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DYNAMIC STEREOCHEMISTRY OF *cis*-OCTAHEDRAL BIS(β-DIKETONATO) COMPLEXES

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Summary

The dynamic aspects of the stereoisomerizations of some bis(β-diketonato) complexes have been investigated with the aid of permutational analysis and topological representations. The analysis indicates that the lowest energy rearrangement mode (M_4) occurring in such complexes, and involving a reversal of the helicity of the structure, is permutationally equivalent to the "one-ring flip" mechanism of diaryl derivatives of the type Ar_2ZX, which are shown to be stereochemically correspondent to the bis-chelate molecules.

The activation energies associated with such rearrangements have been determined by variable temperature NMR studies. Only for bis(acetylacetonato)bis(triphenylphosphine)ruthenium(II) is the activation barrier high enough to allow resolution of the two enantiomers at ambient temperatures.

Introduction

In continuation of our studies on the static and dynamic stereochemistry of propeller-like molecules [1], we have recently investigated the stereochemical behaviour of some β-diketonate complexes of the elements of Group IVA and IVB and of transition metals. In this paper we will concentrate on investigation of the dynamic stereochemistry of some representative bis-chelate molecules with the aid of permutational analysis and topological representations.

This approach has enabled us to determine the lowest energy (threshold) rearrangement mode occurring in the stereoisomerizations of these complexes and to recognize systems which are stereochemically correspondent to these bis-chelate molecules.

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Static stereochemistry and permutational analysis

Of the two possible symmetry differentiable structures (*cis* and *trans*) which can be adopted by an octahedral complex when four of the six ligands are connected pairwise by a chemical bond (Fig. 1), several techniques such as dipole moment data [2a—2d], NMR spectroscopy [2e—2m] leave no doubt that bis-chelate derivatives of the Group IVA and IVB elements adopt a *cis* conformation in solution. This structure, whose molecular skeleton has C_2 point group symmetry, is therefore chiral, and can be regarded as a two-bladed molecular propeller [1c]. That is, the two cyclic moieties are twisted in the same direction in order to impart an helical [1c] motion to the structure.

In previous related studies, dealing with the analysis of chemical isomers and isomerizations in two-, three-, and four-bladed molecular propellers [1], we established the relevance of permutational analysis and group theory to the description of the stereochemical aspects of such systems. Furthermore, this approach led inter alia to the description of the concept of stereochemical correspondence, which implies that two systems, no matter how chemically disparate, can be analyzed in the same way provided they possess the same point group

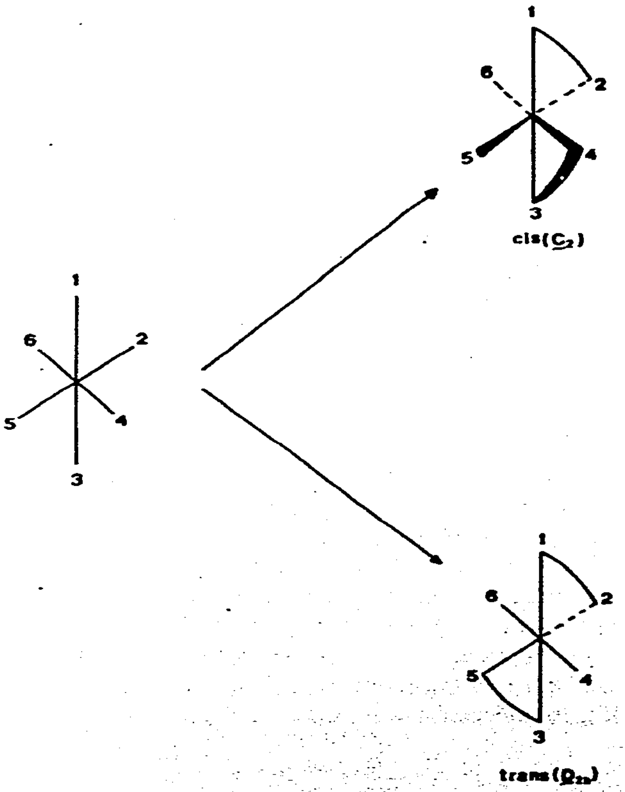
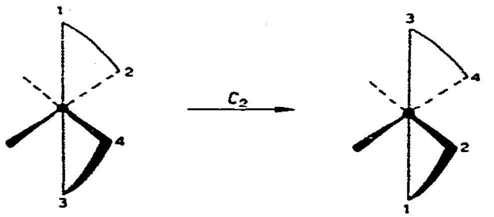


Fig. 1. The two symmetry differentiable isomers for an octahedral (β-diketonato) complex.

symmetry (or proper subgroup) and the same permutation group [1c,d]. In this context we have previously observed that diaryl derivatives of the type Ar_2ZX and spirocyclic phosphoranes, which can be both regarded as two-bladed molecular propellers, are stereochemically correspondent [1d]. That is, both systems allow the same number and kind of stereoisomers and the permutational consequences of the possible stereoisomerizations can be described by the same number and type of rearrangement modes.

As pointed out above, *cis*-(β-diketonate) complexes of the elements of Group IV can be viewed as two-bladed propeller molecules, and thus the permutational analysis of such systems should be analogous to that previously reported for diaryl derivatives.

Consider a *cis*-octahedral complex in the C_2 conformation in which the two monodentate ligands are identical. An isomerization can be represented as a permutation of ligands on these numbered sites. Thus, a C_2 rotation corresponds to the permutation (13)(24).



If we restrict our analysis to isomerizations which occur by nonbond-rupture twist mechanism [2m] and follow the procedure described in previous papers [1], the group of permutations associated with each "edge exchange" [3] and C_2 rotation can be show to be:

(1)(2)(3)(4) = E
(13)(24) = C_2
(12) = "one-edge exchange"
(34) = "one-edge exchange"
(1324) = "one-dege exchange" x C_2
(1423) = "one-edge exchange" x C_2
(12)(34) = "two-edge exchange"
(14)(23) = "two-edge exchange" x C_2

where E denotes the identity and the x stands for "followed by".

Considering also inversion of helicity (*) of the structure we need to consider also the following permutations:

(1)(2)(3)(4) *
(13)(24) *
(12) *
(34) *
(1324) *
(1423) *
(12)(34) *
(14)(23) *

where the asterix denotes the reversal of helicity. Thus the full permutational-inversion group is $S_2[S_2] \times C_2$ of order 16.

Since a C_2 rotation is a proper rotation of the molecule and will therefore lead to no new isomer, the number of differentiable isomers for the maximally labeled case (the two β-diketonate ring are different and lack a local C_2 axis) is eight (4 *dl* pairs). These eight isomers are schematically depicted in Fig. 2. Possible degeneracies in the system will reduce the number of differentiable stereoisomers as shown in Table 1.

Use of double co-sets allows us to partition the permutational group into six rearrangement modes [4—6], where a mode is a set of permutations which are either rotationally equivalent or symmetry equivalent [4]. These six modes * are termed M_0, M_1, M_2, M_3, M_4 and M_5. (See Table 2). It is readily seen that three of these modes (M_3, M_4 and M_5) include a reversal of the helicity of the structure whereas modes M_0, M_1 and M_2 do not.

We note at this point that for diaryl derivatives of the type Ar_2ZX and spirocyclic phosphoranes also, in the maximally labeled case eight isomers (4 *dl* pairs) are possible and six rearrangement modes describe the permutational isomeriza-

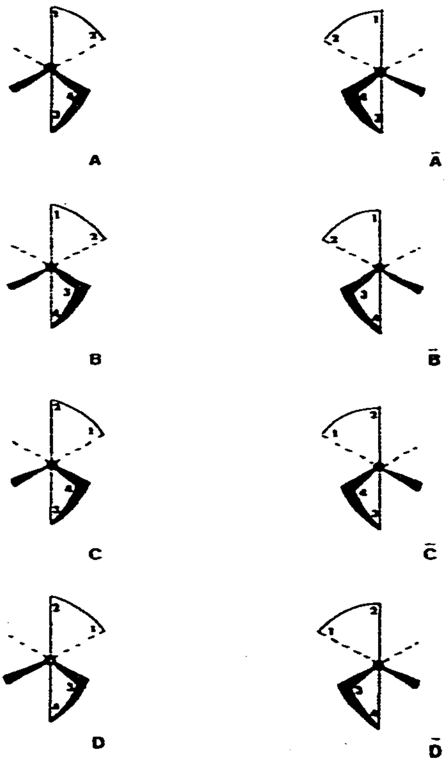


Fig. 2. The eight stereoisomers of a *cis*-(β-diketonato) complex of the type $X_2M(chel)_2$. Barred letters denote enantiomeric relationship.

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* These six modes correspond to the "averaging sets" described by Bickley and Serpone [2m] for bis-chelates of the type $XYM(chel)_2$ as follows: $M_0 \rightarrow A_1$; $M_1 \rightarrow A_6$; $M_2 \rightarrow A_7$; $M_3 \rightarrow A'_1$; $M_4 \rightarrow A'_6$; $M_5 \rightarrow A'_7$.

TABLE 1

NUMBER OF ISOMER FOR SUBSTITUTED *cis*-OCTAHEDRAL BIS-CHELATE COMPLEXES OF THE TYPE $X_2M(CHEL)_2$

Number of identical chelate rings	Number of rings with C_2 axes		
	0	1	2
0	8	4	2
2	6	—	2

tions in these systems [1d]. A stereochemical correspondence between these bis-chelate molecules and other two-bladed propeller molecules is therefore established.

Isomerizations in Ar_2ZX molecules have been described more specifically in terms of ring-flips [1d,g] which include a net reversal of the helicity of the structure, and in terms of rearrangements which do not. Previous works have shown that in Ar_2ZX systems only stereoisomerizations which lead to an helicity change need to be considered as feasible rearrangement pathways, and within these pathways the one-ring flip is the threshold mechanism [1d,g]. Inspection of the permutational consequences associated with each mode for the bis-chelate systems reveals that a correspondence can be established among these modes and the ring flip pathways in Ar_2ZX. Thus mode M_4 correspond to the one-ring flip, mode M_5 to the two-ring flip and mode M_3 to the zero-ring flip.

The principle of stereochemical correspondence tells us nothing about mechanism and energetics. That is evidenced by the fact that the threshold mechanism for the stereoisomerization of Ar_2ZX molecules and spirocyclic phosphoranes are mode non-equivalent [1d]. Therefore, in order to ascertain the threshold rearrangement mode occurring in such bis-chelate molecules we turned to experiments, focusing our attention on the dynamic NMR behaviour of some selected substrates.

The threshold mechanism in bis-chelate complexes

Our first study of the dynamics of the stereoisomerization processes in such complexes involved dichloro bis(acetylacetonato)tin (I) and dichloro bis(dipivaloylmethanato)tin (II). In these compounds the two chelate rings within each molecule are identical and possess a local C_2 axis and therefore only two

TABLE 2

REARRANGEMENT MODES FOR *cis*-OCTAHEDRAL BIS-CHELATE COMPLEXES OF THE TYPE $X_2M(Chel)_2$

M_0	M_1	M_2	M_3	M_4	M_5
(1)(2)(3)(4)	(12)	(12)(34)	(1)(2)(3)(4) *	(12) *	(12)(34) *
(13)(24)	(34)	(14)(23)	(13)(24) *	(34) *	(14)(23) *
	(1324)			(1324) *	
	(1423)			(1423) *	

enantiomeric forms are possible (Table 1). The two enantiomers differ in helicity, and when their interconversion is kinetically restricted on the NMR time scale the two pairs of methyl groups in I (or tert-butyl groups in II) reside in diastereotopic environments and so the NMR spectrum should show two separate signals of equal intensity in the methyl region. The ^{1}H-NMR spectra at ambient temperatures do show indeed in the methyl region two signals at $\delta(CDCl_3)$ 2.11 and 2.20 ppm for I, and two signals for the tert-butyl groups at $\delta(CDCl_3)$ 1.12 and 1.25 ppm (TMS) for II (1.10 and 1.20 ppm in chlorobenzene). Increasing the temperature causes these signals to broaden and finally coalesce to a single peak, indicating that rapid enantiomerization is occurring on the NMR time scale at these temperatures. From the knowledge of the chemical shift separation of the peaks and the coalescence temperature, by employing the Gutowsky-Holm [7] approximation in conjunction with the Eyring equation the free energy of activation for the enantiomerization processes in I and II, were calculated. The values are as follows: for compound I $\Delta G^{\neq}_{81}$ 19.1 kcal/mol, in close agreement with values previously reported in the literature [2k]; for compound II $\Delta G^{\neq}_{67}$ 18.26 kcal/mol (in chloroform) and $\Delta G^{\neq}_{67}$ 18.1 kcal/mol (in chlorobenzene). These values indicate that the enantiomerization process in these tin complexes is occurring at a rate which precludes resolution into optical andipodes except at very low temperatures (T — 60° C). Secondly, a comparison of $\Delta G^{\neq}$ data obtained for I and II reveals that increasing the basicity of the diketonate ligand leads to a more stereochemical rigid complex. Finally for compound II, the $\Delta G^{\neq}$ data clearly show how insensitive the stereoisomerization process is with respect to the nature of the solvent employed [2e].

In connection with the more general question concerning the threshold rearrangement mode in the stereoisomerizations of these complexes derivatives I and II due to their degeneracies, are unfortunately inconclusive. If we disregard mode M_3, the effect of which is not directly observable in the experiment performed because it exchanges only enantiotopic environments, and M_0 because it denotes the identity, the remaining four modes can in principle explain the experimental results. However, we recently provided compelling evidence that in such octahedral complexes also, stereoisomerizations are accompanied by reversal of helicity [8]: it follows, that of the six possible rearrangement modes only modes M_3, M_4 and M_5 need be considered as the lowest energy stereoisomerization pathways in such molecules. Mode M_3 is disregarded because its concomitant occurrence cannot be detected and so only models M_4 and M_5 are candidates for the threshold mechanism.

In order to distinguish between these two modes we studied the DNMR behaviour of dichloro-bis(benzoylacetonate)tin(III).

For III, which possesses two identical chelate rings but lacks a local C_2 axis, six isomers (3 *dl* pairs) are possible (Table 1): these forms are depicted in Fig. 3. It can be easily seen that of the six isomers, four have C_2 symmetry (forms $B\bar{B}$, $C\bar{C}$), while forms $A\bar{A}$ have C_1 symmetry. Therefore the two methyl groups within forms $B\bar{B}$ and $C\bar{C}$ are rotationally equivalent, whereas both methyl group of forms $A\bar{A}$ reside in diastereotopic environments. It follows that when the interconversion among these three diastereomers is kinetically restricted, a mixture of these isomers should in the methyl region of the NMR spectrum show four signals (in a achiral solvent) two of which must have equal intensity.

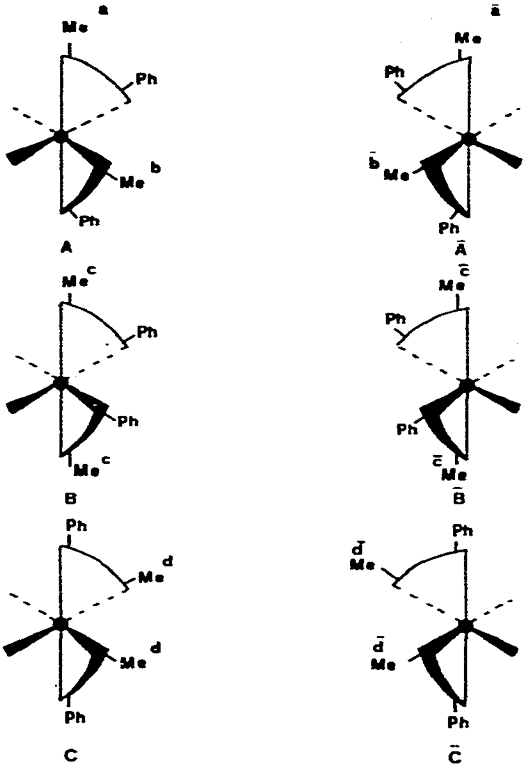

Fig. 3. The six stereoisomers of dichloro-bis(benzoylacetonato)tin (III). Barred letters denote enantiomeric relationship.

The topological analysis shown in Fig. 4 reveals that only mode M_4 can interconvert all three diastereomers, whereas mode M_5 enantiomerizes forms A and Ā and diastereomerizes forms BB̄ and CC̄. It follows that mode M_4 results in a isoenergetic averaging of the four methyl signals to a singlet; in contrast, mode M_5 has the net effect of coalescing the four signals to two singlets. The effect of mode M_3, although shown in Fig. 4, is not directly observable in an achiral medium because its effect is to exchange enantiotopic environments.

On the basis of this analysis we can now discuss the stereoisomerization phenomena observed for III when the temperature is raised.

At 38°C the 60-MHz ^{1}H NMR spectrum of III in chlorobenzene shows four signals in the methyl region (Fig. 5) the relative intensities of the signal are ca. 0.50, 0.518, 0.50 and 0.334, respectively. The two signals of equal intensity (numbered 1 and 3 in Fig. 5) must correspond to forms AA, while assignment of peaks 2 and 4 to each of the other two diastereomers is not obvious from these data alone. Thus, in chlorobenzene solution at ambient temperatures, the ^{1}H-NMR spectrum of III is consistent with a mixture of the three diastereomeric forms in the ratio A : B : C of 1.00 : 0.518 : 0.334, assuming that of the two diastereomeric forms B and C, isomer B is the more populated.

Upon warming the solution of III, the four peaks in the methyl region broaden

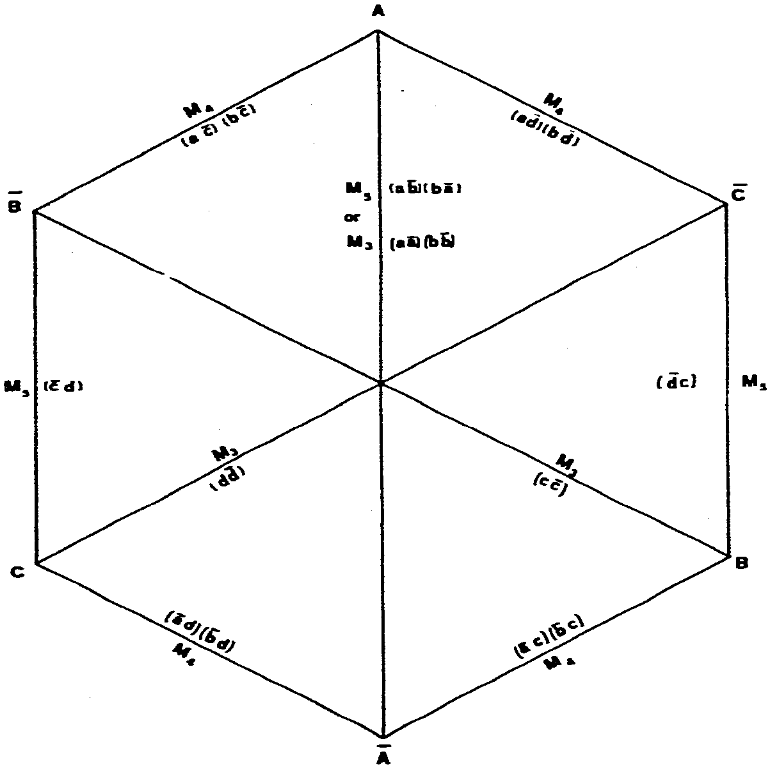

Fig. 4. Topological representation of the effect of the various rearrangement modes on the six stereoisomers of III. Permuted sites are parenthesized. See Fig. 3 for significance of letters.

and on further increase in the temperature the four signals coalesce to a singlet at 83°C (Fig. 5). This behaviour indicates that the diastereomerization has become a fast process on the NMR time scale.

The analysis above reveals that the only pathway which can explain such behaviour is mode M_4, which interconverts all diastereomers and averages the four signals to a singlet. NMR line-shapes based upon this rearrangement mode were calculated * in the temperature range 61—83°C. A satisfactory fit between the calculated and experimental spectra was obtained in the methyl region at five temperatures (see Fig. 5).

The rate data determined by line-shape analysis were used to calculate free energies of activation for the various exchange processes at 83°C. The results are shown schematically in Fig. 6. For the equilibrium $A\bar{A} \rightleftharpoons B\bar{B}$, ΔG°_{83} is 0.46 kcal/mol and for the conversion of $A\bar{A}$ into BB the calculations give $\Delta G^{\neq}_{83}$ 19.38 kcal/mol, and for the reverse process $B\bar{B} \rightarrow A\bar{A}$, $\Delta G^{\neq}_{83}$ 18.92 kcal/mol. For the equi-

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* The computer program used was adopted from one developed by Prof. Saunders (see ref. 9). We are grateful to Prof. Saunders for providing us with a copy of his program, and to Dr. Joseph D. Andose for the modification.

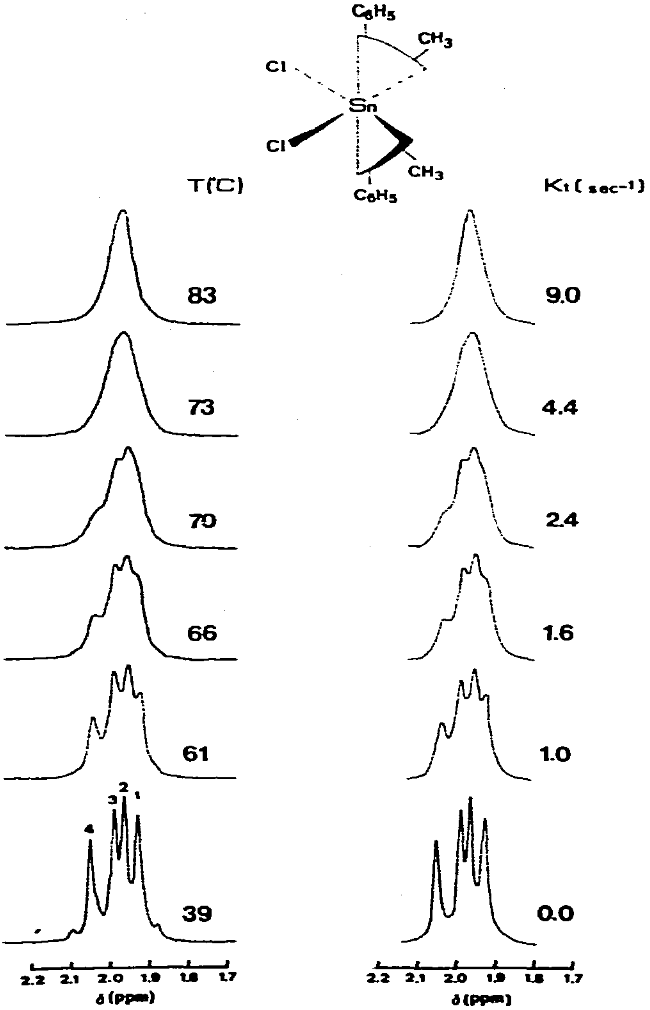


Fig. 5. Temperature-dependent 60-MHz ^{1}H NMR spectrum (methyl region) of III in chlorobenzene (left), and corresponding calculated spectra (right).

librium $A\bar{A} \rightleftharpoons C\bar{C}$ ΔG°_{83} is 0.77 kcal/mol, and for the conversion of $A\bar{A}$ to $C\bar{C}$ the calculations yielded $\Delta G^\ddagger_{83}$ 19.25 kcal/mol, and for the reverse process $C\bar{C} \rightarrow A\bar{A}$ $\Delta G^\ddagger_{83}$ 18.48 kcal/mol.

The ^{1}H NMR spectrum of III in $CDCl_3$ solution shows a similar behaviour. In this solvent the population ratio of the three diastereomers is A : B : C of 1.0 : 0.56 : 0.44. Computer line-shape analysis based upon M_4 was performed [9] as described above and a good match between experimental and calculated spectra was obtained at six temperatures (see Fig. 6). Free energy data obtained in this solvent are consistent with those calculated in chlorobenzene solution and reported above (see Fig. 6). Thus, the experimental evidence shows that for III

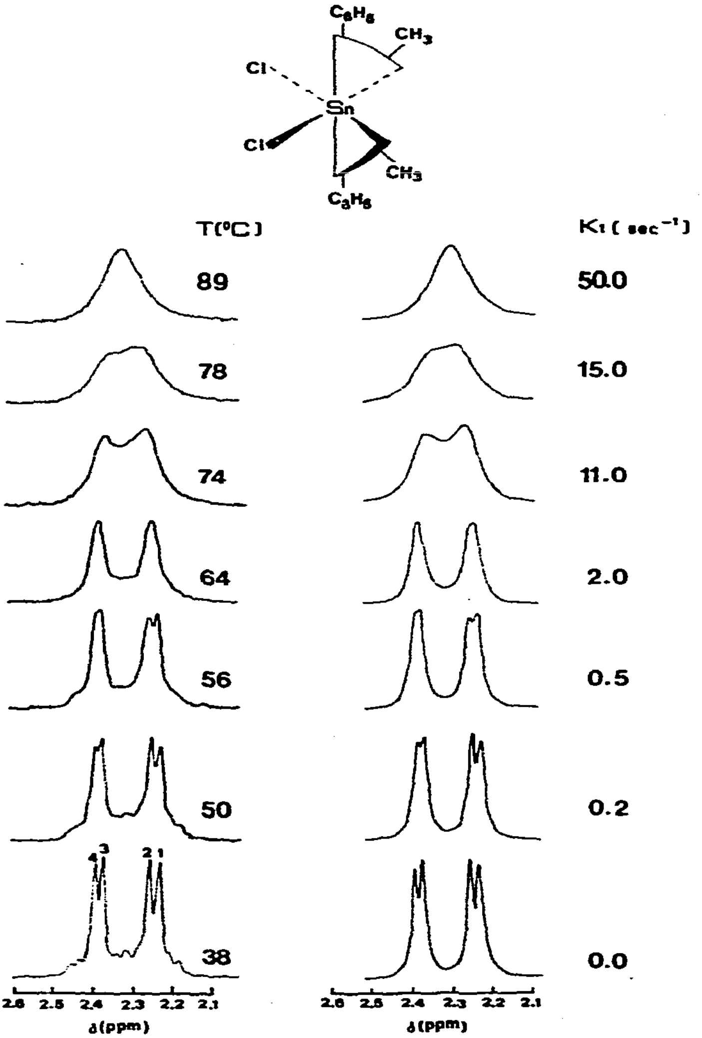
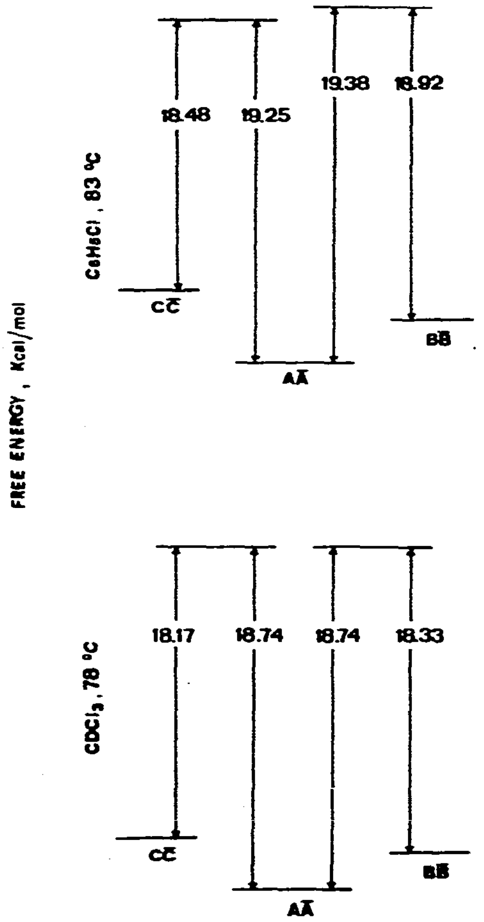


Fig. 6. Temperature-dependent 60-MHz ^{1}H NMR spectrum (methyl region) of III in $CDCl_3$ (left), and corresponding calculated spectra (right).

the stereoisomerization process of lowest energy, i.e., the threshold rearrangement mode is M_4.

It is noteworthy that for bis(acetylacetonato)bis(triphenylphosphine)-ruthenium(II) (IV) the two possible enantiomeric forms are not interconverted in the NMR time scale even at high temperatures. In fact, when the 1,2,4-trichlorobenzene NMR solution of IV is warmed the two diastereotopic acetylacetonato methyl signals do not coalesce or broaden even at 190°C (Fig. 8). This behaviour indicates that the process which results in the averaging of the two methyl group environments in IV involves such a high barrier that it cannot be detected on the NMR time scale even at 190°C. By employing the Gutowsky-



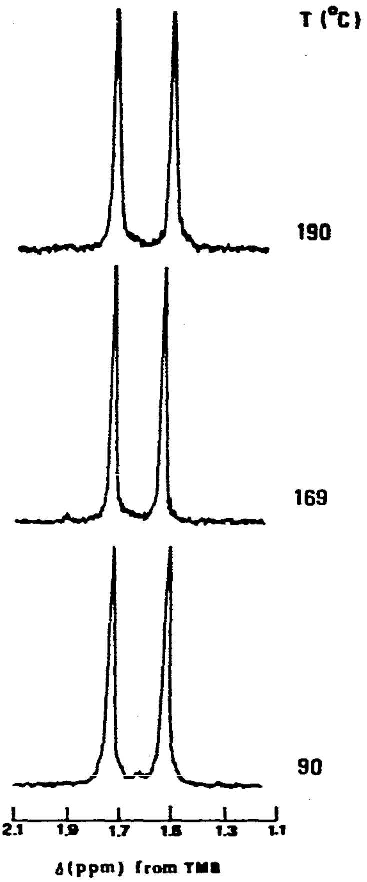


Fig. 7. A schematic representation of the energies of the stereoisomerizations of III.

Fig. 8. 60-MHz ^{1}H NMR spectra (methyl region) of IV in 1,2,4-trichlorobenzene as a function of temperature.

Holm approximation [7] in conjunction with the Eyring equation a lower limit of $\Delta G^{\neq}_{190} > 24.5$ kcal/mol for such barrier was thus calculated. Granted that for IV also the lowest energy mechanism occurs with reversal of helicity and leads to enantiomerization, a threshold barrier of such magnitude implies that IV can be obtained in optically active form at ambient temperatures.

Thus IV can be regarded as an example of a two-bladed propeller molecule in which chiroptical properties can easily be investigated. The theoretical interest of such studies in propeller-shaped molecules was recently pointed out [10].

Conclusions

As mentioned above, in diaryl derivatives of the type Ar_2ZX the one-ring flip was found to be the lowest energy rearrangement mode [1g] which permutationally corresponds to mode M_4 in bis-chelates. Thus in this example of stereochemically correspondent molecules, the same rearrangement mode is demonstrated to be the threshold pathway. It follows that under these circumstances in appropiately substituted bis-chelate derivatives, residual isomerism and diastereotopism phenomena [1e] are conceivable and the strategy for the design of suitably substituted derivatives capable of showing such phenomena is exactly the same of that described for diaryl derivatives of the type Ar_2ZX [1d,g]. Under these circumstances in a bis-chelate derivative in which the two cyclic moieties are constitutionally different and lack a C_2 axis, two residual enantiomers must be expected, even when interconversion of the possible diastereomers by mode M_4 is fast on the time scale of observation.

Experimental

The compounds used in this work were synthesized by published procedures: *Dichloro-bis(acetylacetonato)tin (I)* m.p. 207—209°C (lit. [11]: 203—204°C); *Dichloro-bis(dipivaloylmethanato)tin (II)* m.p. 134—135°C (lit. [12]: 132°C); *Dichloro-bis(benzoylacetonato)tin (III)* m.p. 223—224°C (lit. [2k]: 222—23°C); *Bis(acetylacetonato)bis(triphenylphosphine)ruthenium (IV)* m.p. 189—90°C (lit. [13]: 189—90°C).

NMR measurements

^{1}H NMR spectra were recorded on a Varian A60-D spectrometer equipped with variable-temperature accessories. Temperature measurements were based on the chemical-shift separation of the protons of an ethylene glycol sample and utilized the temperature-shift correlation of Van Geet [14]. Temperatures are believed to be accurate to ±2°C, although within a given series of measurements smaller differences (ca. 0.5°C) are considered significant. Saturation of the NMR signals was avoided. NMR samples were ca. 25% v/v solutions with ca. 5% v/v tetramethylsilane as internal reference (TMS). The line-shape analyses were performed [9] on a CDC-6600 computer.

In the methyl region, the 60-MHz ^{1}H NMR spectrum of III at 38°C consists of four lines: $\delta(CDCl_3)$ 2.22 (peak 1), 2.26 (2), 2.37 (3), and 2.40 (4); δ(chlorobenzene) 1.93 (1); 1.97 (2); 2.00 (3); 2.06 (4) ppm (TMS). An exchange matrix for use in the Saunders computer program [9] was constructed according to mode M_4 and the best fitting between calculated and experimental spectra in chlorobenzene solution (Fig. 5) was obtained employing a ratio of the two rate constants, k_1/k_2, of 1 : 0.834, where k_1 and k_2 refer to the processes (AA) → (BB) and $(\mathrm{A\bar{A}}) \rightarrow (\mathrm{C\bar{C}})$, respectively. Thus, the rate constants of the two reverse processes $(\mathrm{B\bar{B}}) \rightarrow (\mathrm{A\bar{A}})$ and $(\mathrm{C\bar{C}}) \rightarrow (\mathrm{A\bar{A}})$ will be given by $(p_{\mathrm{A\bar{A}}}/p_{\mathrm{B\bar{B}}})k_1$ and $(p_{\mathrm{A\bar{A}}}/p_{\mathrm{C\bar{C}}})k_2$, respectively, where $p_{\mathrm{A\bar{A}}}$, $p_{\mathrm{B\bar{B}}}$, and $p_{\mathrm{C\bar{C}}}$ are the populations of the three diastereomeric forms of III. The calculated rates at five temperatures (see Fig. 5) for the various processes involved were used to calculate $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for each process from a least-squares treatment of $\ln(k/T)$ vs. $1/T$ *, and the resulting parameters were employed to derive $\Delta G^{\neq}_{80}$ for each process. The values of $\Delta S^{\neq}$ calculated for all interconversions of III were positive, but since the

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* The transmission coefficient was assumed to be unity [15].

values obtained for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ from line-shape methods are sometimes questionable [15] and because the relevance of $\Delta S^{\neq}$ values to mechanistic aspects has been claimed to be tenuous in such complexes [2m], their figures are not reported here.

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