Table I

Time, h	Frequency, cm^{-1}					
	984	953	945	922	890	882
0.15	7		30	70		
1.0	8		13	61		
3.0	10		10	47		67
21	18	25	10	24	58	55
44	23	20	10	20	50	48
140	36	28	13	26	54	49

$(PEt_3)_2$: mp 114–115° dec; ir (Nujol) 3030 vw, 2900 vs, 1580 m, 1495 s, 1460 ms, 1440 vs, 1430 ms, 1380 m, 1335 m, 1255 w, 1095 w, 1070 m, 1050 s, 1040 s, 1010 w, 952 vs, 768 s, 748 w, 740 s, 724 ms, 708 w, 697 cm^{-1}; NMR ($CDCl_3$) δ 8.0–6.8 (m, 10), 1.53 (m, 12), 1.07 (quint, 18, J_{HH} = 8 Hz, $J_{PH} + J_{P'H}$ = 17 Hz).

Anal. Calcd for $C_{30}H_{40}F_5PdP_3$: C, 51.85; H, 5.80; F, 13.67; P, 13.37. Found: C, 51.63; H, 5.89; F, 13.29; P, 13.25.

***trans*-Bromo(pentafluorophenyl)bis(triethylphosphine)nickel(II).** This compound (mp 127–129° (lit.[20] mp 130–131°)) was prepared from Ni(1,5-COD)$(PEt_3)_2$ and bromopentafluorobenzene following a procedure to be reported separately.[8]

Attempted Preparation of *trans*-(Pentafluorophenyl)(diphenylphosphido)bis(triethylphosphine)nickel(II). A solution of 0.27 g (1.0 mmol) of $LiPPh_2 \cdot OEt_2$ in 3 ml of ether was added to 0.54 g (1.0 mmol) of *trans*-$NiBr(C_6F_5)(PEt_3)_2$ in 3 ml of ether at 0° causing the solution to turn green. On cooling to −72°, only a small amount of *trans*-$NiBr(C_6F_5)(PEt_3)_2$ was successfully isolated from the solution.

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Kinetics, Steric Course, and Mechanism of Stereoisomerization of Aluminum β-Diketonates[1]

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Abstract. The activation parameters for the stereoisomerizations of tris(2,6-dimethyl-3,5-heptanedionato)aluminum(III) and bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(2,6-dimethyl-3,5-heptanedionato)aluminum(III) have been determined by dynamic nuclear magnetic resonance (DNMR) spectroscopy and are reported. The reactions are found to be first order and intramolecular. Permutational analysis of the combined results of this study and those of all other DNMR studies of tris(β-diketonato)aluminum chelates reported reveal that the steric course of stereoisomerization involves the effective simultaneous interchange of the terminal groups within two of the three bidentate ligands and enantiomerization at the metal center. Consideration of the magnitudes of the activation parameters, the effective steric course, and a topological analysis leads to the following mechanistic conclusions. Chelates with alkyl or aryl substituents on the β-diketonate rings most likely stereoisomerize by a rhombic twist mechanism. Chelates with fluorocarbon substituents on the β-diketonate rings stereoisomerize by a bond-rupture mechanism which proceeds via an actual square pyramidal–apical five-coordinate intermediate.

Introduction

It has been more than 10 years since the pioneering study by Fay and Piper reported on the stereochemical nonrigidity of tris(β-diketonato)aluminum(III) chelates.[2] This work stimulated much interest in the dynamic stereochemistry of tris chelates in general,[3] and, subsequently, the "steric courses"[4] of the stereoisomerizations of other tris chelates, specifically certain tris(N,N-disubstituted dithiocarbamato) complexes,[5] and certain tris(α-substituted tropolonato) complexes,[6] have been uniquely determined. Nevertheless, despite more than a decade of investigation,[1b,2,7-12] the question of the steric course of the stereoisomerization of tris(β-diketonato)-

aluminum(III) chelates has not been settled. The results reported in the present paper, together with the previous studies, provide for a unique determination of the effective steric course of this reaction and a probable determination of its mechanism.

Experimental Section

Preparation of Complexes. All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Al(dibm)$_3$. Tris(2,6-dimethyl-3,5-heptanedionato)aluminum(III), Al(dibm)$_3$, was prepared from the reaction of aluminum trichloride and H(dibm) (Eastman) in an aqueous ethanol solution using a procedure similar to that described by Hammond, Nonhebel, and Wu for the synthesis of Al(thd)$_3$.[13,14] The white solid product was recrystallized from ethanol/water; mp 153.5–154.5 °C. Anal. Calcd: C, 65.82; H, 9.20; Al, 5.47. Found: C, 65.24; H, 9.16; Al, 6.27.

Al(acac)$_3$. Tris(2,4-pentanedionato)aluminum(III), Al(acac)$_3$, was prepared according to the literature;[15] mp 192.5–195.0 °C (lit. 194.6 °C).

Al(hfa)$_3$. Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)aluminum(III), Al(hfa)$_3$, was prepared according to the method of Morris, Moshier, and Sievers[16] and purified by sublimation in vacuo at 70 °C; mp 73–74.5 °C (lit. 73–74 °C).

Rh(dibm)$_3$. Tris(2,6-dimethyl-3,5-heptanedionato)rhodium(III), Rh(dibm)$_3$, was prepared by the addition of H(dibm) to an aqueous solution of rhodium(III) ions (pH $\simeq$ 4) according to procedures similar to those described for the preparation of Rh(hfa)$_3$[17] and Rh(bzac)$_3$.[18] The yellow solid product was recrystallized from methylene chloride, mp 86–92 °C. ^{1}H NMR spectrum (0.23 M in 84% TFT, 16% CH_2Cl_2): CH_3, 1.07 ppm (J = 7.0 Hz), 1.10 (J = 7.0 Hz); CH(i-Pr), 2.54 ppm (J = 7.0 Hz); CH, 5.46 ppm (TFT = trifluorotoluene).

Mixed Ligand Aluminum(III) Chelates. The mixed ligand chelates Al(dibm)(hfa)$_2$ and Al(dibm)$_2$(hfa) cannot be isolated in pure form because of a reasonably rapid ligand exchange disproportionation reaction to form an equilibrium mixture with the parent tris complexes Al(dibm)$_3$ and Al(hfa)$_3$. Thus, they were prepared in situ by equilibrating mixtures of the appropriate ratios of the parent chelates at ~70 °C for ca. 13 h in sealed, degassed NMR tubes.

The analogous preparation of the chelate Al(dibm)(acac)$_2$ was described previously.[1b] The equilibrium quotient of the reaction shown below

$$\text{Al(acac)}_3 + \text{Al(dibm)}_3 \rightleftarrows \text{Al(dibm)(acac)}_2 + \text{Al(dibm)}_2\text{(acac)} \quad (1)$$

was determined, by integrating the appropriate NMR peaks of the various chelates, to be 5.0 ± 0.8 in chlorobenzene at ambient temperature.[1b] This is consistent with a subsequent, more careful, investigation of the Al(acac)$_3$/Al(bzbz)$_3$ system where the analogous equilibrium quotient was found to be 5.5 in benzene at 25 °C.[19] These reactions have quotients very nearly equal to the statistical value (9) because of negligible enthalpy changes.[19]

In contrast, the reaction to form Al(dibm)(hfa)$_2$ and Al(dibm)$_2$(hfa),

$$\text{Al(hfa)}_3 + \text{Al(dibm)}_3 \rightleftarrows \text{Al(dibm)(hfa)}_2 + \text{Al(dibm)}_2\text{(hfa)} \quad (2)$$

strongly favors the formation of the mixed ligand chelates. We have estimated the equilibrium quotient to be ~3×10^3 in CCl_4 at 32 °C by procedures similar to that reported earlier.[10] It is expected that this value should be similar to that found in a careful study of the Al(acac)$_3$/Al(hfa)$_3$ system, which varied from 4×10^4 to 9×10^4 in different solvents at 25 °.[19] The latter reactions have significant negative $\Delta H°$ values.[19] The Al(dibm)$_3$/Al(hfa)$_3$ system was chosen for this work specifically because of the possibility of generating solutions in which either of the mixed ligand chelates is the dominant species (vide infra).

NMR Solutions. Trifluorotoluene (TFT, Eastman) was distilled and dried over molecular sieves (Linde, Type 4A). All other solvents used in this work [C_6H_5Cl, CCl_4, $Si(CH_3)_4$, and CH_2Cl_2] were of commercial spectroscopic grade and were dried over molecular sieves prior to use. All NMR solutions were degassed and sealed in precision 5-mm tubes on a vacuum line.

NMR Spectroscopy. Fluorine-19 magnetic resonance spectra were obtained on a Varian DP-60-IL spectrometer at 56.4 MHz. Proton spectra were obtained on either a Varian A-60 or the DP-60-IL at 60 MHz. Both spectrometers were equipped with Varian V-6040 variable-temperature controllers. The A-60 sample temperatures were calibrated using the methanol and ethylene glycol shift separations as described by Van Geet.[20] The DP-60-IL sample temperatures were calibrated by thermocouple measurements. Chemical shift measurements on the A-60 were calibrated by using the standard Me_4Si in $CHCl_3$ sample. The DP-60-IL frequency sweep (internal lock mode; lock signal: Me_4Si or CH_2Cl_2 for ^{1}H, TFT singlet for ^{19}F) was calibrated with a frequency counter which monitored the difference frequencies between the lock and sweep oscillator outputs.

NMR Line Shape Analysis. The DP-60-IL is interfaced with an IBM 1800 computer, and as the spectra were recorded they were simultaneously digitized (up to 1024 points/spectrum) and stored on magnetic tape and punched cards. Spectra obtained on the A-60 were either machine digitized onto punched paper tape and subsequently transferred to punched cards, or were hand digitized and keypunched directly onto cards. The subsequent processing of the data for the total line shape analyses was completely computer controlled and has been described previously.[21]

The values of the chemical shift difference in the absence of exchange ($\Delta\nu_\infty$) used were extrapolated from plots of the temperature dependence in regions where no exchange was detectable. This compensates for temperature dependence of $\Delta\nu_\infty$ in the region of exchange.[22] The values of T_2 (reciprocal line width) in the absence of exchange were obtained and corrected for temperature dependence in either of two ways. Straight-line plots of the log of the line width at half-height ($\Delta H_{1/2}$) as a function of $1/T$ from regions where exchange was not observable were interpolated through the exchange region.[23] Alternatively, values of T_2 for the ^{19}F peaks were obtained from the temperature dependence of the line width of the resonance of Al(hfa)$_3$ (0.2 M in 73% TFT, 27% CH_2Cl_2) and the T_2 values for the dibm methyl resonances from the temperature dependence of the methyl quartet line widths of Rh(dibm)$_3$ (0.23 M in 84% TFT, 16% CH_2Cl_2). The latter compound is inert toward enantiomerization, and the quartet persists at the highest temperature studied by us (84 °C).

Results

Stereoisomerization of Al(dibm)$_3$. The evidence that Al(dibm)$_3$ undergoes labile enantiomerization in solution has been presented earlier.[1b] This is indicated by the fact that the quartet which appears in the isopropyl methyl region of the proton NMR spectrum at ambient temperatures coalesces to the expected spin-coupled doublet at higher temperatures (>~120 °C in chlorobenzene, see Figure 1 in ref 1b). The diastereotopic environments of the methyl groups in the isopropyl substituents are exchanged every time the molecule enantiomerizes and thus the methyl resonance peaks serve as probes for the lifetime of the molecule in each chiral form.

We have performed a total line shape analysis of the coalescence of the downfield doublet of the isopropyl quartet in order to obtain the Arrhenius parameters for the process

$$\text{H}_3\text{C}(1)^\delta|\alpha\rangle + \text{H}_3\text{C}(2)^\lambda|\alpha\rangle \rightleftarrows \text{H}_3\text{C}(2)^\delta|\alpha\rangle + \text{H}_3\text{C}(1)^\lambda|\alpha\rangle \quad (3)$$

where (1) and (2) simply label the methyl groups, the superscripts δ and λ designate the two diastereotopic environments, and $|\alpha\rangle$ represents the spin function of the methine proton.[1b] This exchange is, of course, caused by the molecular rearrangement given by

$$\Lambda\text{-Al(dibm)}_3 \rightleftarrows \Delta\text{-Al(dibm)}_3 \quad (4)$$

which is the process of interest.[24] The numerical data and results of the line shape analysis are given in Table I, the Arrhenius plot is shown in Figure 1, and the activation parameters are set out in Table II. Less extensive data for both doublets of the quartet of a solution less than half as concentrated as the first are included. The activation energy found (19 kcal/mol) is more consistent with expectation than the value of 15 kcal/mol previously estimated on the basis of an approximate graphical analysis.[1b] It can be compared with the value of 22 kcal/mol found for the rearrangement of Al(acac)$_2$(bzbz) in o-$Cl_2C_6H_4$[7] and also given in Table II.

Table I. Kinetic Data for Stereoisomerization of Aluminum(III) β-Diketonates

Temp, °C	$\delta\nu_\infty$, Hz	$\Delta H_{1/2}$, Hz	$T_2 = 1/\pi\Delta H_{1/2}$, s	τ, s	$k = 1/2\tau$, s^{-1}
	$Al(dibm)_3$ (0.294 M in ClC_6H_5) (downfield doublet of isopropyl methyl quartet)[a,d]				
100.6	2.93	0.42	0.750	0.274	1.82
105.2	2.93	0.41	0.782	0.211	2.37
109.7	2.93	0.39	0.817	0.149	3.36
109.0	2.93	0.38	0.830	0.159	3.14
115.1	2.93	0.38	0.845	0.114	4.38
118.0	2.93	0.37	0.857	0.0989	5.05
119.5	2.93	0.37	0.870	0.0851	5.88
120.6	2.93	0.36	0.883	0.0728	6.87
123.1	2.93	0.35	0.897	0.0643	7.78
125.5	2.93	0.35	0.910	0.0586	8.53
125.8	2.93	0.34	0.925	0.0527	9.49
129.9	2.93	0.34	0.937	0.0456	10.96
130.9	2.93	0.33	0.952	0.0410	12.19
136.2	2.93	0.32	0.988	0.0303	16.50
140.7	2.93	0.31	1.020	0.0219	22.83
	$Al(dibm)_3$ (0.120 M in ClC_6H_5) (both doublets of isopropyl methyl quartet)[b,d]				
115.1	2.93	0.38	0.845	0.113	4.42
115.1	2.93	0.38	0.845	0.100	5.00
119.5	2.93	0.37	0.870	0.090	5.56
119.5	2.93	0.37	0.870	0.090	5.56
123.1	2.93	0.35	0.897	0.069	7.25
125.8	2.93	0.34	0.925	0.063	7.94
125.8	2.93	0.34	0.925	0.060	8.33
130.9	2.93	0.33	0.952	0.044	11.36
130.9	2.93	0.33	0.952	0.048	10.42
	$Al(dibm)(hfa)_2$ (initial $f_{Al(hfa)_3} = 0.772$, [Al(III)] $\simeq$ 0.06 M in CCl_4)[a,d] (downfield doublet in isopropyl methyl quartet)				
36.9	2.94	0.86	0.370	0.180	2.78
41.2	2.94	0.84	0.378	0.109	4.59
45.9	2.94	0.83	0.383	0.0678	7.37
49.8	2.94	0.82	0.388	0.0420	11.90
54.9	2.94	0.81	0.392	0.0257	19.46
58.7	2.94	0.80	0.398	0.0170	29.41
67.7	2.94	0.77	0.413	0.00782	64.10
	$Al(dibm)(hfa)_2$ (initial $f_{Al(hfa)_3} = 0.610$, [Al(III)] = 0.26 M in TFT (22 mol % Me_4Si) (downfield doublet of isopropyl methyl quartet)[c,f]				
35.8	1.64	0.99	0.322	0.231	2.16
39.0	1.61	0.99	0.322	0.139	3.61
42.3	1.59	0.98	0.325	0.0722	6.92
57.8	1.43	0.94	0.339	0.0144	34.5
68.8	1.34	0.91	0.350	0.00770	64.9
	(^{19}F doublet of CF_3 groups)[c,d]				
39.0	2.49	1.09	0.292	0.152	3.30
42.3	2.62	1.09	0.292	0.0903	5.54
47.4	2.70	1.09	0.292	0.0576	8.68
57.8	2.97	1.10	0.289	0.0196	25.5
68.8	3.27	1.11	0.287	0.00590	84.7
	$Al(dibm)(hfa)_2$ [initial $f_{Al(hfa)_3} = 0.689$, [Al(III)] = 0.14 M in TFT/CH_2Cl_2 (45 mol % CH_2Cl_2)] (upfield and downfield doublets of isopropyl methyl quartet)[c,f]				
35.8	2.13	1.00	0.318	0.167	2.99[g]
35.8	2.13	1.08	0.295	0.156	3.20
39.0	2.13	0.99	0.322	0.104	4.81[g]
39.0	2.13	1.07	0.297	0.0942	5.31
42.3	2.13	1.05	0.303	0.0672	7.44
42.3	2.13	1.05	0.303	0.0633	7.90
42.3	2.13	0.98	0.325	0.0511	9.79[g]
42.3	2.13	0.98	0.325	0.0467	10.7[g]
47.4	2.13	1.03	0.309	0.0266	18.8
52.5	2.13	0.96	0.332	0.0183	27.3[g]
63.2	2.13	0.91	0.350	0.00771	64.8[g]
68.8	2.13	0.98	0.325	0.00410	121.9

[a] Experimental spectra hand digitized; see Experimental Section. [b] Experimental spectra machine digitized; see Experimental Section. [c] Experimental spectra directly computer digitized; see Experimental Section. [d] $\Delta H_{1/2}$ determined by interpolation; see Experimental Section. [e] $\Delta H_{1/2}$ obtained from $Al(hfa)_3$ data; see Experimental Section. [f] $\Delta H_{1/2}$ obtained from $Rh(dibm)_3$ data; see Experimental Section. [g] Downfield doublet.

Table II. Activation Parameters for Stereoisomerization of Aluminum(III) β-Diketonates

Compd	Solvent	$k_{25\,°C}$, s^{-1}	E_a, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
Al(dibm)$_3$	ClC_6H_5[a]	2.9×10^{-3}	19.1 ± 1	11.4 ± 0.6	18.3 ± 1[b]	−8.6 ± 1.5[b]	This work
Al(acac)(thd)$_2$[c]	ClC_6H_5		~19			−6	22
Al(acac)$_2$(bzbz)	o-$Cl_2C_6H_4$	2.2×10^{-3}	22.0 ± 0.6	13.43 ± 0.33		0.9 ± 1.5[d]	7
Al(acac)(hfa)$_2$	C_6H_6	8.4×10^{-1}	19.0 ± 1.3	13.87 ± 0.82[e]		2.9 ± 4.2[d]	7
Al(acac)(hfa)$_2$	$O_2NC_6H_5$	1.5	19.5 ± 0.6	14.47 ± 0.41		5.7 ± 1.9[d]	7
Al(acac)(hfa)$_2$	CH_2Cl_2	8.6×10^{-1}	21.3 ± 0.7	15.55 ± 0.45		10.7 ± 2.2[d]	7
Al(dibm)(hfa)$_2$ (dibm quartet)	CCl_4[f]	6.9×10^{-1}	21.5 ± 1	65.59 ± 0.7	20.7 ± 1[b]	10.3 ± 3[b]	This work
Al(dibm)(hfa)$_2$ (^{19}F doublet)	TFT[f]	6.0×10^{-1}	22.9 ± 1	16.5 ± 0.7	21.5 ± 1[b]	12.9 ± 4[b]	This work
Al(dibm)(hfa)$_2$ (dibm quartet)	TFT[f]	7.1×10^{-1}	22.2 ± 1.5	16.2 ± 1.0	20.8 ± 1.5[b]	10.7 ± 5[b]	This work
Al(dibm)(hfa)$_2$ (dibm quartet)	TFT/ CH_2Cl_2[f]	1.0	22.9 ± 2	16.8 ± 1.2	21.5 ± 2[b]	13.7 ± 6.5[b]	This work
Al(acac)$_2$(hfa)	CH_2Cl_2	8.0×10	18.4 ± 0.7	15.41 ± 0.53		10.0 ± 2.4[d]	7
Al(pmhd)$_3$	ClC_6H_5		27.6–30.2	16.18–17.62	26.8–29.4[b]	12.9–19.5[b]	8[g]

[a] Only data obtained at 0.294 M were used to determine activation parameters. [b] Derived from Eyring plots. [c] Original data published in ref 10. [d] Calculated at 25 °C using the Eyring equation. [e] This value appears incorrectly as 3.87 in ref 7; personal communication from the authors. [f] Concentration given in Table I. [g] See the text for a discussion of these activation parameters.

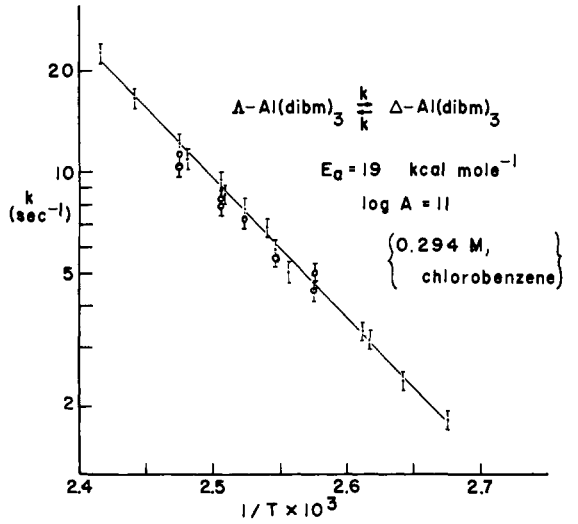


Figure 1. Arrhenius plot for the stereoisomerization of Al(dibm)$_3$ in chlorobenzene solution. Data points for two different concentrations are shown: (·) 0.294 M, downfield doublet; (○) 0.120 M, both doublets. See text and Table I for details.

Stereoisomerization of Al(dibm)(acac)$_2$. The study of Al(dibm)$_3$ tells us very little about the steric course and mechanism of the labile reorganization process. More stereochemical detail is needed to elucidate the operative pathway. We have studied molecules of the type Al($\widehat{AA}$)($\widehat{BB}$)$_2$ (where $\widehat{AA}$ and $\widehat{BB}$ represent different symmetric β-diketonate ligands). The two ends of the $\widehat{BB}$ ligands are rendered stereochemically nonequivalent in the chelates and are often anisochronous in the NMR spectrum.[1b,7,10,11] It is possible, therefore, to study the rate of interchange of the B terminal groups between the axial and equatorial environments.[7,10] If the $\widehat{AA}$ ligand is dibm, a simultaneous measurement of the rate of enantiomerization between the Λ and Δ environments is possible. The ratio of these rates is a function of the steric course and mechanism.

The mixed ligand chelate Al(dibm)(acac)$_2$ fits the above requirements because the methyl groups of the acac ligands have different resonant frequencies when in the axial and equatorial environments, while the isopropyl methyl resonance is a quartet at ambient temperatures (see Figure 2 of ref 1b). Although the acac methyl doublet collapses to a singlet while the quartet coalesces to a doublet, indicating the simultaneity of the two processes, the quantitative study of this molecule is hindered by its low equilibrium quotient of formation (see Experimental Section). In an equilibrium mixture where the initial mole fraction of Al(acac)$_3$, $f_{Al(acac)_3}$, was equal to 0.576 (concentration of Al(III) = 0.363 M), the Al(dibm)(acac)$_2$ species is present in significant amounts, but there is still considerable Al(acac)$_3$ and Al(dibm)$_2$(acac) present. The acac methyl and isopropyl methyl resonances of these latter species overlap severely with those of the desired compound. Even after careful hand resolutions of the acac methyl doublet and the doublets of the isopropyl methyl quartet and digitization of the component curves, subsequent line shape analyses yielded Arrhenius plots with unacceptable scatter. Although the results are in qualitative agreement with a preliminary graphical analysis,[1b] the activation energy of the enantiomerization process cannot be as low as initially estimated.[1b] It does seem clear that the enantiomerization proceeds at a rate faster than that of the axial/equatorial environmental interchange, perhaps by a factor of 2, over most of the temperature range studied. However, the scatter in the Arrhenius plots is such that it is impossible to give a precise value for the ratio of these rates or to state whether the activation energies for the two processes differ significantly. The implications of these results will be discussed below. The problems with the study of Al(dibm)(acac)$_2$ have been avoided in the study of Al(dibm)(hfa)$_2$.

Stereoisomerization of Al(dibm)(hfa)$_2$. With the large equilibrium quotient of reaction 2 (see Experimental Section), Al(dibm)(hfa)$_2$ can be produced in a solution which contains Al(hfa)$_3$ as the only other observable species. A clean quartet is observed in the *i*-Pr methyl region of the spectrum while the ^{19}F doublet of the Al(dibm)(hfa)$_2$ molecule is well resolved from the ^{19}F singlet of the Al(hfa)$_3$ parent (Figure 2).

A total line shape analysis of the coalescence of the downfield doublet of the isopropyl quartet of a CCl_4 solution of initial mole fraction Al(hfa)$_3$, $f_{Al(hfa)_3}$, equal to 0.772 (concentration of Al(III) ≃ 0.06 M) was performed. The numerical data and results are given in Table I, the Arrhenius plot is shown in Figure 3, and the activation parameters are set out in Table II. The activation parameters for the axial-equatorial exchange of the CF_3 groups in Al(acac)(hfa)$_2$, derived from the coalescence of the ^{19}F doublet by Case and Pinnavaia,[7] in several solvents are also given in Table II. The parameters for this process in CH_2Cl_2 are identical within experimental error with the values for the Λ to Δ process of Al(dibm)(hfa)$_2$ in CCl_4. The data of Case and Pinnavaia are also plotted in Figure 3. This is very strong evidence for a mechanism in which the lifetime of the molecule in each chiral form is equal to the

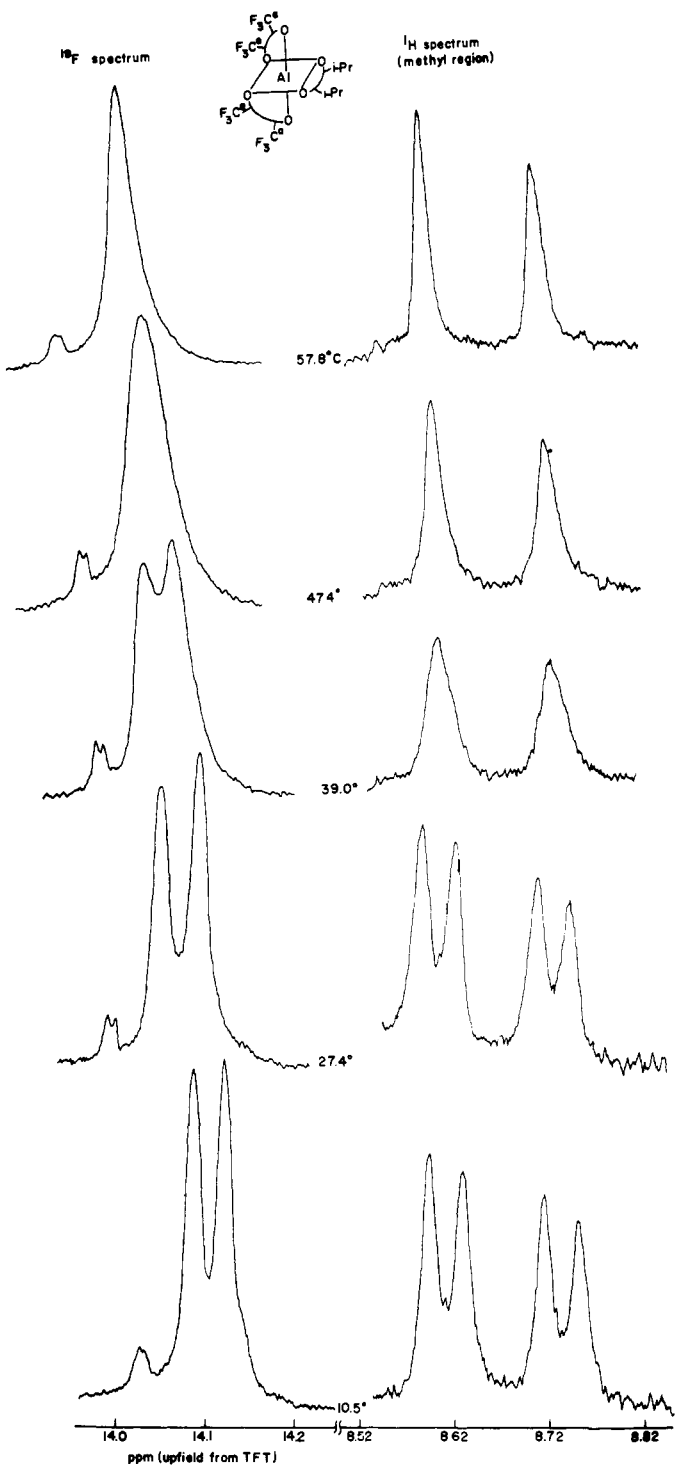


Figure 2. Temperature dependence of the ^{1}H and ^{19}F NMR spectra of Al(hfa)$_2$(dibm) in TFT solution (22 mol % Me_4Si). Initial mole fraction of Al(hfa)$_3$, $f_{Al(hfa)_3}$ = 0.610, concentration of Al(III) = 0.26 M. The small downfield peak in the ^{19}F spectrum is due to Al(hfa)$_3$.

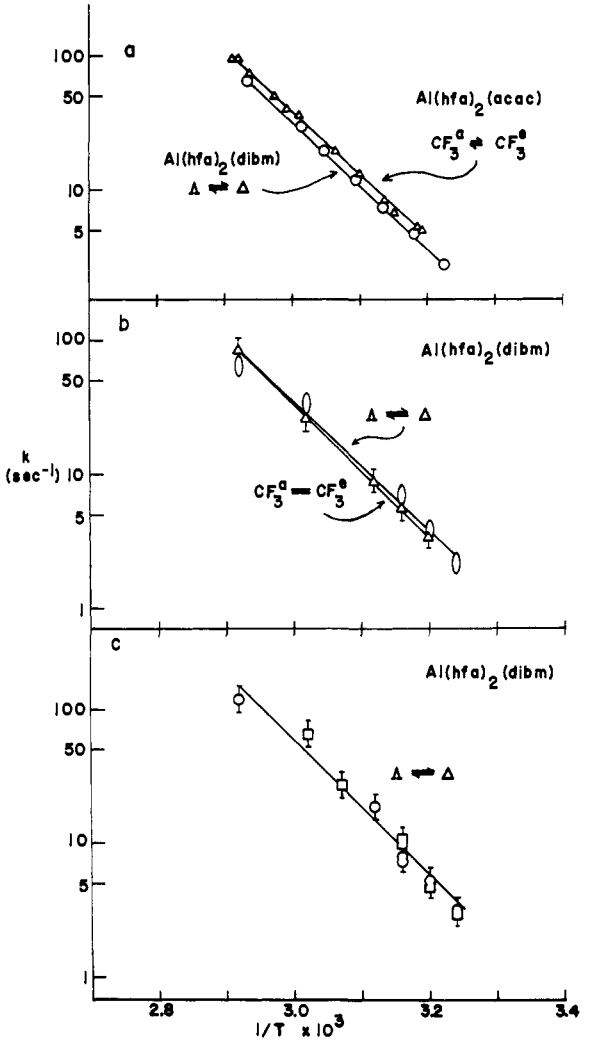


Figure 3. Arrhenius plots for stereoisomerizations of: (a) Al(hfa)$_2$(acac) in CH_2Cl_2 (data from ref 7); and Al(hfa)$_2$(dibm) in CCl_4, initial $f_{Al(hfa)_3}$ = 0.772, [Al(III)] ≃ 0.06 M, downfield doublet. (b) Al(hfa)$_2$(dibm) in TFT (22 mol % Me_4Si), initial $f_{Al(hfa)_3}$ = 0.610, [Al(III)] = 0.26 M; Δ, ^{19}F data; 0, ^{1}H data from downfield doublet. (c) Al(hfa)$_2$(dibm) in TFT (45 mol % CH_2Cl_2), initial $f_{Al(hfa)_3}$ = 0.689, [Al(III)] = 0.14 M; O, ^{1}H data, upfield doublet; □, ^{1}H data, downfield doublet.

lifetime of a CF_3 group in an axial or equatorial environment. However, because of possible small solvent effects[7] (Table II) and the fact that Al(dibm)(hfa)$_2$ and Al(acac)(hfa)$_2$ differ slightly (by C_4H_8), it is important to confirm this result with a more direct study.

The results of total line shape analyses of the ^{19}F doublet and the downfield doublet of the isopropyl methyl quartet of a solution of initial $f_{Al(hfa)_3}$ equal to 0.610 (concentration of Al(III) = 0.26 M) in TFT (22 mol % Me_4Si) are given in Table I. The activation parameters are set out in Table II, and the Arrhenius plots are shown in Figure 3. It is clear that the two processes have Arrhenius plots which are identical within experimental error.

The numerical data and results of an additional analysis of the isopropyl methyl quartet of a solution of initial $f_{Al(hfa)_3}$ equal to 0.689 (concentration of Al(III) = 0.14 M) in TFT/CH_2Cl_2 are given in Table I. The Arrhenius plot is shown in Figure 3, and the activation parameters are set out in Table II.

Stereoisomerization of Al(dibm)$_2$(hfa). In principle, the isopropyl methyl resonance of the Al(dibm)$_2$(hfa) molecule could exhibit eight peaks. The isopropyl groups can occupy either the axial or equatorial environment while still sensing the total chirality of the molecule. Thus, one might expect to observe a doublet of quartets. At ambient temperature, however, only one spin-coupled doublet is observed. Figure 4 shows the temperature dependence of the isopropyl methyl region of the NMR spectrum of a solution of initial $f_{Al(hfa)_3}$ = 0.32 (concentration of Al(III) ≃ 0.1 M) in CH_2Cl_2. It is interesting to note that the doublet splits into only a quartet upon initial cooling. Since Serpone has observed greater splitting in Ti(dibm)$_2$Cl$_2$ at lower temperatures,[25] the indication is that the rates of axial to equatorial interchange and enantiomerization

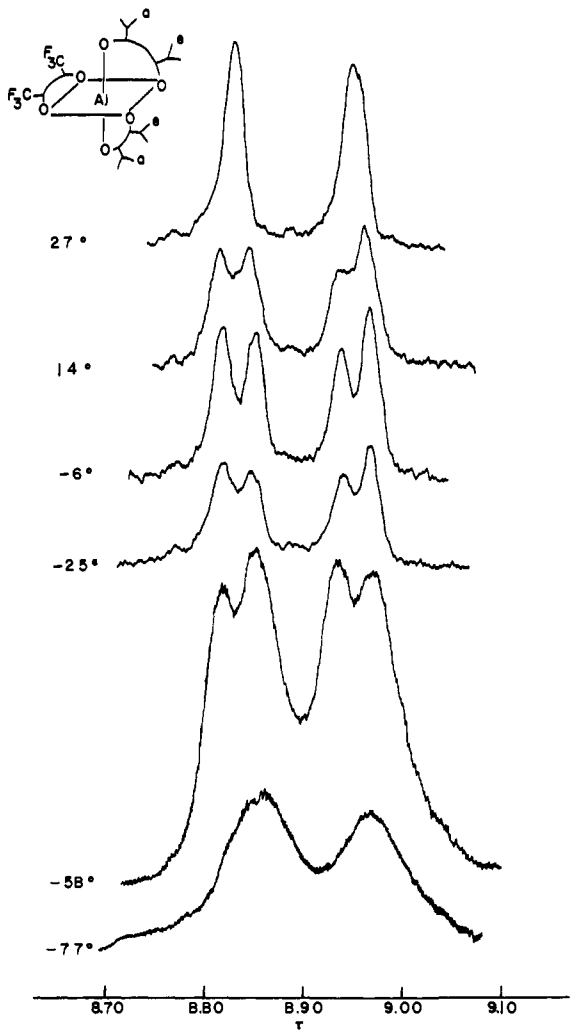


Figure 4. Temperature dependence of the ^1H NMR spectrum of Al(dibm)$_2$(hfa) in CH_2Cl_2, initial $f_{Al(hfa)_3} = 0.32$, [Al(III)] $\simeq$ 0.1 M.

are different for the process causing the splitting. The implications of this result for the steric course and mechanism of this reaction will be discussed below.

Discussion

Kinetics. The data given in Table I and depicted in Figure 1, revealing the concentration independence of the enantiomerization of Al(dibm)$_3$, demonstrate the first-order nature of the rate of this reaction. This has also been shown previously for the environmental interchange of ligand terminal substituents in other tris(β-diketonato) Al(III) chelates.[10]

Although it is conceivable that the stereoisomerization reaction could be first order and intermolecular[26] (the dissociation mechanism of Thomas[27a]), the fact that the ^{19}F doublet of Al(dibm)(hfa)$_2$ coalesces independently of the Al(hfa)$_3$ singlet (Figure 2) is strong evidence for the intramolecularity of the stereoisomerization reaction. This observation has been made repeatedly for mixtures of different tris(β-diketonate) Al(III) chelates[7,8,10-12] and for mixtures of the tris chelates with free (protonated) β-diketonate ligands.[2,10-12] The fact that equilibration of ligand exchange disproportionation requires ~13 h at 70 °C (see Experimental Section) is also proof of this point. The rate of exchange of acetyl acetonate between Al(acac)$_3$ and ^{14}C-labeled H(acac) in various organic solvents has also been studied and found to be quite slow compared with the stereoisomerizations discussed here.[27b] Thus, there is no doubt that the stereoisomerization reactions of tris(β-diketonato) Al(III) chelates in weakly polar solvents are intramolecular in nature. Simple point charge calculations in the original study by Fay and Piper[2] indicate the probable reason why the energetics of the dissociation mechanism (proposed by Thomas for tris(oxalato)metal chelates[27a]) are prohibitive in the case of the neutral tris aluminum β-diketonates. [This mechanism may be operative in the case of Sc(triac)$_3$.[8]]

The activation parameters determined for the stereoisomerizations studied in this work are set out in Table II. The results of others are also included for comparison purposes. Although there have been many determinations of the activation parameters for stereoisomerizations of tris(β-diketonato) Al(III) chelates, many of these[1b,2,9,10-12] involve approximations of one kind or another[28] and are not included in Table II.[29]

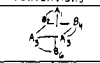
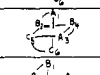
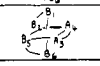
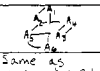
The exhaustive study of the stereoisomerization of Al(pmhd)$_3$ in chlorobenzene by Hutchison, Gordon, and Holm[8] does not involve any approximations in the DNMR analysis. However, the spectrum is sufficiently complicated that the rate constants and thus the activation parameters obtainable from a total line shape analysis depend upon the assumption of a particular steric course. Thus, the investigators report a range of activation parameters (E_a from 27.6 ± 1.4 to 30.2 ± 1.4 kcal/mol; log A from 16.18 ± 0.45 to 17.62 ± 0.45; $\Delta H^{\ddagger}$ from 26.8 ± 1.4 to 29.4 ± 1.4 kcal/mol; and $\Delta S^{\ddagger}$ from 12.9 ± 3.5 to 19.5 ± 3.5 eu) for different steric courses which are most compatible with the observed line shapes. Compared with the others given in Table II, the values of E_a ($\Delta H^{\ddagger}$) and log A ($\Delta S^{\ddagger}$) seem a bit large, but using the data given in Figure 3 of ref 8 and the simple approximate technique of ref 2, a value of $\Delta G^{\ddagger}_{398}$ equal to 20.6 kcal/mol for the stereoisomerization of Al(pmhd)$_3$ in chlorobenzene can be estimated. This is in good agreement with the similarly estimated values for other tris(β-diketonato) Al(III) chelates.[29]

The data in Table II can be viewed in two ways. Focusing on the activation energies (or $\Delta H^{\ddagger}$ values), one sees that, with the exception of the Al(pmhd)$_3$ data discussed above, there is a narrow range of values (<5 kcal/mol). This tends to confirm the intuitive opinion that all Al(β-diketonate)$_3$ chelates isomerize via a common mechanism. Alternatively, if one concentrates on the less accurate values of $\Delta S^{\ddagger}$, it is observed that the molecules which contain the hfa ligand have magnitudes ranging from 10.0 to 13.7 [with the exception of solvent effects of $O_2NC_6H_5$ and C_6H_6 on Al(acac)(hfa)$_2$], while the other molecules [again, with the exception of Al(pmhd)$_3$] have values of $\Delta S^{\ddagger}$ which are almost zero or negative. Thus, the latter data would seem to indicate two distinct mechanisms. These observations will be expanded upon below.

Steric Course. In order to determine the steric course of the stereoisomerization of tris aluminum β-diketonates, one must undertake a permutational analysis to delineate all possible steric courses. Rigorous permutational analyses have been applied to tris chelates in general by Musher,[31] the Eatons,[32] and Klemperer[4] with, as must be, identical results. We shall use the formalisms and conventions of the Eatons.

For a tris chelate with six distinguishable ligating ends, there are sixteen possible rearrangement permutations or permutation-inversions.[32] These constitute an Abelian group and the complete representative group used by Eaton and Eaton[32] is set out in Table III. Also given in Table III is a list of all of the Al(β-diketonate)$_3$ chelates studied by DNMR. For each distinct type of chelate [Al($\widehat{AB}$)$_3$, Al($\widehat{AB}$)$_2$($\widehat{CC}$), Al($\widehat{AA}$)($\widehat{BB}$)$_2$, and Al($\widehat{AA}$)$_3$] studied, a numbering convention, keyed to the group of permutations, is depicted. By noting the change in NMR signal multiplicity, during any coalescence, caused by stereoisomerization, one can determine which rearrangement permutations are consistent with the spectral change and which are not.[32] This is indicated in Table III by the cross-hatching out of permutations inconsistent (as the *sole* permutation) with the coalescence of the spectrum of a particular molecule. It

Table III. Permutational Analysis of Stereoisomerization of Al(β-diketonate)$_3$ Chelates

Molecule(s) Studied	Abelian Group of All Rearrangement Permutations and Permutation-Inversions: E	(12)(34)(56)	(56)	(12)	(34)	(34)(56)	(12)(56)	(12)(34)	E*	(12)(34)(56)*	(56)*	(12)*	(34)*	(34)(56)*	(12)(56)*	(12)(34)*	Numbering Conventions[a]	Ref.
Al(tfa)$_3$	×	×							×	×								2
Al(tfa)$_2$(acac)	×	×	×				×	×	×	×	×					×		12
Al(acac)$_2$(hfa)	×				×				×				×					11
Al(acac)$_2$(thd) Al(thd)$_2$(acac) Al(thd)$_2$(hfa) Al(acac)$_2$(afa) Al(hfa)$_2$(acac) Al(hfa)$_2$(thd)	×				×				×				×				Same as Al(acac)$_2$(hfa) above	10
Al(fod)$_3$	×	×							×	×							Same as Al(tfa)$_3$ above	9
Al(pmhd)$_3$	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	Same as Al(tfa)$_3$ above	8
Al(hfa)$_2$(acac) Al(acac)$_2$(hfa) Al(acac)$_2$(bzba)	×				×				×				×				Same as Al(acac)$_2$(hfa) above	7
Al(dibm)$_3$	×	×	×	×	×	×	×	×										1b
Al(hfa)$_2$(dibm)	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	Same as Al(acac)$_2$(hfa) above	this work

[a] It should be noted that the allowed permutations depend, of course, on the numbering conversions. The important point here is the fact that there is a type of permutation-inversion, exemplified by (12)(56)*, consistent with all experiments. The numbering conventions were designed to emphasize this fact.

should be emphasized that the eliminations of permutations for the first eight rows of the table are based solely on the observed changes in signal multiplicity and are independent of the values of rate constants and activation parameters that may have also been determined from the spectra. From Table III we can see that, if there is a common mechanism, only three rearrangement permutation-inversions are consistent (as *sole* process) with the coalescence patterns of all the molecules represented in the first eight rows. These are exemplified by (12)*, (34)(56)*, and (12)(56)*. We shall now see that the study of the Al(hfa)$_2$(dibm) molecule reported in this paper eliminates the first two of these.

There are only two possible stereoisomers of the Al(hfa)$_2$(dibm) molecule: Λ and Δ (Figure 5a). However, the coalescences of the ^{1}H and ^{19}F NMR spectra can differentiate[4] more detail in the rearrangement process. Consider the labels defined in Figure 5b (there are, of course, also the four enantiomers of these species, Δ_{25}, etc.). The species are labeled according to their chirality and according to which indexed B terminal groups are situated in equatorial environments (that is, in the same plane as the unique $\widehat{AA}$ ligand). The finding obtained in this study that, for Al(hfa)$_2$(dibm), the lifetime of a CF_3 group (a B group) in the axial or equatorial environment is equal to the lifetime of the molecule in the Λ or Δ form means, most simply, that the predominant rearrangments allowed (as *sole* process) are those which take Λ_{25}, for example, to Δ_{16} (of course, equally allowed are $\Lambda_{26} \rightleftarrows \Delta_{15}$, $\Lambda_{15} \rightleftarrows \Delta_{26}$, or $\Lambda_{16} \rightleftarrows \Delta_{25}$). The results of operating on Λ_{25} with the group of rearrangements in Table III are set out in Table IV. It is clear that only the rearrangement permutation-inversions (12)(34)(56)*, and (12)(56)* are consistent (as *sole* process) with experiment. This is shown in the last row of Table III. As implied above, the rearrangement (12)(34)(56)* has been ruled out by the coalescence patterns observed in a number of earlier studies[2,8,9,12] including the original investigation of Fay and Piper.[2]

Thus, *there is only one rearrangement consistent (as sole process) with all DNMR studies of Al(β-diketonate)$_3$ chelates.* This is the rearrangement exemplified by (12)(56)* in Table III and is thus the steric course of the stereoisomerization

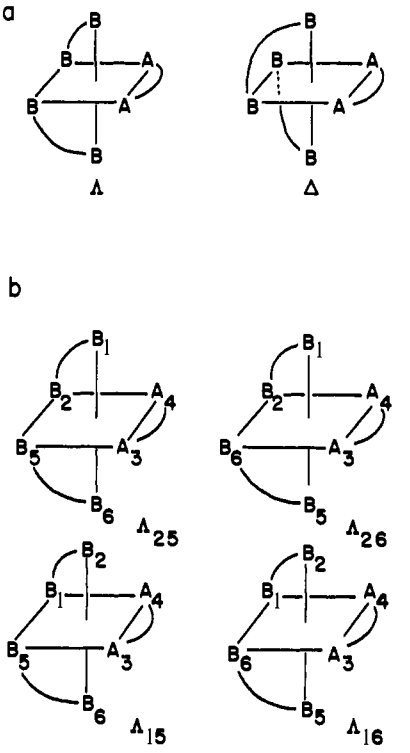


Figure 5. Labeling conventions for M($\widehat{BB}$)$_2$($\widehat{AA}$) molecules.

process if there is a single steric course. If there is more than one steric course, this rearrangement is the average or effective steric course (vide infra). It involves *the effective simultaneous interchange of the terminal groups within two of the three bidentate ligands and enantiomerization at the metal center.* This permutation-inversion has been variously designated as A_8 (or A_9'),[32] M_3'',[31] and $h_5'^{U*U}$.[4]

Mechanism. All of the papers dealing with permutational analyses[4,31,32] have taken great pains to carefully distinguish between steric course and mechanism. The steric course is a

Table IV

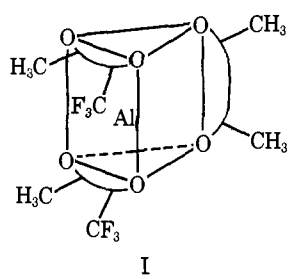
Operation	Resulting species	Operation	Resulting species
E	Λ_{25}	E*	Δ_{25}
(12)(34)(56)	Λ_{16}	(12)(34)(56)*	Δ_{16}
(56)	Λ_{26}	(56)*	Δ_{26}
(12)	Λ_{15}	(12)*	Δ_{15}
(34)	Λ_{25}	(34)*	Δ_{25}
(34)(56)	Λ_{26}	(34)(56)*	Δ_{26}
(12)(56)	Λ_{16}	(12)(56)*	Δ_{16}
(12)(34)	Λ_{15}	(12)(34)*	Δ_{15}

"permutational isomerization reaction" which is "differentiable in a chiral environment"[4] and is simply a definite permutation consistent with experiment. The mechanism, on the other hand, is "a description of the actual physical pathway followed by the molecule during the reaction".[33] The mechanism cannot be determined by a permutational analysis alone whereas, as we have just seen, the effective steric course can be. However, the elimination of certain steric courses, of course, eliminates certain mechanisms as well. The following is a discussion of the probable mechanisms of the stereoisomerization of Al(β-diketonate)$_3$ chelates.

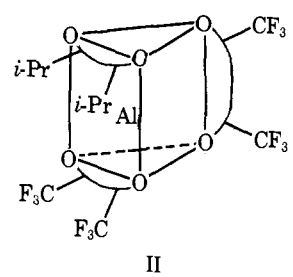
The kinetic data given above indicate that the mechanism is intramolecular. Intramolecular mechanisms for the isomerizations of tris chelates have been generally divided into two categories: nonbond rupture and bond rupture.[3,5,6,8]

Most of the nonbond-rupture mechanisms previously considered are associated with steric courses which have been eliminated for the Al(β-diketonate)$_3$ chelates. Thus, the trigonal-squash mechanism first envisioned by Stiefel and Brown for other chelates[34] is associated with the E* permutation-inversion and, as seen in Table III, cannot be operative in this case. Likewise, the trigonal (or Bailar) twist about the real or pseudo-C(3) axis,[35] proceeding through a trigonal prism with the bidentate ligands situated along the rectangular edges, is associated with the permutation-inversion (12)(34)(56)*. Although this mechanism is allowed for Al(hfa)$_2$(dibm) (Table III) as mentioned above, it has been ruled out by a number of the earlier studies.[2,8,9,12] The remaining nonbond-rupture mechanism previously considered is the rhombic (or Ray and Dutt) twist about the imaginary-C(3) axis.[35] In this process the molecule is visualized as isomerizing via a trigonal prism with two of the bidentate ligands situated along triangular edges and is associated with the rearrangements (34)(56)*, (12)(56)*, and (12)(34)*. Obviously, there are rhombic twists consistent with all studies of Al(β-diketonate)$_3$ complexes. Unfortunately, as seen below, there are bond-rupture mechanisms also consistent with the same steric course. Thus, the distinction between the rhombic-twist mechanism and certain bond-rupture mechanisms cannot be accomplished by the determination of the steric course.

There are only two types of rhombic twists formally eliminated as *sole* processes by the permutational analysis. These are characterized by the trigonal prisms I for Al(tfa)$_2$(acac) and II for Al(hfa)$_2$(dibm), for example. Since I appears to have less in common with II than it does with the other formally allowed rhombic twists characterized by III for Al(tfa)$_3$ and IV for Al(hfa)$_2$(dibm), it seems very hard to seriously consider the rhombic twist as a viable mechanism, at least for the chelates of fluorinated ligands (tfa, hfa, and fod).



I



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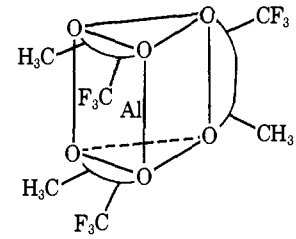
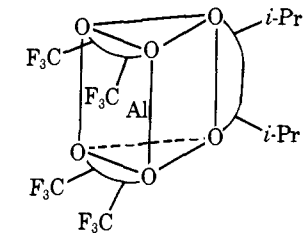


III

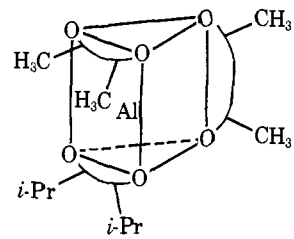


IV

Recent DNMR studies and their accompanying permutational analyses have fairly clearly indicated that the trigonal twist mechanism is operative for neutral tris(N,N-disubstituted dithiocarbamato) chelates[5] and tris(α-substituted tropolonato) chelates.[6] The driving force for the operation of this mechanism has been attributed in large part to the small "bite" sizes of these ligands and the consequent structural distortions of the chelates toward the trigonal prismatic (although this is apparently not the only factor in the case of the tropolonates[6]). The "bite" sizes of β-diketonate ligands are not as small as those of the above mentioned ligands,[6] and thus this particular driving force is not expected to be as important.

For the complexes mentioned above, where there is good evidence for twist mechanisms, it is interesting to note the values of the activation entropies found. Thus, for the dithiocarbamate chelates, the values range from 1.5 to 4.1 eu,[5] and for the tropolonate complexes, the values range from −16 to 5.4 eu.[36] It has been pointed out a number of times that twisting processes, because of their relative improbability, would be expected to manifest small or negative entropies of activation (2, 5-8, 10, 22, 23, 26, 36-38). The gas-phase stereoisomerizations of Cr(tfa)$_3$, for which arguments in favor of twist mechanisms have been advanced, exhibit $\Delta S^{\ddagger}$ values ranging from −1.7 to −5.5 eu.[38] In contrast, the stereoisomerizations of Co(β-diketonate)$_3$ chelates in solution, for which the evidence for bond-rupture mechanisms is reasonably clear,[26,33,37] are accompanied by activation entropies ranging from 1.5 to 11.0 eu.[26,37]

Thus, in the light of the activation entropy criterion, the chelates listed in Table II which do not contain hfa ligands [with the possible exception of Al(pmhd)$_3$, discussed above] most likely isomerize via rhombic-twist mechanisms.[39] Their activation entropies compare favorably with those of the Al(α-substituted tropolonate)$_3$ chelates which range from −11 to −4.3 eu.[36] The values for Al(acac)$_2$(dibm), studied by us (vide supra), although not very accurate, are less than zero. A contribution from the rhombic twist characterized by the trigonal prism V would ensure a rate of enantiomerization faster than the rate of axial–equatorial site interchange,[10] as is observed.



V

The activation entropy data in Table II pretty clearly indicate bond-rupture mechanisms for the isomerizations of the chelates containing the hfa ligand. This is consistent with a

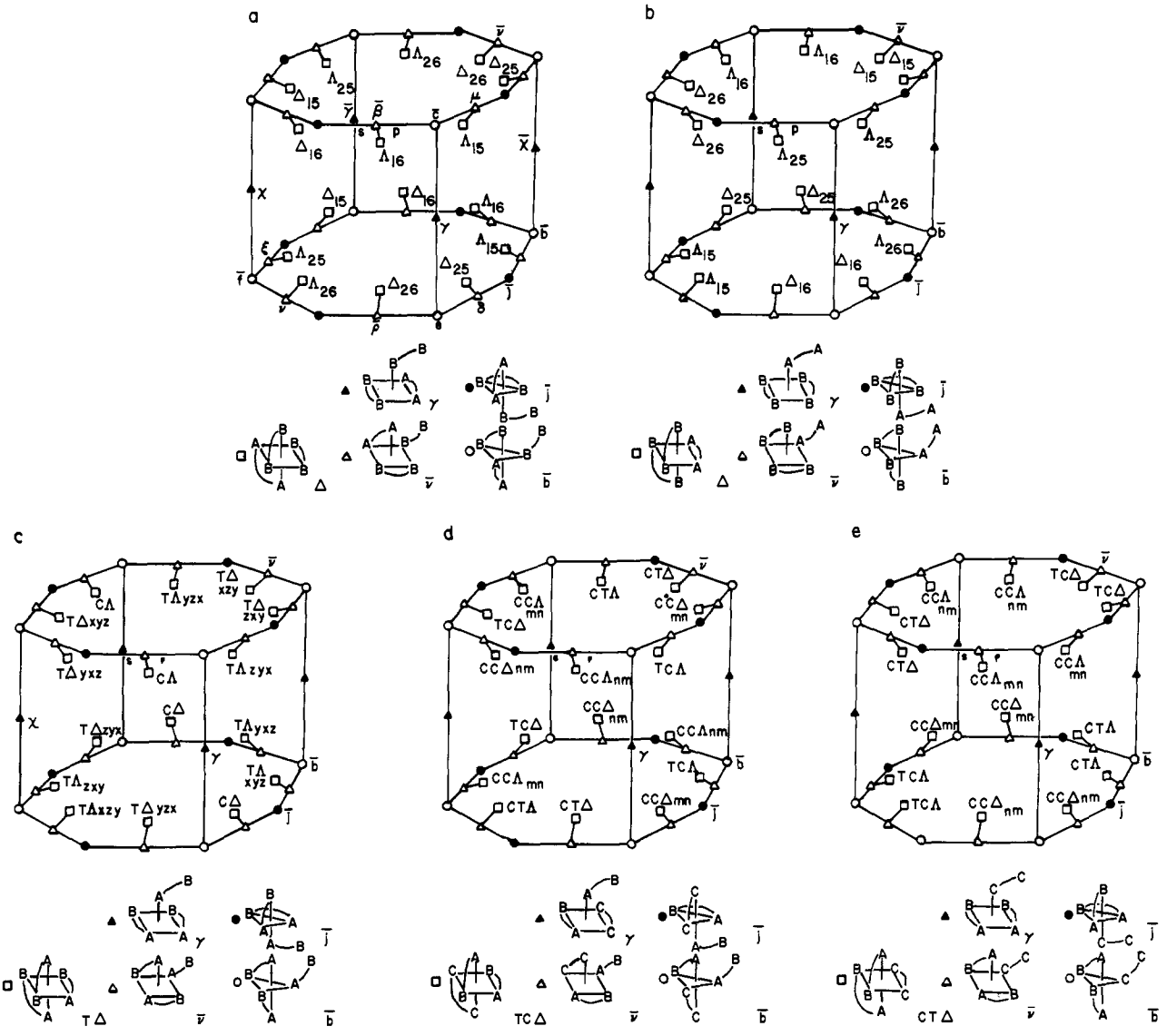


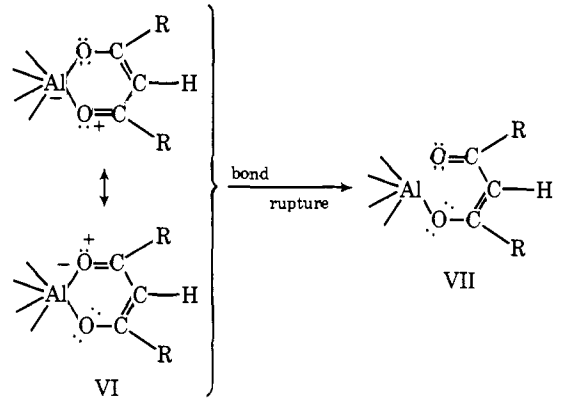
Figure 6. Compound topological graphs for the bond-rupture mechanism. The letter labels are defined in ref 33. (a) M-B bond rupture of an $M(\widehat{BB})_2(\widehat{AA})$ molecule. The numbered terminal groups in ref 33 have the following equivalences: 1 = 2 = 5 = 6 = B, 3 = 4 = A. The isomers shown are simply examples. (b) M-A bond rupture of an $M(\widehat{BB})_2(\widehat{AA})$ molecule. The numbered terminal groups in ref 33 have the following equivalences: 1 = 2 = 3 = 4 = B, 5 = 6 = A. The isomers shown are simply examples. (The octahedral isomers are named as if B = 1 = 2 = 5 = 6 and A = 3 = 4, in accordance with Figure 5.) (c) M-B bond rupture of an $M(\widehat{AB})_3$ molecule. The numbered terminal groups in ref 33 have the following equivalences: 1 = 3 = 5 = A, 2 = 4 = 6 = B. The isomers shown are simply examples. The *x*, *y*, and *z* environments are related to those of ref 32 and are depicted in XVI in the text. (d) M-B bond rupture of an $M(\widehat{AB})_2(\widehat{CC})$ molecule. The numbered terminal groups in ref 33 have the following equivalences: 1 = 5 = A, 2 = 6 = B, 3 = 4 = C. The isomers shown are simply examples. The isomer labels are depicted in XVII, XVIII, and XIX in the text. The *m* and *n* environments are related to those of ref 32 and are depicted in XIX in the text. (e) M-C bond rupture of an $M(\widehat{AB})_2(\widehat{CC})$ molecule. The numbered terminal groups in ref 33 have the following equivalences: 1 = 3 = A, 2 = 4 = B, 5 = 6 = C. The isomers shown are simply examples. See the caption to Figure 6d.

number of independent observations that the metal bond to the oxygen on the side of a β-diketonate ligand bearing a fluorocarbon substituent is significantly weaker than the analogous bonds to the ends of ligands bearing the common nonfluorinated substituents (CH_3, $C(CH_3)_3$, C_6H_5, etc.) because of the electron-withdrawing inductive effect of the fluorocarbon substituent.[7,10,19,22,26,40,41] Arguments have been made citing the results of force constant[10] and formation constant[22] determinations.

The bond-rupture mechanism for these chelates involves a coordination number change of 6 → 5 → 6. Arguments have been given for ascertaining the stereochemical role of the five-coordinate intermediate by allowing it to rearrange via the Berry pseudorotation mechanism (BPR).[33] Recently, "convincing support to the postulated Berry physical mechanism for intramolecular rearrangement in five-coordinate molecules" has been obtained from a careful analysis of the solid-state distortions observed in the structures of monodentate complexes determined by x-ray crystallography.[42] Of course, any physical mechanism within the same steric course, called the "Berry Permutation" by Whitesides and co-workers[43] and found to be operative for most of the five-coordinate stereoisomerizations which have been carefully studied,[44a-e] could be used. It does seem now that no other five-coordinate steric courses need be realistically considered.[44f] However, as discussed in ref 33, the BPR mechanism seems most appropriate for compounds entering the five-coordinate surface from an initial octahedral six-coordinate structure. Accordingly, the appropriate compound topological graphs[33] for the various kinds of chelates employed in the studies of Al(β-diketonate)$_3$ complexes are shown in Figure 6. The octahedral isomers are indicated by squares, the square (or tetragonal) pyramidal (SP) intermediates by triangles, and the trigonal bipyramidal (TBP) intermediates by circles. Before we proceed to analyze each graph in detail, let us consider the implications of the recent results of related studies.

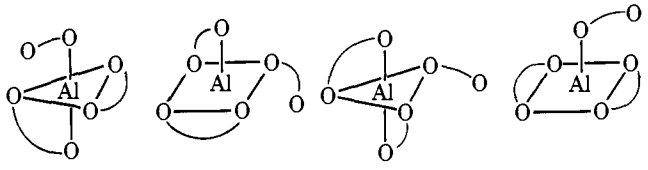
The Al(III) central atom is, of course, formally isoelectronic with Si(IV), P(V), and S(VI). The stereochemistries of a number of the reactions of four-coordinate Si(IV)[45,46] and S(VI)[47] compounds have been interpreted in terms of associative mechanisms involving coordination number changes of $4 \rightarrow 5 \rightarrow 4$. The ability of the five-coordinate intermediate to rearrange plays an important role in the stereochemistry of these reactions. The importance of this same type of mechanism in biological reactions of four-coordinate P(V) compounds is currently being investigated.[43,44a,b,48,49] There are, of course, large numbers of stable five-coordinate P(V) compounds, and their stereoisomerizations have been the subjects of extensive study.[43,44a,b,48,49] Because of the immense amount of experimental investigation into the rearrangement of five-coordinate compounds, there have been a number of theoretical studies made of the energetics of the five-coordinate surface. Thus, the structural consequences of ligand-ligand repulsion have been investigated,[50] molecular orbital electronic energy calculations of σ-bonding[44c,45,51-53] and π-bonding[44c] effects have been made, and the effects of the presence of two chelate rings on ligand-ligand repulsion[54] have been studied. The combination of all of these experimental and theoretical studies results in three conclusions of importance to the problem at hand. (1) The most electropositive ligands will be preferentially located in the equatorial positions of the TBP structure and the apical position of the SP structure.[44b,c,45,51] (2) The best π-donor ligands will be preferentially located in the equatorial position of the TBP structure and the apical position of the SP structure (for central atoms with empty d orbitals).[44c] (3) Chelate rings tend to occupy axial-equatorial positions in the TBP structure to avoid ring strain,[44b] and bis bidentate five-coordinate compounds of moderate to small "bite" have a strong tendency to have both rings occupying basal-basal positions in the SP structure.[44b,54] This latter aspect is so pronounced that many spirocyclic phosphorus compounds may actually have ground states[44b] or fairly clearly defined real kinetic intermediates[44c] with bis(basal-basal) SP structures.

Combining the above conclusions with three simple postulates, we can derive a single consistent mechanism for all of the stereoisomerizations of Al(β-diketonate)$_3$ complexes of ligands bearing fluorinated substituents which have been studied. The postulates are the following. First, breaking of only the aluminum oxygen bonds to the ends of ligands bearing fluorinated substituents is mechanistically significant. We have mentioned evidence for this postulate above. Second, in the five-coordinate intermediate, the oxygen atom remaining bound to the aluminum in the monodentate ligand will not be as electronegative as the oxygens of the chelated bidentate ligands. This has been noted previously by Fay and Piper,[2,55] and its reasonableness should be evident after consideration of the important resonance forms of the bidentate (VI) and monodentate (VII) ligands. Third, the monodentate ligand is a better π-donor ligand than the bidentate ligand. This should also be evident after consideration of VI and VII. Although none of the three postulates may alone be strong enough to have important structural consequences for the five-coordinate intermediate, taken together, along with chelate ring effects, they determine the shape for the five-coordinate surface.



VI VII

For the process under discussion here, there are four generalized types of five-coordinated intermediates to be considered.[33] These are the TBP-axial (VIII), SP-basal (IX), TBP-equatorial (X), and SP-apical (XI) structures. From the



TBP-ax SP-basal TBP-eq SP-apical

VIII IX X XI

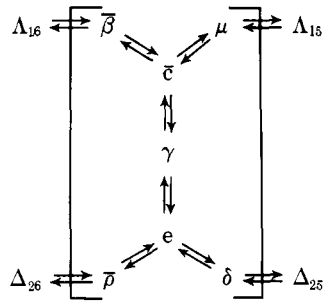
combination of the conclusions from the study of five-coordinate compounds with the postulates given above, it is reasonably certain that the energies of these intermediates decrease in the order VIII > IX $\gg$ X $\geq$ XI. The TBP-axial form (VIII) should be high in energy; chiefly because of the ring strain present in the equatorial-equatorial ring, but also because the most electropositive and best π-donor ligand is in the unfavored axial position. The SP-basal form (IX) has some ring strain in the apical-basal ring (but certainly less than the TBP-axial form) and also has the most electropositive and best π-donor ligand in the unfavored basal position. The TBP-equatorial form (X) should be considerably lower in energy because virtually all of the ring strain has been released and the most electropositive and best π-donor ligand (the monodentate ligand) is now in the favored equatorial position. Finally, the SP-apical form (XI) has the monodentate ligand in the electronically favored apical position. With the spirocyclic effect[44b] also in operation, it is likely that XI is lower in energy than X. Even if only ligand-ligand repulsion is considered, the "normalized bite", b[54], of the Al-β-diketonate ring [1.44 for Al(acac)$_3$[56]] is such that X and XI would be expected to have very similar depths on the same floor of a continuous potential-energy valley.[54] Some idea of the energy profile of the structures VIII–XI, if postulate two is correct, before the effects of π bonding and ring strain are introduced, can be obtained from Figure 8 of ref 45 and Figure 6 of ref 51.

Let us now return to Figure 6 and consider the Al(β-diketonate)$_3$ rearrangements which have been studied. Immediately after bond rupture, the activated molecule finds itself on the five-coordinate surface with a structure identical with or equivalent to the SP-basal (IX).[33] This structure is symbolized in Figure 6 by an open triangle. The SP-basal form can undergo ½ BPR motions of the "primary" or "secondary" type to produce the TBP-eq (X, open circles) or TBP-ax (VIII, closed circles) forms, respectively.[33] In the complexes under discussion here, the "primary" process should be favored to the almost complete exclusion of the "secondary" process because of the relative energies of the five-coordinate structures noted above. This has the following consequences in the various systems which have been studied.

Al(hfa)$_2$(dibm) and Similar Molecules. Figures 6a and 6b are appropriate for molecules of the type M($\widehat{BB}$)$_2$($\widehat{AA}$). Figure 6a represents the case where an M–B bond ruptures, Figure 6b represents the case where an M–A bond ruptures. As seen in Tables II and III, a number of Al(β-diketonate)$_3$ chelates in this class, where $\widehat{BB}$ = hfa and $\widehat{AA}$ = acac,[7,10] thd,[10] or dibm, have been studied. In these cases, postulate one requires the breaking of only M–B bonds, and thus Figure 6a is to be used.

In Figure 6a we see that, for example, if an M–B bond

Scheme I

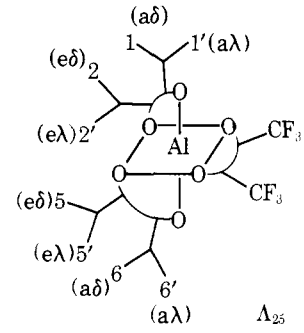


rupture occurs in Λ_{16} to produce the SP-basal form β, the SP-apical form γ is the ultimate intermediate because the excursion from $\bar{\beta} \rightarrow \bar{c} \rightarrow \gamma$ is energetically downhill. If $\bar{\beta}$, μ, $\bar{p}$, and δ are of very similar energies,[57] the decomposition of γ re-forms Λ_{16} or forms Λ_{15}, Δ_{26}, and Δ_{25}, all with equal probabilities. This is indicated by the reaction sequence in Scheme I. In such a sequence, it is clear that the average lifetime for enantiomerization is equal to the average lifetime for axial to equatorial interchange.[10] This is what is measured for $Al(hfa)_2(dibm)$ and $Al(hfa)_2(acac)$ (Figure 3). There are, of course, three other equivalent reaction sequences (characterized by χ, $\bar{\gamma}$, and $\bar{\chi}$) shown in Figure 6a. These are all isolated from each other by the high-energy TBP-axial structures.

If postulate one were not operative and M–A bond rupture were occurring, the result would be the same in this particular class. This can be seen in Figure 6b. For example, Λ_{25} would form SP-apical intermediate γ (note that the greek letter symbols have different meanings in each graph in Figure 6), which can only re-form Λ_{25} or form Δ_{16} with equal probabilities. However, arguments were given above in support of postulate one, and additional stereochemical results will be given below which mitigate against the breaking of M–A bonds in this class. The stereoisomerization of $Al(hfa)_2(thd)$ presumably follows the same pathway although the reported results[10] are insufficient to prove this directly.

We have also investigated the ^{19}F NMR spectrum of $Al(hfa)_2(+atc)$ [prepared from the ligand interchange reaction of $Al(hfa)_3$ with $Al(+atc)_3$] where +atc is a chiral, unsymmetrical β-diketonate ligand.[58] This molecule has only two isomers, Δ and Λ, but eight distinguishable environments for the CF_3 group. Seven of the eight possible resonances can be differentiated in $CFCl_3$, and all eight can be observed at low temperatures (−20 °C) in TFT. The mechanism given above for $Al(hfa)_2(dibm)$ would predict the coalescence of the eight resonances into a doublet. As the temperature of the TFT solution is raised, the coalescence of the eight resonances is complex, and a quantitative analysis is precluded by severe overlap with the strong singlet of $Al(hfa)_3$. However, at the highest temperature studied (90 °C), it does seem that two major resonances are emerging from the kinetically broadened pattern. A very small splitting (~1 Hz) of the downfield resonance in the 8,9,10-"camphor" methyl region of the ^1H spectrum of a CCl_4 solution of $Al(hfa)_2(+atc)$ is observed to coalesce between 30 and 40 °C. This indicates that the complex is indeed undergoing rapid enantiomerization. In order for the study of this chelate to be definitive, however, a more quantitative analysis of the spectrum is necessary.

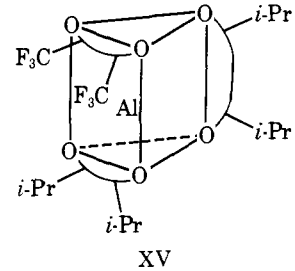
If $\widehat{AA}$ = hfa and $\widehat{BB}$ = acac,[7,10,11] thd,[10] or dibm, then postulate one requires M–A bond rupture and the use of Figure 6b. The Λ_{25} form of the $Al(dibm)_2(hfa)$ molecule is symbolized in XIV. As noted in the Results section, there are four different methyl group environments (aδ, aλ, eδ, and eλ in XIV, where a and e represent axial and equatorial and δ and λ represent the two diastereotopic environments of each *i*-Pr group[1b]). With spin-spin coupling from the methine proton, this could give rise to eight methyl resonances, in principle, and six distinct resonances have been observed, in fact, for *cis*-$Ti(dibm)_2Cl_2$.[25] However for $Al(dibm)_2(hfa)$, Figure 4 shows that, for the lowest temperature studied, only extremely broadened resonances are observed. As the temperature is raised, four distinct resonances emerge. If the broadening at low temperatures is due to chemical exchange ($T_c \simeq -60$ °C), this is exactly the behavior expected for M–A bond rupture as can be seen in Figure 6b. The Λ_{25} molecule can form only the SP-apical intermediate γ which can only re-form Λ_{25} or form Δ_{16}. If Δ_{16} is formed the only environments averaged will be aδ with eλ and aλ with eδ. Thus, with spin-spin coupling, four methyl resonances would be expected. The coalescences of the axial–equatorial *t*-Bu doublet of $Al(thd)_2(hfa)$ ($T_c = -9$ °C in ClC_6H_5[10]) are also presumably due to the same mechanism. The activation parameters for $Al(acac)_2(hfa)$ (Table II) are consistent with the bond rupture mechanism (vide supra). The activation energy is somewhat lower than those for molecules with two hfa ligands, presumably because the Al ion is less acidic in $Al(acac)_2(hfa)$.



XIV

M–B bond rupture for $Al(dibm)_2(hfa)$ would cause exchange of all four environments and thus coalescence to two spin-spin coupled methyl peaks. For example, Λ_{25} could be converted to Λ_{26} via the sequence ($\Lambda_{25} \rightleftarrows [\xi \rightleftarrows \bar{f} \rightleftarrows \chi \rightleftarrows \bar{f} \rightleftarrows \nu] \rightleftarrows \Lambda_{26}$, Figure 6a). If this occurred, methyl 5 (XIV) would be exchanged from environment eδ to environment aδ. The simultaneous formation of Δ_{15} and Δ_{16} from Λ_{25} would cause exchange between all four environments. Thus, the rupture of the aluminum–oxygen bond to the dibm ligand can be ruled out for the low-temperature process (LTP) which gives rise to four methyl methyl resonances for $Al(dibm)_2(hfa)$ at −60 °C or at 0 °C.[59]

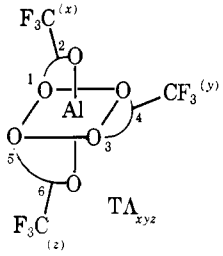
When the temperature is raised to 20 °C, the four resonances do broaden and coalesce to a spin coupled doublet. This high-temperature process (HTP) could involve the rupture of the Al-dibm bond but more likely involves a rhombic twist process, characterized by the trigonal prism XV, as discussed above.



XV

Al(tfa)$_3$ and Similar Molecules. The original aluminum β-diketonate reported by Fay and Piper was $Al(tfa)_3$.[2] They found that all four ^{19}F resonance peaks of the equilibrium mixture of cis and trans isomers simultaneously broaden and coalesce as the temperature is raised. The appropriate graph for this compound is shown in Figure 6c. It depicts the rearrangements of an $M(\widehat{AB})_3$ chelate following M–B bond rup-

ture. Postulate one requires that the B end be considered the CF_3 end of the tfa ligand. It is clear from the graph that CF_3 groups in the three trans environments (*x*, *y*, and *z*, XVI) are

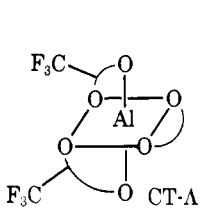


XVI

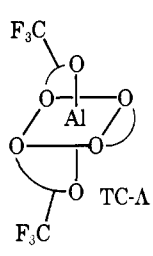
all exchanged into the cis environment by bond rupture and rearrangement through the SP-apical intermediate. For example, intermediate γ exchanges $T\Lambda(zyx)$ with $C\Lambda$, $C\Delta$, and $T\Delta(yzx)$. It is also clear that although no single SP-apical intermediate exchanges CF_3 groups among all three trans environments, simultaneous transit through different intermediates does cause such exchange. For example, although intermediate γ does not exchange CF_3 groups out of *x* to *y* or *z*, intermediate χ does. Thus the general mechanism is entirely consistent with the observed results. The same mechanism is presumably operative for $Al(fod)_3$.[9]

Al(tfa)$_2$(acac). Palmer, Fay, and Piper report that all four ^{19}F resonances of the equilibrium mixture of *cis,cis*-, *cis,trans*-, and *trans,cis*-$Al(tfa)_2(acac)$ simultaneously broaden and coalesce into a single sharp peak.[12] The compound graphs appropriate for an $M(\widehat{AB})_2(\widehat{CC})$ complex such as this are shown in Figures 6d and 6e.

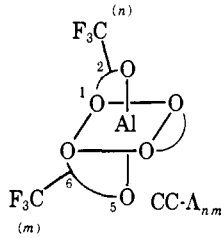
Figure 6d represents M–B bond rupture and thus postulate one requires that B represent the CF_3 end of the tfa ligand. It is quite clear that the bond rupture mechanism characterized by the SP-apical intermediate is consistent with the exchange of CF_3 groups among the cis–trans (XVII), trans–cis (XVIII), and two cis–cis (XIX) environments (the *m* and *n* labels are



XVII



XVIII



XIX

related to those of the Eatons[32]). For example, intermediate γ connects isomers $CC\Lambda(nm)$, $TC\Lambda$, $CT\Delta$, and $CC\Delta$ (mn).

Consideration of Figure 6e gives strong proof of postulate one. This graph represents M–C bond rupture; that is, Al–acac bond rupture. If this pathway were operative, via the SP-apical intermediate, it is clear that the CF_3 groups would never be exchanged out of the two cis–cis environments into the cis–trans and trans–cis environments and vice versa. Thus, rupture of the M–$\widehat{AB}$ chelate ring is required and this would seem to be almost certainly at the CF_3 end.

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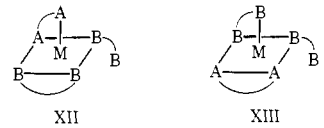

XII XIII

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(59) A referee has suggested that the coalescence observed at ~−60 °C is due to viscosity broadening. Since the coalescence temperature of Al(acac)$_2$(hfa) is 1 °C (CH_2Cl_2[7]), one might expect the coalescence temperature for the analogous LTP of Al(dibm)$_2$(hfa) to be similar. The referee points out that this might indeed be the case and that the expected eight resonances are simply accidently degenerate as a quartet below 0 °C.

Solvent Specific Photochemistry Involving an Intramolecular Amino Ketone Triplet Exciplex[1]

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Abstract: β-Naphthyl γ-dimethylaminopropyl ketone (**1**) undergoes inefficient ($\Phi \leq 0.01$), unquenchable type II photoelimination to 2-acetonaphthone in protic and aprotic solvents. The efficiency of **1** as a photosensitizer indicates that it forms long-lived ($\tau \geq 10^{-6}$ s) triplets in good yield ($\Phi_{isc} = 0.76$–0.88). Only in protic solvents does this easily quenchable triplet yield acetonaphthone ($\Phi = 0.17$ in methanol). It is concluded that the π,π^* triplet undergoes efficient CT interaction with the amine group in all solvents; only specific protonation of the exciplex catalyzes its rearrangement into a diradical. The lack of such rearrangement in aprotic solvents indicates a rather restricted cyclic geometry to the exciplex.

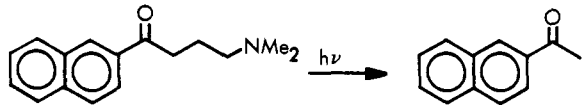
It is now well established that the triplet states of ketones are quenched by charge transfer (CT) interactions with amines, with efficient photoreduction often following.[2] Whereas the reactivity differences between n,π^* and π,π^* ketone triplets are now pretty well defined for hydrogen abstraction reactions,[3] they are not so well defined for CT reactions. Thermodynamic factors (redox potentials and electronic excitation energy) clearly affect quenching rate constants,[4] but from the limited data in the literature it is not possible to tell whether any fundamental reactivity differences exist between the two triplet types.

Another aspect of CT quenching of triplet ketones which is not well understood involves the structure of the nonluminescent exciplex presumably formed in the quenching process. In this regard, the photochemistry of amino ketones is particularly interesting because of the conformational limitations of intramolecular bifunctional reactions.

In this paper we report the strongly solvent dependent photochemistry of β-naphthyl γ-dimethylaminopropyl ketone, **1**. This compound was chosen because the π,π^* lowest triplets of naphthyl ketones do not abstract hydrogen atoms directly[5,6] and because γ-amino phenyl ketones undergo facile intramolecular CT triplet quenching.[7]

Results

Irradiation at 313 or 365 nm of degassed benzene or acetonitrile solutions 0.02–0.05 M in **1** results in inefficient (Φ =



0.010), completely unquenchable (by 3.4 M 1,3-pentadiene) type II elimination[8] to 2-acetonaphthone. The quantum yield is unaffected by 0.56 M pyridine. We presume that some cyclobutanol is also formed[9] but did not analyze for it. In methanol as solvent, the type II quantum yield is 0.17, 0.163 of which is readily quenchable by low concentrations of dienes and stilbene, both of which quench triplet naphthyl ketones.[10] After subtraction of the residual unquenchable reaction, linear Stern-Volmer plots were obtained for the quenchable portion of the reaction, with slope ($k_q\tau$) values of 780 M^{-1} for 1,3-pentadiene and 6100 M^{-1} for *trans*-stilbene. In methanol-*O*-*d*, the total quantum yield is only 0.12; in 2,2,2-trifluoroethanol, 0.05. Table I lists quantum yields in benzene as a function of added methanol concentration.

In benzene, 0.05 M **1** is 76 ± 2% as efficient as 0.05 M benzophenone or 2-acetonaphthone at photosensitizing the cis–trans isomerization of 0.04–0.20 M 1,3 pentadiene.[11] Consequently, the intersystem crossing yield of **1** is 0.76 relative to 1.0 for 2-acetonaphthone.[12] In methanol, 0.03 M **1** is 88% as efficient as 0.03 M benzophenone at sensitizing the isomerization of 0.2 M diene. In benzene, 10^{-3} M **1** is 30% as effective as benzophenone and 2-acetonaphthone at sensitizing