of the trigonal-bipyramid system is considered both with and without the addition of a second set of operations that can add to the rate of environmental averaging but will not cause optical inversion. Complete dissociation of the bidentate ligand as proposed by Thomas¹⁶ can be discounted for reasons stated above.

Owing to the electron-withdrawing tendency of the fluorines, one of the metal-oxygen bonds of the hfa ligands might be expected to break more easily than those of the nonfluorinated ligands. Therefore, the effect of only the fluorinated ligand rupturing, as opposed to random rupturing of any one of the six bonds, is also considered. Any difference in the relative likelihood of bond rupture of thd *vs.* acac would be expected to be more subtle, assuming, of course, that steric crowding by the bulky *t*-butyl groups does not play a significant role. If one compares the rates of environmental averaging for $Al(acac)_2(thd)$ and $Al(acac)(thd)_2$, the similarity of these values indicates that steric crowding is not a significant factor in the complex.

The Twist Mechanisms.—In Figure 2 are pictured the Bailar twists about the four octahedral face axes. The first of these might be labeled a twist about the pseudo- C_3 axis (as defined by Fay and Piper⁸) while the other three are about imaginary C_3 axes (as defined by

Springer and Sievers²¹). It is noted that in the figure the three ligands are designated as A_1A_2 , B_1B_2 , and B_3B_4 , where AA and BB represent different symmetrical ligands and the subscripts are simply identifying labels. When a B end is *trans* to an A group, a prime is used.

For the twist about the pseudo- C_3 axis $\Lambda(C_2)$ to $\Delta(C_2)$ inversion is accompanied by environmental changes for all four B groups. This is also seen to be true for the second case which is a twist about an imaginary C_3 axis. In the third case optical inversion is accompanied by environmental changes of only B_1 and B_2 while B_3 and B_4 are unaffected. The fourth case has B_3 and B_4 exchanging environments, but B_1 and B_2 remaining unchanged while the complex goes from the $\Lambda(C_2)$ to the $\Delta(C_2)$ form. If it is assumed that the four motions described in Figure 2 can occur with approximately equal ease, then the rate of optical inversion would be equal to $4/3$ of the rate of environmental averaging found from the nmr experiments.

The first of the four motions in Figure 2 can also be used to represent changes that would occur for the rigid ring mechanism proposed recently.²¹ This would result in a rate of optical inversion equal to the rate of environmental averaging. The other three show the possible conversions of the Rây and Dutt mechanism. The relationship of the optical inversion rate to the environmental averaging rate would then be $3/2$ (assuming equal likelihood of occurrence of the Rây and Dutt versions of the last three transitions in Figure 2).

The Trigonal Bipyramid.—In Figure 3 are pictured the transitions of a bond-rupture mechanism going through a trigonal-bipyramidal intermediate. All six possibilities can cause optical inversion. The bond rupture of one end of the mono ligand causes environmental exchange of half of the terminal groups of the bis ligands, while rupture at the other end causes the other half to change. The third and the sixth pictured possibilities combined also causes all four B ends to change environments, but the fourth and the fifth cause no environmental changes whatsoever. If all six are considered equally probable, the ratio of the rate of optical inversion to the environmental averaging rate would be 3:1. If only the mono ligand is considered likely to rupture (perhaps an hfa ligand), the value would be 2:1. The ratio of 4:1 is found if only the bis ligand bonds are considered likely to rupture.

Figure 4 pictures three doubly degenerate combinations (either end of the ligand may dissociate) which will contribute to the environmental averaging but not to optical inversion. The ratio of rate of optical inversion to rate of environmental averaging will be affected as follows if these are added to the possibilities causing environmental averaging: the ratio considering all rupture equally probable becomes 3:2, the ratio with only the bonds of the mono ligand rupturing remains 2:1, and where bonds of only the bis ligands are considered likely to rupture the ratio is 4:3.

By considering various data one can argue that the type of mechanism producing environmental averaging

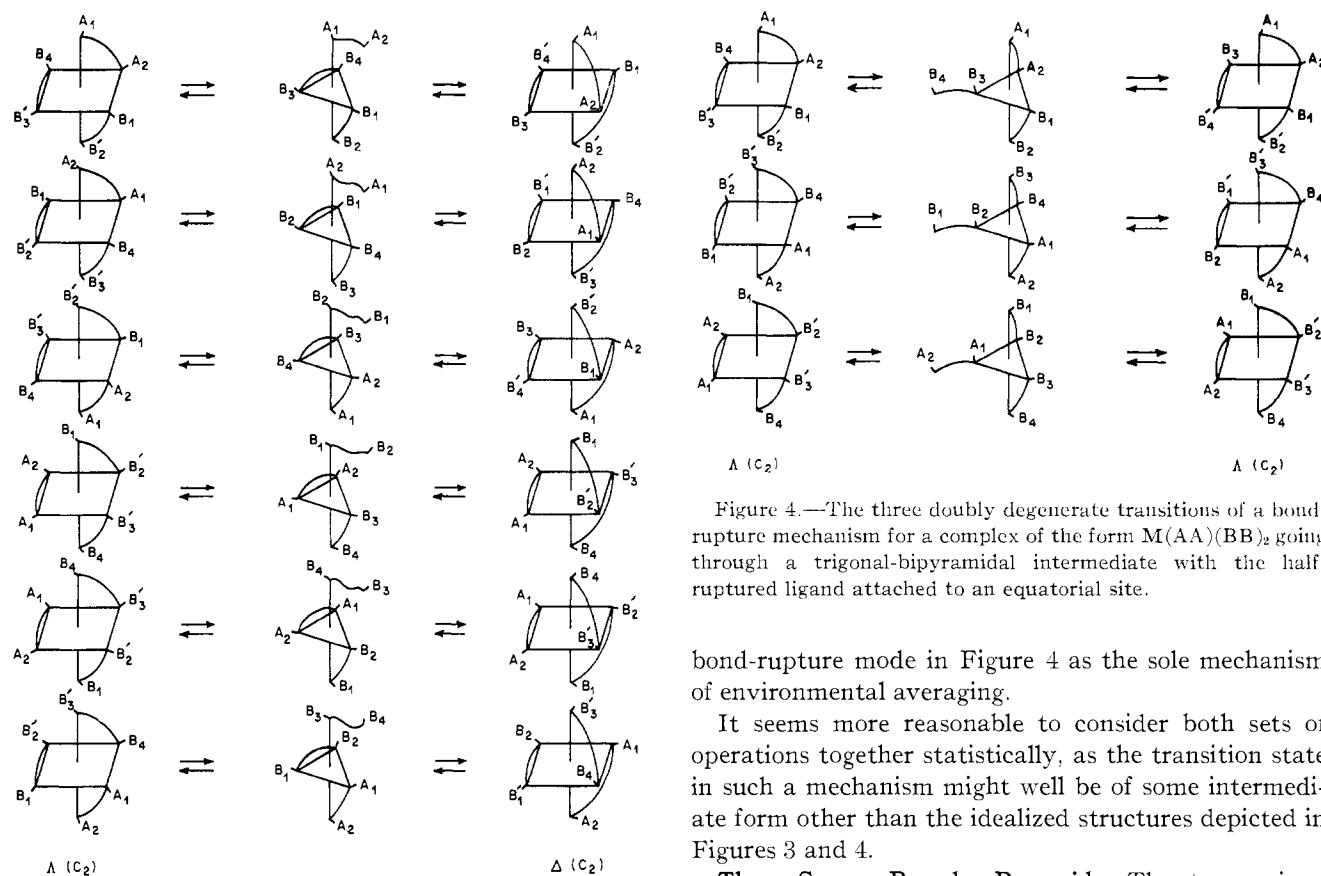


Figure 3.—The six transitions of a bond-rupture mechanism for a complex of the form $M(AA)(BB)_2$ going through a trigonal-bipyramidal intermediate with the half-ruptured ligand attached to an axial site.

Figure 4.—The three doubly degenerate transitions of a bond-rupture mechanism for a complex of the form $M(AA)(BB)_2$ going through a trigonal-bipyramidal intermediate with the half-ruptured ligand attached to an equatorial site.

without optical inversion depicted in Figure 4 cannot be the sole pathway for the reactions in the cases studied. If it were operative to the exclusion of the mechanisms depicted in the other figures and, if the logical assumption is made that the metal-oxygen bond of the one type of ligand is more likely to rupture than the other type, coalescence could not be produced for both the AA terminal groups of $Al(AA)_2(BB)$ and the BB terminal groups of $Al(AA)(BB)_2$. If one assumed that the AA ligand was more susceptible to rupture (as would seem a good assumption for the electron-deficient hfa ligand), this could cause coalescence for the $Al(AA)_2(BB)$ complex but not for the $Al(AA)(BB)_2$ complex. In the $Al(AA)(BB)_2$ complexes a rupture of the AA ligand pictured in the third mode of Figure 4 would not average the environments of the distinct terminal groups of the BB ligands. As was noted above, the methyl groups of the acac ligands in $Al(acac)_2(thd)$ coalesce as well as the *t*-butyl resonances of the thd ligands in $Al(acac)(thd)_2$ under comparable conditions. Perhaps more convincing are the observations²⁴ that the fluorine resonance peaks of $Al(hfa)_2(acac)$ coalesce as do those of $Al(hfa)_2(thd)$. These observations, in addition to the occurrence of coalescence of the methyl peaks in $Al(hfa)(acac)_2$ and the *t*-butyl resonances in $Al(hfa)(thd)_2$ described herein, would eliminate the

bond-rupture mode in Figure 4 as the sole mechanism of environmental averaging.

It seems more reasonable to consider both sets of operations together statistically, as the transition state in such a mechanism might well be of some intermediate form other than the idealized structures depicted in Figures 3 and 4.

The Square-Based Pyramid.—The two unique systems of a bond-rupture mechanism going through a square-based pyramidal intermediate are pictured in Figure 5. The first process is doubly degenerate when both ends of the unique ligand are considered and the second system is fourfold degenerate due to the possibilities of either end of either of the bis ligands being the one that dissociates. Of the 48 possibilities 24 cause optical inversion, 12 have environmental changes of all 4 of the B ends, and 24 have environmental changes for 2 of their 4 B ends. This mechanism produces a 1:1 relationship of rate of optical inversion to rate of terminal group environmental averaging, whether all metal ligand bonds are considered equally probable to rupture or whether either the mono or bis ligands are favored.

Further Considerations.—The relationships between rates of optical inversion and rates of environmental averaging for complexes of the form $M(AA)(BB)_2$ offer some interesting possibilities. If a system could be found in which the rate of environmental averaging can be determined by nmr studies and in which the rate of optical inversion can be measured by an independent method, the comparison of the rates determined may allow the assignment of a specific mechanism, or at least elimination of some possibilities.

Furthermore, examination of mixed complexes of symmetric bidentate ligands may prove useful in determining the structure of complexes for which there has been some question as to whether the structures are octahedral, distorted octahedral, or trigonal prismatic in solution. In particular nmr may be helpful in studies of complexes of bidentate sulfur-donor ligands

(24) J. J. Fortman and R. E. Sievers, unpublished results.

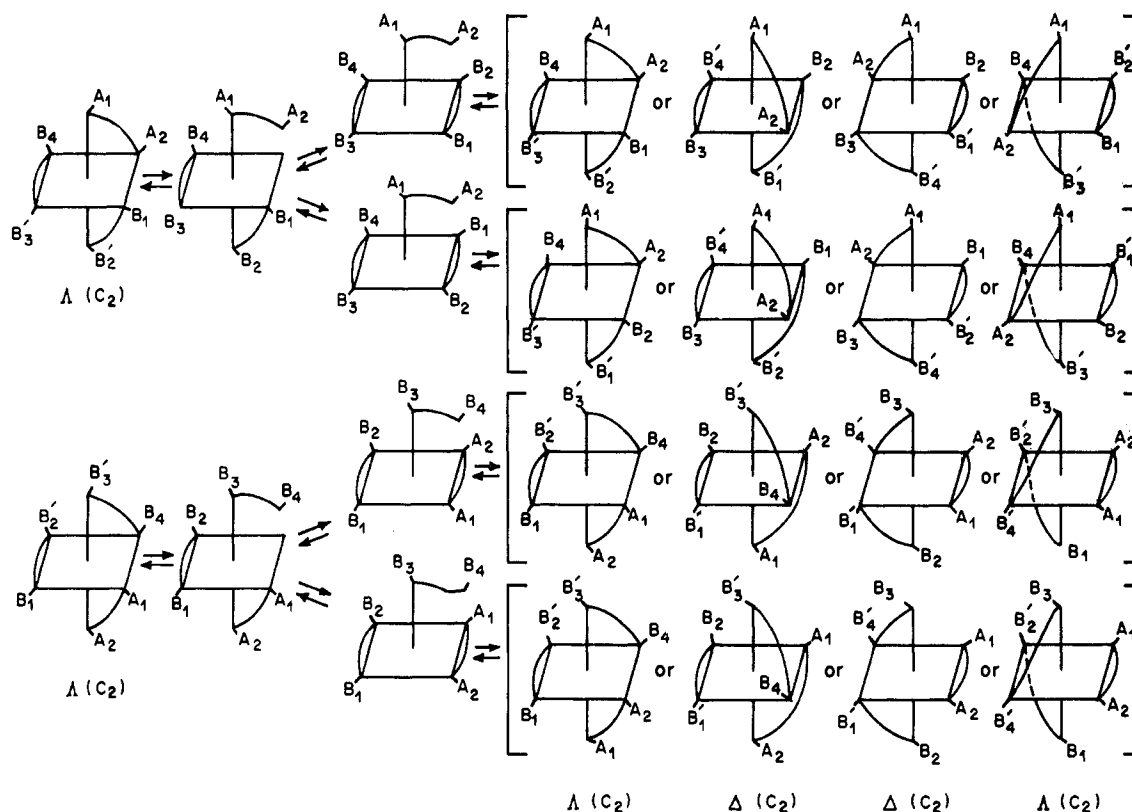


Figure 5.—The transitions of a bond-rupture mechanism for a complex of the form $M(AA)(BB)_2$ going through a square-pyramidal intermediate. The first process is doubly degenerate and the second system is fourfold degenerate. (It should be noted that the first species shown with a ruptured ligand is a square-based pyramid and the total process can be considered only if this first species exists long enough to allow the rearrangements indicated thereafter.)

of the α -dithiolate type.^{25, 26} An nmr study of mixed-ligand complexes of the form $M(CC)_2(DD)$, where CC and DD are symmetrical bidentate sulfur-donor ligands, could possibly allow the determination of whether these complexes have octahedral or intermediate trigonally distorted octahedral structures as opposed to perfect trigonal prismatic structures in solution. As mixed-ligand complexes of nickel have now been prepared by ligand-interchange reactions,²⁷ hexacoordinate analogs of such compounds should also exist.

(25) E. I. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 4012 (1965).

(26) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *ibid.*, **86**, 2958 (1964).

If the terminal groups of CC produce two resonance peaks, a trigonal-prismatic structure with rectangular edge coordination can be eliminated.

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(27) A. Davison, J. A. McCleverty, E. T. Shaw, and E. J. Wharton, *ibid.*, **89**, 830 (1967).