Contribution from the Department of Chemistry,
Sir George Williams University, Montreal, Quebec, Canada H3G 1M8

Permutational and Mechanistic Analysis of the Configurational Rearrangements in $R_2Sn(acac)_2$ and $RClSn(acac)_2$ Complexes[1]

DOUGLAS G. BICKLEY and NICK SERPONE*

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A permutational and mechanistic analysis of the coalescence behavior of acetylacetonate (acac) methyl and ring proton signals in the nmr spectra of $RClSn(acac)_2$ complexes is presented. The analysis suggests that configurational rearrangements in these systems probably proceed *via* twist motions through trigonal-prismatic transition states, if the exchange process occurs by a sole reaction pathway. Comparison of the rate constants for the rearrangements in $(C_6H_5)ClM(acac)_2$ (M = Sn, Ge, Si) tend to support the twist mechanism. Environmental averaging of methyl groups in $(C_6H_5)_2Sn(acac)_2$ are also believed to proceed *via* a twist process on the basis of activation parameters and those obtained from the intermolecular ligand-exchange process in the $(C_6H_5)_2Sn(acac)_2$-$(CH_3)_2Sn(acac)_2$ system.

Introduction

A recent study[2] from this laboratory has reported on the stereochemistry (cis) and on the stereochemical fluxionality of $(C_6H_5)_2Sn(acac)_2$ and $RClSn(acac)_2$ (acac = $CH_3COCHCOCH_3^-$; R = C_6H_5 or CH_3) complexes investigated by means of variable-temperature line-broadening nmr techniques. We now wish to present a permutational and mechanistic analysis carried out on these C_1-type $XYM(acac)_2$ complexes.

Permutational analyses have been applied to six-coordinate molecules[3-7] to describe mathematically all the possible permutations of nuclei without having to specify how atoms move from one position to another. From such a description, actual configurational changes (diastereomerization and/or enantiomerization) and proton nmr observable site interchanges may be deduced from the possible permutations. In turn, the most probable physical pathway which produces a particular permutation may be inferred provided the observed site interchanges are unique to that one permutation; however, the pathway need not be unique to this particular permutation. We analyze here all permutations pertaining to a neutral bis-bidentate six-coordinate chelate of the type $XYM(AA)_2$ (M = Sn; AA = a bidentate ligand, *e.g.*, acac) following the method of Longuet-Higgins[8] of treating fluxional complexes by molecular symmetry groups for nonrigid molecules and recently employed by Eaton and Eaton[7] to analyze labile $M(AB)_3$ and $M(AB)_2(CC)$ chelates.

Permutational Analysis

A symmetry group of a nonrigid molecule is defined[8] as the set of all feasible permutations (P) of the positions and spins of identical nuclei, including the identity E, and of all feasible permutation-inversions ($P^* = E^*P = PE^*$) which simultaneously permute and invert the relative coordinates of all atoms in the center of mass of the molecule (E^* is the inversion of all atomic positions and may or may not be among the feasible operations).

In the case under consideration, the set of all P and P* operations is a group of order 384[9] comprised of a group of order 24 consisting of the 24 rigid-body rotations about the proper symmetry axes of the octahedral skeleton and an Abelian group of order 16[10] representing the complete set of all the possible rearrangements in stereochemically nonrigid $XYSn(acac)_2$ complexes. There is thus a unique set of 16 permutational isomers (8 enantiomeric pairs) each one of which is permuted into the other 15 by 8 P and 8 P* operations. These isomers are referred to by the six indices that label the ligating atoms;[7] hence, the permutational isomer shown in Figure 1 is the [163-542] isomer.[11] The effect of performing the 16 permutations and permutation-inversions on this isomer to yield the remaining 15 is summarized in Table I, where numbers in parentheses denote the operations. For example, (12)(56) describes the net effect of the interchange of groups 1 and 2 and of groups 5 and 6, without specifying the motion involved in this interchange.

When all 16 operations are performed on the 16 permutational isomers, it is observed that certain permutations lead to equivalent configurational changes and site interchanges (see Table I). Those permutations that yield the same net exchange pattern are placed in the same averaging set, A_i; however, permutations within each set may have different effects on a particular isomer. Configurational changes, site interchanges, and averaging sets are summarized in Table I. Only averaging sets A_4, A_6, and A_7 (and the corresponding A_i') lead to net site interchange of methyl groups and ring protons. Sets A_4', A_6', and A_7' in addition lead to $\Lambda \rightleftarrows \Delta$ interconversion. Axial-axial (ax-ax) and equatorial-equatorial (eq-eq) exchange of methyl groups is afforded by A_4; A_7 affords inter-ring ax-eq, ax-eq exchange while A_5 leads to intraring ax-eq, ax-eq exchange. The expectation from

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[1] Presented before the Division of Inorganic Chemistry, 168th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1974, Abstract INOR-64.

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[7] S. S. Eaton and G. R. Eaton, *J. Amer. Chem. Soc.*, 95, 1825 (1973), and references therein.

[8] H. C. Longuet-Higgins, *Mol. Phys.*, 6, 445 (1963).

[9] For an octahedral complex $ML_1L_2L_3L_4L_5L_6$ there are 6! = 720 permutations of the six indexed monodentate ligands L_i. This set of permutations factors into a set of 24 rigid-body rotations of the skeleton and a unique set of 30 permutational isomers. If ligands L_5 and L_6 are restricted to positions cis to each other, there will be 6 fewer permutational isomers and 144 fewer permutations reducing the set to 576 permutations. With the additional constraint that L_1L_2 and L_3L_4 represent ligating atoms of a bidentate ligand and that such a ligand cannot span trans positions, the unique set of permutational isomers is further reduced to 16 and the set of permutations by 192 to yield the group of order 384.

[10] The complete 16 × 16 group multiplication table has already been given elsewhere (see Table II of ref 7).

[11] The [163-542] notation is obtained by viewing the complex down one of the threefold axes with index 1 in the upper vertex of the octahedron. The indices of the ligating atoms positioned toward the viewer are then read in a clockwise manner; thus, 163 (Y is 6) for the permutational isomer of Figure 1. Next, the index trans to 3 is read followed by the other two indices, also in a clockwise direction.

Table I. Permutational Analysis for the *cis*-$XYSn(acac)_2$ Complex

Operation	Permutational isomer	Site interchange $R_1R_2R_3R_4; H_1$	Net configurational change CH_3	-CH=	Inversion	Averaging set
E	[163-542]	abcd; m	No exch	No exch		A_1
(12)	[145-362]	bacd; m	ax–eq	No exch		A_2
(34)	[164-532]	abdc; m	ax–eq	No exch		A_3
(56)	[153-642]	dcba; n	ax–ax eq–eq	Exch		A_4
(12)(34)	[135-462]	badc; m	ax–eq ax–eq	No exch		A_5
(12)(56)	[146-352]	cdba; n	Total scrambling	Exch		A_6
(34)(56)	[154-632]	dcab; n				
(12)(34)(56)	[136-452]	cdab; n	ax–eq ax–eq	Exch		A_7
E*	[136-245]	abcd; m	No exch	No exch	$\Lambda \rightleftarrows \Delta$	A_1'
(12)*	[154-263]	bacd; m	ax–eq	No exch	$\Lambda \rightleftarrows \Delta$	A_2'
(34)*	[146-235]	abdc; m	ax–eq	No exch	$\Lambda \rightleftarrows \Delta$	A_3'
(56)*	[135-246]	dcba; n	ax–ax eq–eq	Exch	$\Lambda \rightleftarrows \Delta$	A_4'
(12)(34)*	[153-264]	badc; m	ax–eq ax–eq	No exch	$\Lambda \rightleftarrows \Delta$	A_5'
(12)(56)*	[164-253]	cdba; n	Total scrambling	Exch	$\Lambda \rightleftarrows \Delta$	A_6'
(34)(56)*	[145-236]	dcab; n				
(12)(34)(56)*	[163-254]	cdab; n	ax–eq ax–eq	Exch	$\Lambda \rightleftarrows \Delta$	A_7'

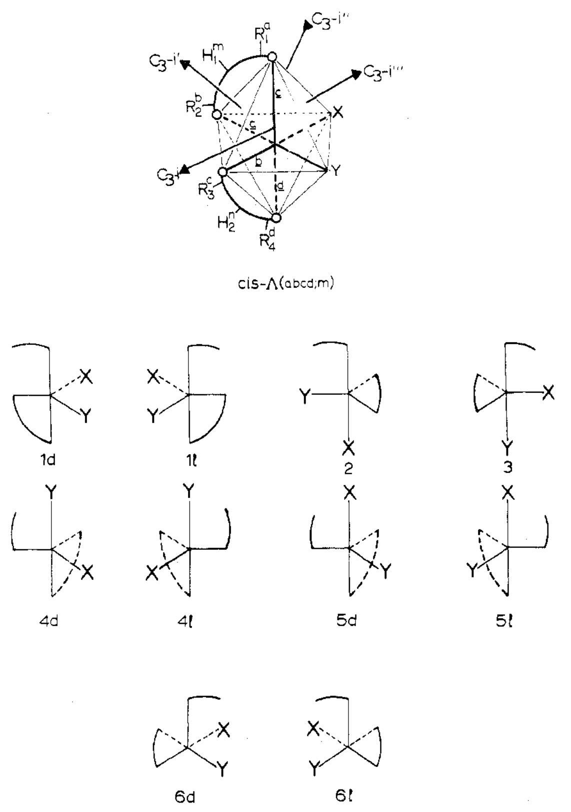

Figure 1. View of a cis-Λ isomer of $XYSn(acac)_2$ complex along the threefold axis $C_3 i$. R's represent the methyl groups on the acetylacetonate ligands. Numerical subscripts label R groups and ring protons; letter superscripts label the nonequivalent environments. It also illustrates the [163-542] permutational isomer of $XYSn(acac)_2$ where Y is number 6 and X is 5. The letters a, b, c, and d define the four Sn–O bonds which can be ruptured. The letters between parentheses, (abcd; m), denote the site occupied by R_1, R_2, R_3, R_4 in this order, while m defines the site occupied by H_1. Also shown are the possible TBP-axial, TBP-equatorial, and SP-axial intermediates arising from a metal–oxygen bond rupture.

A_4 is coalescence of the four methyl and two ring proton nmr resonances to yield a doublet and a singlet, respectively, in the fast-exchange limit (see Figures 1 and 2 of ref 2a). Set A_6 leads to total scrambling of the methyl groups between the four nonequivalent sites with the consequence that the four nmr signals coalesce into a single resonance under conditions of fast exchange. A_7 should yield the same coalescence expectations as A_6, but because of the difficulty of assigning the components of the two doublets to the particular methyl groups, the methyl doublet at fast exchange may be experimentally observed only if the chemical shifts of the two components are large enough to be resolved and may not be otherwise.[12] In the latter case, A_6 and A_7 cannot be distinguished. Distinction between A_i and A_i' averaging sets may be accomplished by incorporating diastereotopic groups into the complex. We have observed that $Ti(dibm)_2X_2$ (X = F, Cl, Br; dibm = diisobutyrylmethanate), $Ti(dibm)_2Cl(OCH_3)$, and $Sn(dibm)_2Cl_2$ complexes undergo, simultaneously, exchange of terminal isopropyl groups and inversion of the molecular configuration.[13] In addition, it is interesting to note that $(C_6H_5)_2Sn(bzbz)_2$ and $Cl_2Sn(bzbz)_2$ complexes (bzbz = dibenzoylmethanate) exhibit the Pfeiffer effect.[14]

The experimental observations[2a] impose the following constraints on the mechanism of the exchange process: (i) configurational rearrangements in $RClSn(acac)_2$ complexes proceed *via* a mechanism which simultaneously exchanges -CH= protons and methyl groups between the two and four, respectively, nonequivalent sites of the cis isomer to yield singlets under conditions of fast exchange; (ii) although not observed for $RClSn(acac)_2$ complexes, rearrangements most probably occur with $\Lambda \rightleftarrows \Delta$ interconversion. Therefore, the mechanism for the rearrangement process must produce A_6' (and/or possibly A_7'), if we restrict the rearrangements to a sole reaction pathway.

Physical Mechanisms

Various mechanisms that can lead to averaging of ring proton and methyl group environments in neutral β-ketoenolate complexes of the type $M(dik)_2X_2$ have been discussed in some detail.[15] These include (a) dissociation of a mono-

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(12) We have tested this possibility by computing line shapes in the fast-exchange limit using the program DNMR3 (QCPE, University of Indiana) for the averaging sets A_1 through A_7.

(13) D. G. Bickley and N. Serpone, unpublished results.

(14) V. Doron, W. Durham, and D. Frazier, *Inorg. Nucl. Chem. Lett.*, 7, 91 (1971). See also, S. Kirschner, *Coord. Chem. Rev.*, 2, 461 (1967), and references therein.

(15) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, 17, 391 (1972).

dentate ligand to give a five-coordinate intermediate, (b) complete dissociation of a diketonate ligand to yield a four-coordinate intermediate, (c) momentary rupture of one metal-oxygen bond to give a trigonal-bipyramidal (TBP) transition state with the dangling ligand in the axial or equatorial positions or a square-pyramidal (SP) transition state with a basal or axial dangling ligand, and (d) twist motions of the ligands to give an idealized trigonal-prismatic (TP) transition state.

Dissociation of a methyl or phenyl group in a medium such as CH_2Cl_2, $CDCl_3$, or $CHBr_3$ is not likely owing to a high bond dissociation energy (of the order of *ca.* 100 kcal/mol);[16] also, an equimolar mixture of $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ in deuteriochloroform (or bromoform) yields no nmr resonances attributable to the mixed complex $(C_6H_5)(CH_3)Sn(acac)_2$. However, equimolar mixtures of $X_2Sn(acac)_2$ and $Y_2Sn(acac)_2$ in 1,1,2,2-tetrachloroethane yield an equilibrium mixture containing the parent complexes as well as the mixed complex $XYSn(acac)_2$ (X = Y = F, Cl, Br, I), but halide exchange appears to be slow compared to methyl group exchange.[17] In addition, ^{36}Cl exchange between $Cl_2Sn(acac)_2$ and tetraethylammonium chloride is slow ($k_{15} = 0.0018\ M^{-1}\ sec^{-1}$).[18] Chloride exchange in $RClSn(acac)_2$ complexes is also expected to be slower than either acac methyl group or ring proton exchange. Available evidence argues against intermolecular mechanism (b). Tin-ring proton coupling in both methylchlorotin and phenylchlorotin complexes is observed before (~2.5-3 Hz) and after (~2 Hz)[19] coalescence; $J(Sn-CH_\gamma)$ is too small to be observed during coalescence. These observations suggest that acetylacetonate ligands remain attached to the tin atom, at least through one oxygen, even though Sn-O bond breaking may be fast.[20] Faller and Davison[21] have also noted retention of $J(Sn-CH_3)$ and $J(Sn-CH_\gamma)$ in dynamic nmr studies of $Cl_2Sn(acac)_2$. Additional support for rejecting complete dissociation of an acac ligand comes from a recent report[22] that the rate of intermolecular exchange of acac ligands between $(CH_3)ClSn(acac)_2$ and Hacac in acetylacetone solvent is 100-fold slower, $k_{25} = 0.03\ sec^{-1}$ (extrapolated; *cf.* Table II in ref 2a). More important, exchange of acetylacetonate ligands between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ affords a rate-controlling step which does not involve complete dissociation of a given bidentate ligand.[23]

We now look at the possible intramolecular pathways (c) and (d). For simplicity and for later reference we have defined in Figure 1 a permutational isomer of $RClSn(acac)_2$[24] and the possible five-coordinate intermediates derived from a one-bond-rupture process.

Table II. Permutational Isomers and Averaging Sets Derived from Rearrangements of the Cis-Λ(Δ)[abcd; m] Isomer of a $XYM(AA)_2$ Complex by Various Mechanisms

(a) Twist Mechanisms[a]

Twist axis	Trigonal-prismatic intermediate	Permutational isomer	Averaging set
$C_3 i$	TP1(TP1)	cis-Δ(Λ)[cdab; n]	A_7'
$C_3 i$	TP2d(TP21)	cis-Δ(Λ)[cdba; n]	A_6'
$C_3 i''$	TP3(TP3)	cis-Δ(Λ)[badc; m]	A_5'
$C_3 i'''$	TP4d(TP41)	cis-Δ(Λ)[dcab; n]	A_6'

(b) Bond Rupture–TBP Intermediates[b]

Bond broken	Intermediate	Permutational isomer	Averaging set
		TBP-Axial	
a	1d(1l)	cis-Δ(Λ)[dcba; n]	A_4'
b	1l(1d)	cis-Δ(Λ)[dcba; n]	A_4'
c	3(3)	cis-Δ(Λ)[abdc; m]	A_3'
d	2(2)	cis-Δ(Λ)[bacd; m]	A_2'
		TBP-Equatorial	
a	5d(5l)	cis-Λ(Δ)[bacd; m]	A_2
b	4d(4l)	cis-Λ(Δ)[abdc; m]	A_3
c	5d(5l)	cis-Λ(Δ)[bacd; m]	A_2
d	4d(4l)	cis-Λ(Δ)[abdc; m]	A_3

(c) Bond Rupture–SP Primary Process[b,c]

Bond broken	SP-axial[d] intermediate	Permutational isomers	Averaging sets
a	6d(6l)	cis-Λ(Δ)[abcd; m]	A_1
		cis-Δ(Λ)[dcab, n]	A_6'
		cis-Λ(Δ)[bacd; m]	A_2
		cis-Δ(Λ)[cdab; n]	A_7'
b	6l(6d)	cis-Λ(Δ)[abcd; m]	A_1
		cis-Δ(Λ)[cdba; n]	A_6'
		cis-Λ(Δ)[abdc; m]	A_3
		cis-Δ(Λ)[cdab; n]	A_7'
c	6d(6l)	cis-Λ(Δ)[bacd; m]	A_2
		cis-Δ(Λ)[cdab; n]	A_7'
		cis-Λ(Δ)[abcd; m]	A_1
		cis-Δ(Λ)[dcab; n]	A_6'
d	6l(6d)	cis-Λ(Δ)[abdc; m]	A_3
		cis-Δ(Λ)[cdab; n]	A_7'
		cis-Λ(Δ)[abcd; m]	A_1
		cis-Δ(Λ)[cdba; n]	A_6'

[a] For specification of intermediates and illustration of the mechanism, see Figure 2. [b] For bond labeling and specification of intermediates, see Figure 1. [c] Rearrangements *via* SP-axial intermediates formed by and decaying *via* a secondary process (see ref 15) yield the same averaging sets A_i (or A_i') as from the primary process. [d] SP-basal intermediates are kinetically equivalent to TBP-axial intermediates.

Momentary rupture of a metal-oxygen bond in $XYSn(acac)_2$ yields two chiral and two achiral TBP-axial intermediates, four chiral TBP-equatorial intermediates, and two chiral SP-axial intermediates. These are illustrated in Figure 1. The consequences of reattachment of the dangling ligand end to the central metal ion *via* the above intermediates are presented in Figure 2 and summarized in Table II. Reattachment of the dangling end to tin in TBP-axial intermediates leads to inversion of the molecular configuration but does not exchange ring protons and methyl groups between the appropriate sites according to constraint (i). TBP-equatorial transition states afford retention of the molecular configuration, contrary to constraint (ii), and lead to environmental averaging of only two of the four methyl group environments without exchange of ring protons (*cf.* Figure 2a). Rupture of the metal-oxygen bond a in the isomer cis-Λ (abcd; m) followed by attack of the dangling ligand end at the four basal positions in the SP-axial intermediates (formed and decaying through a primary process)[15] leads to rearrangements identical with those from rupture of any one of the remaining three M-O bonds. Reactions involving SP-axial transition states (Figure 2b) are improbable because, in theory, they

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[16] "Handbook of Chemistry and Physics," 51st ed, Chemical Rubber Co., Cleveland, Ohio, 1970-1971.

[17] R. W. Jones, Jr., and R. C. Fay, *Inorg. Chem.*, 12, 2599 (1973).

[18] J. M. Bull, M. J. Frazer, L. I. B. Haines, and J. Measures, Abstracts of Papers, Fall Meeting of the Chemical Society (London), Southampton, 1969, p A-14.

[19] Y. Kawasaki, *J. Inorg. Nucl. Chem.*, 29, 840 (1967).

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[21] J. W. Faller and A. Davison, *Inorg. Chem.*, 6, 182 (1967).

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[23] N. Serpone and R. Ishayek, *Inorg. Chem.*, 13, 52 (1974).

[24] The four nonequivalent sites in a complex such as $XYSn(acac)_2$ are labeled as follows: the site trans to the ligand Y is always b; the one trans to X is labeled c. Sites c and d are always connected with the same ring, a similar situation prevailing for sites a and b. Thus if R_1 is in site c, then R_2 is in site d, etc. Site m for the ring proton H_1 is the site cis to X; site n is cis to Y.

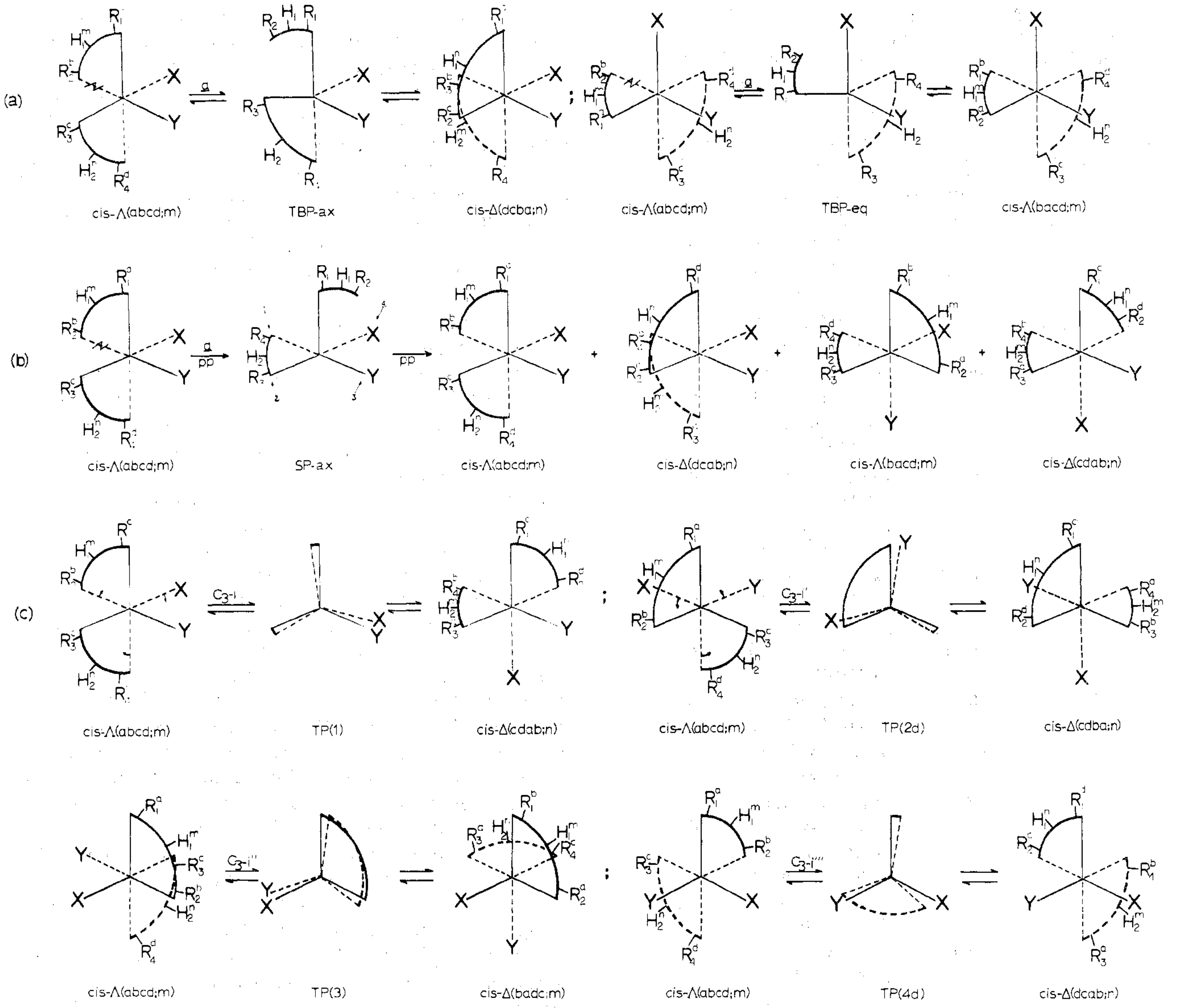

Figure 2. (a) Example of configurational rearrangements proceeding through TBP-axial and TBP-equatorial intermediates derived from rupture of the tin–oxygen bond a. (b) Example of rearrangements occurring *via* an SP-axial intermediate derived from rupture of the tin–oxygen bond a in the isomer cis-Λ (abcd; m) and decaying to products through a primary process (see text). (c) Configurational rearrangements for the isomer cis-Λ(abcd; m) proceeding through trigonal-prismatic intermediates obtained by rotations about the indicated imaginary threefold axes of the complex. Note rotations about the C_3i'' axis may also provide a path to yield the trans isomer (see text).

could provide a route for $\Lambda \rightleftarrows \Delta$ interconversion and for simultaneous exchange of ring protons and methyl groups according to constraints (i) and (ii)—that is, for the A_6' (or A_7') set—if the attack of the dangling end occurs at just one (or possibly two) basal position. Such a case would, of necessity, require implausible discrimination by the attacking ligand end between the four ligand atoms in the basal plane of the SP transition state. Although, *a priori*, attack is not expected to be equally probable at all four basal positions, especially since the atoms at these positions are so different (Cl, O, C), neither is it expected that exclusive preferential attack will occur at any one specific basal position since, for example, A_6' is obtained by attack at one of the two basal oxygens in breaking bonds a and b (*cf.* Table II and Figure 2b). SP intermediates with basal dangling ligands are kinetically equivalent to TBP-axial intermediates and thus are not considered as possible routes to the observed configurational changes. The TBP pathway is also analyzed (Table III) in terms of the eight transition states undergoing pseudorotation (pr) about each of the three metal–ligand equatorial bonds. As is evident from Table III, TBP-axial intermediates 1d and 1l undergo pseudorotation to yield TBP-equatorial intermediates which, upon reattachment of the dangling ligand end, may lead to $\Lambda \rightleftarrows \Delta$ interconversion accompanied by ring proton and methyl group exchange (A_6' and/or A_7'). Pseudorotation of TBP-equatorial intermediates leads to a mixture of TBP-axial and -equatorial intermediates. The configurational consequences from these upon reattachment of the ligand end onto the central metal ion is in some cases (*cf.* Table III) consistent with both constraints (i) and (ii). Configurational changes proceeding through pseudorotated TBP transition states, however, are not considered likely owing to the extensive ligand motion involved in such processes.

Another possible pathway for configurational rearrangements in $XYSn(acac)_2$ complexes, which however does not necessitate metal–ligand bond rupture, is twist motions about the four threefold axes of the octahedral framework. These twist motions, carried out for the cis-Λ (abcd;m) isomer, are illustrated in Figure 2c. Rotations about the imaginary threefold axes of the complex (Figure 1) are thought to occur by keeping one triangular face of the octahedron fixed

Table III. Intermediate and Permutational Isomer Distribution after Pseudorotation of TBP Intermediates Arising from a Bond Rupture in the Initial Isomer Cis-Λ(Δ)[abcd; m] of a $XYSn(acac)_2$ Complex

Bond broken	Intermediate	Intermediate after pseudo-rotation	Permutational isomer	Averaging set
		(a) TBP-Axial Intermediates[a]		
a	1d(1l)	5d(5l)	cis-Λ(Δ)[bacd; m]	A_2
			cis-Λ(Δ)[abcd; m]	A_1
		4l(4d)	cis-Δ(Λ)[dcba; n]	A_4'
			cis-Δ(Λ)[cdba; n]	A_6'
b	1l(1d)	4d(4l)	cis-Λ(Δ)[abdc; m]	A_3
			cis-Λ(Δ)[abcd; m]	A_1
		5l(5d)	cis-Δ(Λ)[dcba; n]	A_4'
			cis-Δ(Λ)[dcab; n]	A_6'
c	3(3)	5l(5d)	cis-Δ(Λ)[bacd; m]	A_2'
			cis-Δ(Λ)[abcd; m]	A_1'
		5d(5l)	cis-Λ(Δ)[badc; m]	A_5
			cis-Λ(Δ)[abdc; m]	A_3
d	2(2)	4l(4d)	cis-Δ(Λ)[abdc; m]	A_3'
			cis-Δ(Λ)[abcd; m]	A_1'
		4d(4l)	cis-Λ(Δ)[bacd; m]	A_2
			cis-Λ(Δ)[badc; m]	A_5
		(b) TBP-Equatorial Intermediates[a]		
a	5d(5l)	1d(1l)	cis-Λ(Δ)[abcd; m]	A_1
			cis-Δ(Λ)[dcba; n]	A_4'
		4l(4d)	cis-Δ(Λ)[dcab; n]	A_6'
			cis-Δ(Λ)[cdab; n]	A_7'
		3(3)	cis-Δ(Λ)[badc; m]	A_5'
			cis-Λ(Δ)[bacd; m]	A_2
b	4d(4l)	1l(1d)	cis-Λ(Δ)[abcd; m]	A_1
			cis-Δ(Λ)[dcba; n]	A_4'
		5l(5d)	cis-Λ(Δ)[cdba; n]	A_6
			cis-Λ(Δ)[cdab; n]	A_7
		2(2)	cis-Δ(Λ)[badc; m]	A_5'
			cis-Λ(Δ)[abdc; m]	A_3
c	5d(5l)	1d(1l)	cis-Λ(Δ)[bacd; m]	A_2
			cis-Δ(Λ)[cdba; n]	A_6'
		4l(4d)	cis-Δ(Λ)[dcab; n]	A_6'
			cis-Δ(Λ)[cdab; n]	A_7'
		3(3)	cis-Δ(Λ)[abdc; m]	A_3'
			cis-Λ(Δ)[abcd; m]	A_1
d	4d(4l)	1l(1d)	cis-Λ(Δ)[abdc; m]	A_3
			cis-Δ(Λ)[dcab; n]	A_6'
		5l(5d)	cis-Δ(Λ)[cdba; n]	A_6'
			cis-Δ(Λ)[cdab; n]	A_7'
		2(2)	cis-Δ(Λ)[bacd; m]	A_2'
			cis-Λ(Δ)[abcd; m]	A_1

[a] For description of intermediates and specification of bond broken, see Figure 1.

(solid lines in Figure 2c) while the opposite triangular face (dashed lines) is rotated clockwise by 60° about C_3i to produce the idealized trigonal-prismatic achiral transition state TP1. Further rotation through 60° in the same direction yields the isomer cis-Δ(cdab; n), and the averaging set A_7'. Rotations about C_3i' and C_3i''' give the same net configurational changes, averaging set A_6', consistent with both constraints (i) and (ii), although they produce different permutational isomers (*cf.* Table I). Twists about C_3i'' produce the achiral TP3 transition state which upon further rotation provides for Λ ⇄ Δ interconversion as well as exchange of methyl groups but does not time-average the ring proton environments (A_5') contrary to constraint (i). Rotations about C_3i'' also provide a path for cis–trans isomerization since the bidentate ligands do not span opposite triangular faces. Restricting the exchange process to a sole pathway, it would appear, on the basis of the above discussion, that configurational rearrangements in $RClSn(acac)_2$ ($R = CH_3, C_6H_5$) complexes occur *via* twist motions about the C_3i' and/or C_3i''' axes (nearly identical stereochemically). Note, however, that twists about C_3i (averaging set A_7') cannot be precluded[25] for reasons noted above. Neither can we unambiguously preclude linear combinations of averaging sets which accomplish -CH= and CH_3 exchange and Λ ⇄ Δ conversion were environmental averaging to proceed through a bond-rupture path (but see below).

In five reported studies on tris chelates, the mechanism has been inferred from direct dnmr evidence (coalescence behavior) owing to resolution of the nonequivalent nuclei.[26-31] Kinetic data were reported in three cases.[26-29] The dithiocarbamate complexes $Fe(R_1,R_2\text{-dtc})_2(tfd)$ [(R_1,R_2 = Me,Me or Et,Et and tfd = $(CF_3)_2S_2C_2$] undergo inversion of the molecular configuration by a twist process;[26] E_a = 8-10 kcal/mol and $\Delta S^\ddagger = -6$ to -7.5 eu. Additional support for the trigonal twist was afforded by the significant distortions toward an effective TP configuration in the structure of the crystalline Et,Et complex; however, such distortions are not a necessary condition for the operation of a twist process since distortions may arise solely from the short bite and the rigid nature of the chelate rings.[32] From ligand repulsion energy calculations,[32b] it appears that the trigonal twist is more likely for short-bite ligands. Tris(tropolonato) complexes of Al(III) and Co(III), $M(\alpha\text{-}C_3H_5T)_3$ and $M(\alpha\text{-}C_3H_7\text{-}T)_3$, also undergo Λ ⇄ Δ interconversion *via* a trigonal-twist mechanism which receives additional support primarily from the rigid planar geometry of the tropolonate ligand; inversion was characterized by E_a = 11-17 kcal/mol and $\Delta S^\ddagger = -16$ to +5 eu.[27] Optical inversion in $Fe(R_1,R_2\text{-dtc})_2(mnt)$ (where R_1,R_2 = Et,Et or Me,Ph and mnt = maleonitriledithiolene) also occurs through rotations about the $C_3(p)$ axis of the complexes: $\Delta H^\ddagger = 8.6$ kcal/mol and $\Delta S^\ddagger = -3.4$ eu for the Et,Et complex.[28] Clear evidence for an operative twist process is provided from intramolecular metal-centered inversion in $M(dtc)_3$ complexes. Inversion for several dithiocarbamates was characterized by $\Delta S^\ddagger = 1.5\text{-}4.1$ eu.[29] In other cases, mechanistic information has been obtained from the ratio of the rate of optical inversion to the rate of CF_3 group exchange in a complex such as $Al(hfac)_2(dibm)$ (hfac = anion of hexafluoroacetylacetone); the ratio is compatible both with twist motion about the $C_3(p)$ and C_3i''' axes and with a bond-rupture process involving SP-axial intermediates.[33]

Where direct evidence has been unobtainable in determinations of the specific pathway for configurational rearrangements, mechanisms have generally been inferred from the magnitudes of the frequency factors (or entropy of activa-

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(25) A linear combination of twisting opposite faces of the octahedron about the four threefold axes also cannot be excluded on the basis of the data reported earlier.[2a]

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tion) and/or the activation energy. Negative activation entropies (low frequency factors) have long been argued as support for a twist mechanism. A low frequency factor ($\log A = 4.10$) in the inversion of $[Co(biguanide)_3]^{3+}$ led Ray and Dutt[34] to propose that inversion occurs through a twist mechanism because of the long time interval needed to acquire enough energy in the appropriate complex vibrational modes necessary to produce the rather improbable twisting motion. Pressure-induced racemization studies[35,36] in the solid state on such complexes as $[Co(C_2O_4)_3]^{3-}$ and $[Ni(phen)_3]^{2+}$ indicate very low activation energies (2-2.4 kcal/mol) and very small frequency factors ($\log A =$ *ca.* -5); negative volumes of activation further support the contention that racemization proceeds *via* trigonal-prismatic intermediates. Evidence has also been presented that the uncatalyzed inversion of configuration in $[Co(C_2O_4)_3]^{3-}$ in solution ($\Delta S^{\ddagger} = +6$ eu) occurs by a twist mechanism, while acid-catalyzed inversion in $[Cr(C_2O_4)_3]^{3-}$ appears to proceed by a bond-rupture process ($\Delta S^{\ddagger} =$ *ca.* -15 eu).[15] More recently, cis → trans ($\Delta S^{\ddagger} = -5.5$ eu) and trans → cis isomerization ($\Delta S^{\ddagger} = -17$ eu) in $Cr(tfac)_3$ ($tfac = CF_3COCHCOCH_3^-$) in the gas phase was said to occur through twist motions on the basis of the magnitude of the activation parameters.[37] It thus appears tenuous to make claims about mechanisms on the basis of activation parameters alone, especially on the basis of activation entropies. Indeed, a literature survey reveals that $\Delta S^{\ddagger}$ values fall in the range -24 to $+20$ eu for about 40 compounds where rearrangements have been thought to occur *via* a bond-rupture process, whereas, in about 11 compounds, $\Delta S^{\ddagger}$ values fall within -23 to $+10$ eu for rearrangements thought to occur *via* a twist mechanism. Of significance is the value of -33 eu for the activation entropy in the intermolecular ligand exchange between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ where the mechanism has been established to be a tin-oxygen bond rupture process.[23] It appears then that, as noted earlier,[38] there may not yet be enough cases studied for which mechanisms have been definitely established to permit use of activation entropies, or frequency factors, as reliable indicators of mechanisms. Further, while twisting motions may in principle be expected to give rise to low frequency factors, these low frequency factors do not necessarily imply twisting processes. Entropies of activation (Table II of ref 2a) are inconsistent neither with a bond-breaking process nor with a twist mechanism.

Nonetheless, certain trends between data presented before[2a] and other data (see below) may lend some support for the twist mechanism proposed for rearrangements in $RClSn(acac)_2$ complexes. Environmental averaging in the corresponding phenylchlorogermanium(IV)- and phenylchlorosilicon(IV) acetylacetonates have also been investigated.[39] Activation energy and entropy in $CDCl_3$-CCl_4 solutions are respectively 12.8 ± 1.2 and 6.4 ± 1.0 kcal/mol and -13.3 ± 3.8 and -22.4 ± 4.8 eu for $(C_6H_5)ClGe(acac)_2$ and $(C_6H_5)ClSi(acac)_2$. Although bond strengths for Sn-O, Ge-O, and Si-O are not available in these and related complexes, the expected relative order[40] of bond strengths is Si-O > Ge-O > Sn-O. The activation energy in these phenylchlorometal complexes is expected to vary as the metal changes in the order Si > Ge > Sn if rearrangements occurred through TBP or SP intermediates. The observed order in E_a is Sn ~ Ge >> Si. Also, stereochemical lability is, at 25°, Si (4.2×10^3 sec^{-1}) >> Ge (9.4 sec^{-1}) > Sn (4.1 sec^{-1}).

More important is the comparison between values of activation parameters from the intermolecular exchange process in the diphenyltin-dimethyltin system[23] with those from the intramolecular process in diphenyltin acetylacetonate in the hope that a mechanism may be deduced for the latter process. If the same mechanism were operative in both processes, namely, a bond-rupture mechanism, it is difficult to understand reasons for a larger entropy of activation (11 eu larger) and the greater lability (100-fold) in the environmental averaging of terminal methyl groups in the diphenyltin complex, especially since the species in solution in both studies are so related, unless of course different mechanisms are operative. It is suggested that intramolecular rearrangements in $(C_6H_5)_2Sn(acac)_2$ also proceed through TP transition states; for every 100 twists ($k_{25} = 369\ \text{sec}^{-1}$)[2a] a tin-oxygen bond ruptures ($k_{25} = 3.8\ \text{sec}^{-1}$ [23]). Further, the free energy surface for the intramolecular pathway in this complex is of lower energy ($\Delta G^{\ddagger}_{25} = 13.95 \pm 0.09$ kcal/mol[2a]) than that of the intermolecular path ($\Delta G^{\ddagger}_{25} = 16.65 \pm 0.09$ kcal/mol[23]).

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