

## Modes of Rearrangements in *cis*-M(AB)<sub>2</sub>XY Six-Coordinate Bis Chelate Complexes. 2. An Experimental 2D NMR Study of Phenylchlorobis(benzoylacetato)tin

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**Abstract:** The 1D slow exchange resolution-enhanced spectra recorded at several temperatures of CDCl<sub>3</sub> solutions of (C<sub>6</sub>H<sub>5</sub>)ClSn(bzac)<sub>2</sub> (**1**) are discussed in terms of a mixture of four six-coordinate diastereomeric pairs of enantiomers all having *cis* configurations. Examination of slow exchange 2D NMR spectra reveals that three modes of rearrangements of the *cis*-M(AB)<sub>2</sub>XY system must be involved in order to explain the presence of at least 10 pairs of cross peaks. The topology of the matrix associated with this 2D spectrum reveals that only 8 of the 15 possible triplets of modes described in the preceding paper of this issue are possible. We examined several mechanistic possibilities to explain the NMR results. It appears that if the results have to be explained in terms of the Bailar twist, only three of the four a priori possible ones do proceed. Under these conditions, two of these twists, which could not be distinguished up to now experimentally, appear to be distinguishable by our 2D NMR experiments. It is further shown that for this system not only the three possible Ray-Dutt twists but also mechanisms involving square-pyramidal intermediates are excluded. Pathways involving single trigonal-bipyramidal intermediates are not allowed unless they are combined according to energetically unacceptable criteria. Finally, isomerizations through a short-lived trans intermediate are also incompatible with our results. The conclusion is therefore that although this system does not contain diastereotopic probes to observe inversion of chirality, 2D NMR results lead not only to the conclusion that the Bailar twist is the only reasonable mechanism possible for **1** but also to a subtle distinction that becomes possible between those Bailar twists which can and those which cannot proceed. Respective merits of 1D and 2D NMR are briefly discussed.

In the preceding paper of this issue,<sup>3</sup> we presented a theoretical study of the modes of rearrangements of six-coordinate bis chelate complexes of the type M(AB)<sub>2</sub>XY without diastereotopic probes. We made a comparative study of the type of stereochemical information that can be obtained from the analysis of residual diastereotopism in a fast exchange 1D (one-dimensional) NMR spectrum and from the examination of the number and position of cross peaks in a slow exchange 2D (two-dimensional) NMR spectrum. The analysis was performed in both possible assumptions that signal assignment is possible or not. In the latter situation, the main conclusions were that (1) information contained in the fast exchange 1D NMR spectrum is also contained in the slow exchange 2D spectrum, but the reverse is not true; (2) possible misinterpretations due to accidental isochronies in 1D spectra become very unlikely with 2D NMR; (3) the slow exchange 2D spectrum allows us to count the modes of rearrangements responsible for the observed dynamic stereochemical process, information which can only seldom be obtained from a 1D fast exchange NMR spectrum. This paper gives a detailed experimental study of the complex (C<sub>6</sub>H<sub>5</sub>)ClSn(bzac)<sub>2</sub> (bzac = benzoylacetate) based on the above theoretical study. A first account on the stereochemistry of this system was already published.<sup>4</sup> We present now a continuation of the study of this molecule based on new experimental results, among which 2D NMR data, which lead to detailed mechanistic considerations.

**Versatility in the Dynamic Stereochemistry of Six-Coordinate Cis Bis Chelate Complexes.** Besides the theoretical descriptions,<sup>3-5</sup>

considerable experimental research has been performed on bis chelates.<sup>6</sup> From the latter point of view complexes of the type Ti(β-diketonate)<sub>2</sub>X<sub>2</sub> or Ti(β-diketonate)<sub>2</sub>XY where X and Y are monodentate ligands (halogen, alkoxy, alkyl, and aryl) have been studied the most extensively.<sup>7-9</sup> All these complexes have exclusively *cis* geometry in solution, except Ti(acac)<sub>2</sub>I<sub>2</sub> (acac = acetylacetonate),<sup>7b,9</sup> which appears as a mixture of *cis* and *trans* isomers. A very recent elegant study of Fay and Lindmark<sup>9</sup> provided strong evidence that Ti(β-diketonate)<sub>2</sub>(OR)<sub>2</sub> systems rearrange most likely through a twist or mixture of twist mechanisms. This work confirmed the general trend toward these types of mechanisms observed before in a larger variety of titanium complexes studied by Serpone and Bickley.<sup>8</sup> In contrast M(β-diketonate)<sub>2</sub>X<sub>2</sub> or M(β-diketonate)<sub>2</sub>XY complexes (M = Si, Ge, and Sn) have been studied much less. In general, the main static stereochemistry in solution is the *cis* one<sup>8b,g,11-28</sup> (see, however,

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ref 11, 21, 23–25 for  $(\text{CH}_3)_2\text{Si}(\text{acac})_2$  and  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ . The rearrangements of the Si and Ge cis complexes have been proposed to be intramolecular with<sup>12</sup> or without<sup>11</sup> metal–oxygen bond rupture or even intermolecular.<sup>13</sup>

Bis(acetylacetonate)tin complexes exhibit an even larger variety of processes.<sup>4,5c,e,17–22,26</sup> *cis*- $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{acac})_2$  undergoes an intramolecular exchange of the axial and equatorial chelate moieties and an intermolecular ligand exchange involving dimeric species with  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ .<sup>20</sup> For the former, no mechanism can be proposed from a permutational analysis, but a twist mechanism was suggested from qualitative energetic considerations.<sup>5e</sup> The complexes  $(\text{C}_6\text{H}_5)\text{ClSn}(\text{acac})_2$  and  $(\text{CH}_3)\text{ClSn}(\text{acac})_2$  have undoubtedly *cis* geometries, but the presence of some additional signals in the NMR spectrum has been attributed to a small quantity of the *trans* isomer.<sup>21</sup> The NMR data<sup>21</sup> are compatible with twist mechanisms,<sup>5e,6,9,27</sup> but bond rupture alternatives are conceivable although considered unlikely. Inversion of chirality cannot be evidenced in these molecules. Intermolecular exchange between  $(\text{CH}_3)\text{ClSn}(\text{acac})_2$  and Hacac was also observed but is 100 times slower than intramolecular exchange.<sup>5e,26</sup> The  $\text{X}_2\text{Sn}(\text{acac})_2$  complexes (X = F, Cl, Br, and I) have *cis* structure in solution and exhibit intramolecular<sup>28</sup> nonrigidity in the order  $\text{F} > \text{I} > \text{Br} \geq \text{Cl}$ .<sup>12</sup> The rupture of the bond between tin and the oxygen *trans* to the halogen has been proposed as a possible mechanism from <sup>13</sup>C NMR and IR studies.<sup>22</sup> Slow intermolecular halogen exchange was also observed.<sup>12b</sup> The complex  $\text{Cl}_2\text{Sn}(\text{dibm})_2$  (dibm = diisobutylmethanate) contains diastereotopic probes to detect chirality inversion. It was shown<sup>8b</sup> that there is simultaneous exchange of terminal isopropyl groups and inversion of the chirality. The most likely mechanisms resulting here are the two Bailar twist mechanisms  $\text{C}_3(i')$  and  $\text{C}_3(i'')$ <sup>5e,6</sup> ((3) and (4) in Figure 5 of ref 9). Tin compounds of the type  $\text{M}(\text{AB})_2\text{X}_2$  were less studied. The complex  $\text{Cl}_2\text{Sn}(\text{bzac})_2$  appears in solution as an equilibrium mixture of three diastereomeric pairs of enantiomers having *cis* geometry.<sup>5c</sup> None of the two possible *trans* isomers were observed. In this compound the double axial–equatorial exchange of chelate bridgeheads can be excluded as unique rearrangement. No mechanistic discussion was provided. *cis*- $\text{Cl}_2\text{Sn}(\text{tibm})_2$  (tibm = 1,1,1-trifluoro-5-methyl-2,4-hexanedionate), although containing diastereotopic probes, did not provide a better insight into the permutational character<sup>8b</sup> of the rearrangement because of the complexity of NMR patterns. Only a few other  $\text{M}(\text{AB})_2\text{X}_2$  complexes, with other metals, were described.<sup>7c,8h,9,14a</sup>

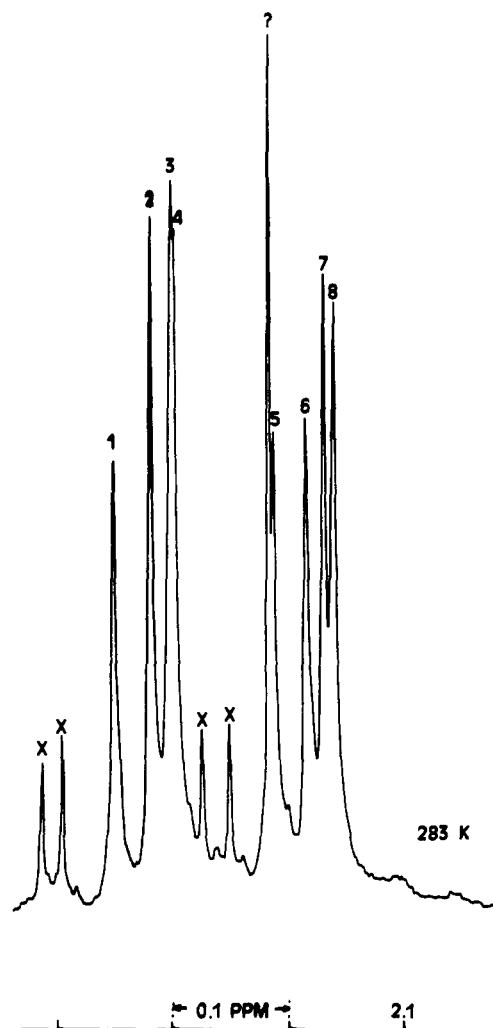


Figure 1. <sup>1</sup>H NMR 270-MHz spectrum of sample A of  $(\text{C}_6\text{H}_5)\text{ClSn}(\text{bzac})_2$  (**1**) at 283 K in  $\text{CDCl}_3$ , in the methyl region.

In contrast to  $\text{M}(\text{AA})_2\text{X}_2$ , and to a less extent,  $\text{M}(\text{AA})_2\text{XY}$  and  $\text{M}(\text{AB})_2\text{X}_2$  systems, those of the type  $\text{M}(\text{AB})_2\text{XY}$  have not been studied extensively, neither theoretically<sup>5d</sup> nor experimentally.<sup>4</sup> The only complex of this type studied up to now was  $(\text{C}_6\text{H}_5)\text{ClSn}(\text{bzac})_2$ <sup>4</sup> (hereafter **1**). We present here a continuation of the study of the stereochemistry of this compound.

Our first aim is the following: the <sup>1</sup>H NMR spectrum<sup>4</sup> at 90 MHz in the methyl region exhibits six signals at  $-26^\circ\text{C}$ , while eight are expected. Indeed, in the *cis* configuration, four  $\text{C}_1$  diastereomeric pairs of enantiomers, having each two diastereotopic methyl groups, are expected for **1**.<sup>3,4,5d</sup> Three interpretations are possible to explain the presence of only six signals: accidental isochrony, as proposed initially,<sup>4</sup> but also partial averaging due to some dynamic process with low-energy pathway or the absence of one of the four diastereomers.<sup>5d</sup> We present here additional data, making an unambiguous choice possible between these alternatives. On the other hand, no mechanistic discussion was given up to now for *cis*- $\text{M}(\text{AB})_2\text{XY}$ . It is our second aim to propose one here in a somewhat different spirit as previously,<sup>8–10</sup> based both on the low symmetry of this system and the new possibilities offered by 2D NMR spectroscopy. It was shown in the preceding paper of this issue<sup>3</sup> that the conjunction of both facts leads to more precise stereochemical information for systems as **1**.

## Results

In the particular case of compound **1**, we are concerned with the symbols A, B, X, and Y in  $\text{M}(\text{AB})_2\text{XY}$  have the following meaning: A = methyl and B = phenyl of the bidentate ligand; X = chlorine and Y = phenyl bound to tin. The only <sup>1</sup>H NMR probes useful to study the dynamic stereochemistry of **1** because

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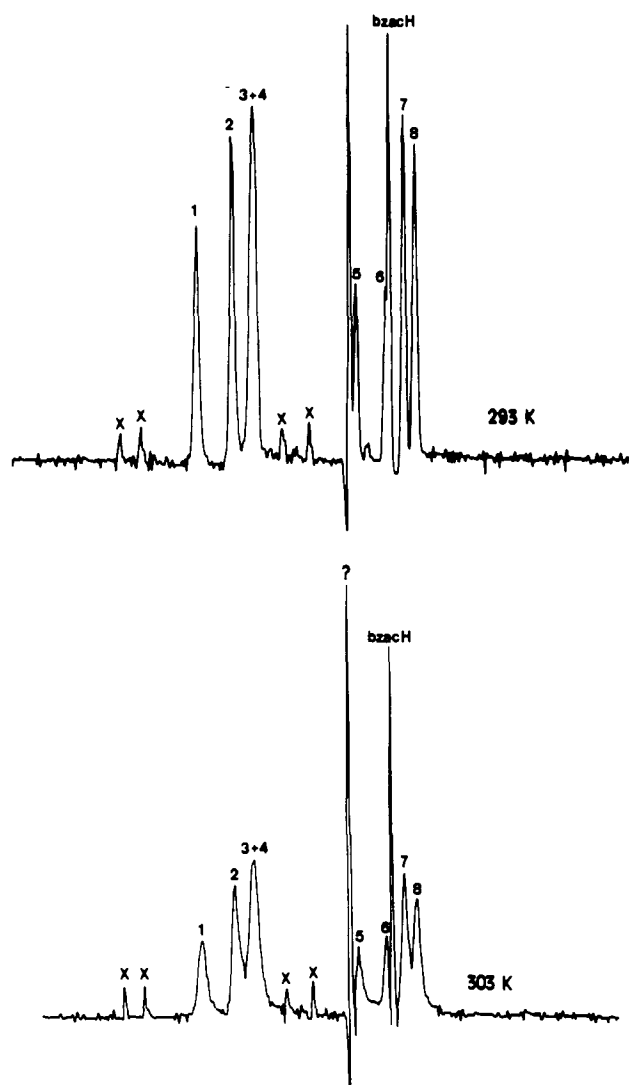


Figure 2.  $^1\text{H}$  NMR 270-MHz resolution-enhanced spectra of sample B of **1**, at 293 and 303 K in  $\text{CDCl}_3$ , in the methyl region.

giving rise to singlets are either the methyl groups and the CH protons of the bidentate ligand. The latter having given rise to more signal overlapping, we only used the former.

**1D Spectra.** We present selected 1D NMR spectra of two samples of impure **1**, indicated A and B, respectively. Since these spectra are quite clear and unambiguous, we did not attempt further purification (see Experimental Section for details).

Figure 1 gives the  $^1\text{H}$  NMR 270-MHz spectrum of sample A of **1** in  $\text{CDCl}_3$  at 283 K in the methyl region. Figure 2 gives the resolution-enhanced<sup>29,30</sup> spectrum (Lorentz–Gauss enhancement) of sample B of **1**, in  $\text{CDCl}_3$  at 293 and 303 K in the same methyl region. Figure 3 gives the methyl spectrum of sample B at 313 K. The eight singlet signals, labeled 1–8 can safely be attributed to compound **1**. It has indeed been shown previously that in resolution-enhanced spectra<sup>29,30a</sup> a strong reduction of intensity occurs for all the lines which undergo a broadening because of exchange phenomena.

Figure 2 shows clearly that this occurs simultaneously and exclusively for these eight lines 1–8 when raising the temperature from 293 to 303 K (signals 3 and 4 are accidentally isochronous at these temperatures but not at 283 K). These eight methyl

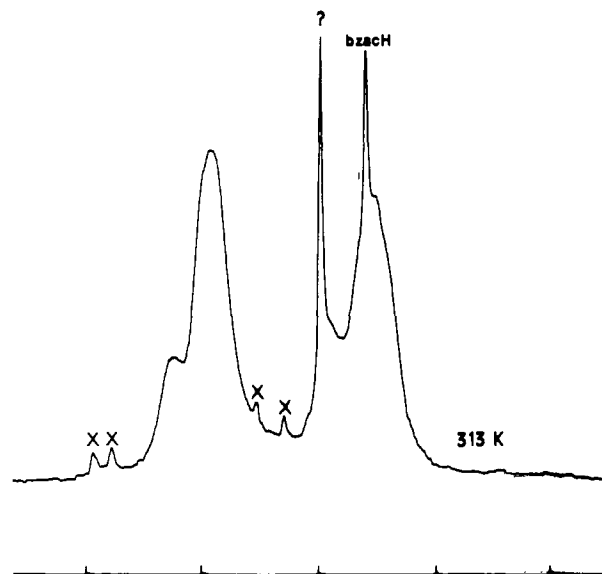


Figure 3.  $^1\text{H}$  NMR 270-MHz spectrum of sample B of **1**, at 313 K in  $\text{CDCl}_3$ , in the methyl region.

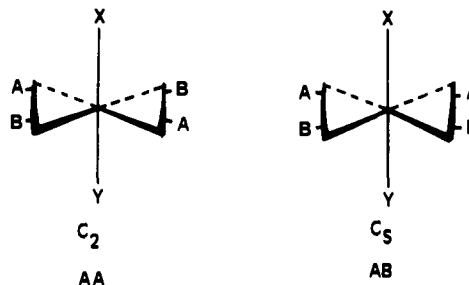


Figure 4. Two possible trans isomers for  $M(AB)_2XY$  systems.

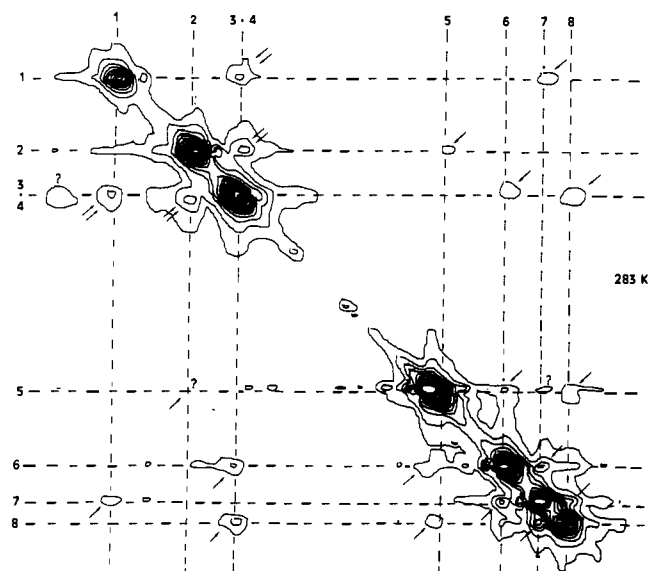
signals characterize unambiguously the four pairs of diastereomers of **1** in its cis geometry (see Figure 2 of ref 3) and therefore exclude the two alternatives pointed out in the introduction.

Although attempts of signal assignments were made for methyl signals of bis(acetylacetonate) complexes in  $\text{CDCl}_3$ ,<sup>21</sup> we consider it as inappropriate to extrapolate this type of argumentation to **1**. Figure 3 confirms that the eight lines do coalesce, indicating exchange processes between all four diastereomeric pairs of enantiomers. At 270 MHz the coalescence is not achieved at 333 K but previous NMR data at 100 MHz settle this point.<sup>4</sup> In all spectra four small X marked signals do appear, but with a larger intensity in sample A than in sample B. Their chemical shifts allow to assign them unambiguously to  $\text{Cl}_2\text{Sn}(\text{bzac})_2$ , a compound studied<sup>5c</sup> previously. Only the spectra of sample B reveal the presence of some free benzoylacetone; its signal is labeled bzacH.

In both samples A and B a unique signal indicated by a question mark is observed at 2.20 ppm. Our proposal is that this signal arises from  $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{bzac})_2$ . It is indeed well-known<sup>31</sup> that  $\text{R}_2\text{SnCl}_3$  compounds dismutate to  $\text{R}_2\text{SnCl}_2$  and  $\text{SnCl}_4$  and that these three products are difficult to separate. Since we indeed obtained  $\text{Cl}_2\text{Sn}(\text{bzac})_2$  in the synthesis of **1**, either from a small amount of  $\text{SnCl}_4$  present in the starting  $\text{C}_6\text{H}_5\text{SnCl}_3$  or generated from the latter during the reaction, it is reasonable to expect the formation of a comparable amount of  $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{bzac})_2$  from  $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$ . That  $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{bzac})_2$  would then give rise to a unique methyl signal instead of the four expected ones for rigid  $M(AB)_2X_2$  systems can readily be explained by the nonrigidity order  $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{acac})_2 \gg (\text{C}_6\text{H}_5)\text{ClSn}(\text{acac})_2 \gg \text{Cl}_2\text{Sn}(\text{acac})_2$  found for the acetylacetonate analogue and confirmed partially for  $(\text{C}_6\text{H}_5)\text{ClSn}(\text{bzac})_2 \gg \text{Cl}_2\text{Sn}(\text{bzac})_2$ .<sup>4,5c</sup>

(29) For technical details about this, see experimental section of ref 30a.  
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(31) For information about equilibria of the type  $2\text{R}_2\text{SnCl}_3 = \text{R}_2\text{SnCl}_2 + \text{SnCl}_4$ , see: (a) Grant, D.; Van Wazer, J. R. *J. Organomet. Chem.* **1965**, *4*, 229. (b) Neumann, W. P. "The Organic Chemistry of Tin"; Wiley: New York, 1970; p 55.



**Figure 5.** Contour display 2D spectrum of sample B of **1**, at 283 K in  $\text{CDCl}_3$ , in the methyl region; arrows indicate the nondiagonal contour signals—cross peaks—of importance for the stereochemical analysis. ? refers to ambiguous contours (see text).

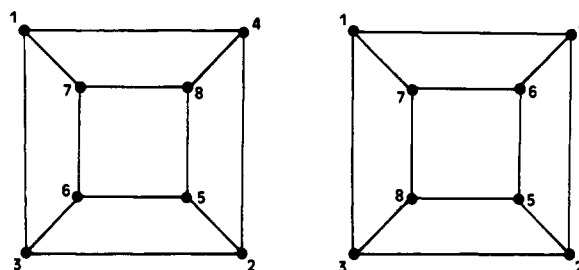
Alternatively, it might be tempting to attribute this signal to the presence of trans isomer(s). Indeed in previous studies of  $(\text{C}_6\text{H}_5)\text{ClSn}(\text{acac})_2$  and  $(\text{CH}_3)\text{ClSn}(\text{acac})_2$  by Serpone and Hersh<sup>21</sup> an additional singlet was also observed and attributed to the trans isomer. While plausible for these compounds<sup>21</sup> an attribution to the trans geometry is certainly cumbersome in our case.

Indeed, for  $\text{M}(\text{AB})_2\text{XY}$ , two trans isomers are conceivable, as shown in Figure 4, one having  $\text{C}_2$  symmetry, the other  $\text{C}_s$  symmetry. Together they give rise to two methyl signals, each of them giving rise to a unique signal. The observation of a unique signal can then only be explained in this context by (1) accidental isochrony which is quite unlikely over a temperature range of 110 °C; (2) absence of one of the isomers, i.e., a significant energy difference between them, also an unlikely interpretation in view of the similar energies of the cis isomers; (3) fast interconversion between both trans isomers, another unlikely explanation since conversion of cis isomers is slow under the same conditions. For all these reasons we do not assign this signal to the trans isomer. In this context it is interesting to outline that in the only system where all possible cis isomers (3) and trans isomers (2) are indeed observed, intramolecular exchanges are equally slow in both geometries ( $\text{Cl}_2\text{Ge}(\text{dhd})_2$ ,  $\text{dhd} = 2,2$ -dimethyl-3,5-hexanedionate).<sup>14a</sup>

These spectra of a priori undesirable mixtures contain important stereochemical information. Indeed, on the NMR time scale at which interconversion of the cis isomers of **1** is observed, exchanges between **1** and free benzoylacetone,  $\text{Cl}_2\text{Sn}(\text{bzac})_2$  and possibly  $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{bzac})_2$  are shown to be very slow, making intermolecular processes very unlikely. In the unlikely case that the unique "impurity" signal would be due to a trans species, and not to  $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{bzac})_2$ , the spectra would then indicate that cis-trans isomerization is slow compared to cis-cis isomerization.

**2D Slow Exchange NMR Spectroscopy.** In order to get stereochemical information from a slow exchange 2D spectrum, it is a necessary condition that this spectrum is recorded at a temperature just below the coalescence region. This is to ensure that sufficient magnetization transfer during the mixing period of the pulse sequence has occurred, since this transfer is responsible for the appearance of the nondiagonal contour signals, i.e., cross peaks, in the slow exchange 2D spectrum.<sup>32</sup> In the coalescence and fast exchange region these signals can no longer be obtained since they lose their own frequency label.<sup>32</sup> Figures 2 and 3 clearly show

**Chart I**



that the most appropriate temperature to satisfy these requirements is 293 K. Since these figures clearly show that only the signals arising from **1** do broaden, we are sure that the cross peaks of interest refer only to the stereochemical process in **1** and not to much slower exchanges, if any, between **1** and other structures.

Figure 5 gives the slow exchange 2D spectrum of sample B of **1** at 293 K in  $\text{CDCl}_3$  at 270 MHz, to which we have superimposed a lattice of rows and columns associated with the signals of **1**. Therefore the signal contours of interest lie at the intersection of rows and columns. All those nondiagonal peaks which do not lie at row and column entries are considered as artifacts. We did not succeed in obtaining a 2D spectrum without artifacts, the one of Figure 5 having optimal artifact/cross peak compromise.

The diagonal elements at the intersection of rows and columns are the signal contours of the slow exchange 1D NMR spectrum. Note that the contour at entry 5/5 is a mixture of the "impurity" singlet at 2.20 ppm and the signal 5 of **1** (see Figure 2), the latter appearing slightly to high field. For this reason we draw the intersection of row and column 5 somewhat at a high field position from the contour maximum.

The cross peaks<sup>32</sup> of stereochemical interest are indicated with arrows and must appear pairwise at row and column entries  $ij$  and  $ji$ , i.e., symmetrically with respect to the main diagonal, since all isomerizations are reversible. However, since an isomerization and its reverse do not proceed with identical rate constants, because the isomers have slightly different energies the cross peaks at a given pair of entries  $ij/ji$  have not necessarily identical intensities. Thus, while a clear cross peak appears at the entry 25, there is no observable one at the entry 52; we attribute this to the low intensity of signal 5 (see Figure 2) making a magnetization transfer with smaller rate constant plausible. We obtained another 2D spectrum, not shown here, with a lower contour threshold, but also with more artifacts, revealing the presence, at entry 52 of the expected cross peak.

An analogous comment holds for the pair 56/65, which is of poor quality here but well-defined in other spectra. In contrast, the contour near to the entry 57 is considered as an artifact since it lies on the same row as the other artifacts lying slightly above row 5, and also since no clear counterpart at the entry 75 does appear, even in other spectra.

The contour 87, although small, is well-defined, while the 78 one appears only as a shoulder; it is worth noting in this context that signals 7 and 8 do strongly overlap. Taking these comments into account, we count 10 pairs of cross peaks. It should be stressed, however, that signals 3 and 4 are accidentally isochronous in the 2D spectrum. However, the number of cross peaks observed in rows (column) 5 and 7, where no accidental isochrony of cross peaks is possible, is three. Tables III and IV of ref 3 show that the number of cross peaks on any row (column) should be the same, namely the number of different modes. Therefore, the pairs of cross peaks  $1(3+4)/(3+4)1$  and  $2(3+4)/(3+4)2$  are superpositions of  $13/31$  and  $14/41$  on one hand,  $23/32$  and  $24/42$  on the other hand. In contrast, the cross peaks  $(3+4)6/6(3+4)$  and  $(3+4)8/8(3+4)$  cannot be superpositions but arise from either the pairs  $36/63$  and  $48/84$  or  $38/83$  and  $46/64$ . The graphs of these two possible exchange patterns, represented in Chart I, are both of type 3B (see Table IV of ref 3)

Attempts to interpret the pairs of cross peaks  $(3+4)6/6(3+4)$  and  $(3+4)8/8(3+4)$  in terms of superpositions of the pairs  $36/63$  and  $46/64$  on one hand, and of the pairs  $38/83$  and  $48/84$

(32) (a) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546. (b) Meier, B. H.; Ernst, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 6441.

on the other hand, forced us to introduce two additional pairs of cross peaks at the entries either 12/21 and 57/75 or 15/51 and 27/72. For the latter possibility absolutely no evidence is found experimentally; the former one, although unlikely, cannot be absolutely excluded. However, the resulting exchange pattern with 16 cross peaks, that should then be interpreted in terms of a combination of four modes, appears to be incompatible with any theoretically predicted pattern of such a combination of four modes.

The conclusion is therefore that this 2D spectrum is to be interpreted in terms of 12 pairs of cross peaks. The graphs of Chart I and Table IV of ref 3 show that a combination of three modes of type 3B is actually proceeding. Of course, these three modes proceed with rate constants of the same order of magnitude in the four diastereomers. This table shows that only 8 triplets of modes from the 15 theoretically possible are compatible with our experimental observations. The seven other triplets include the mode  $\bar{M}_{2n}$  and are rigorously excluded since none of them corresponds to a pattern of type 3B.

This conclusion shows furthermore that in the fast exchange region only one residual signal results, in agreement with the observations made by Finocchiaro et al. on a 100-MHz fast exchange spectrum. However, the presence at a same temperature of all the cross peaks leading to this unique residual signal indicates that the two broad signals observed in the coalescence region of this 100-MHz spectrum at 34 °C are not likely to be due to a possible intermediate residual diastereotopism.<sup>30a,b,32</sup> We believe that these two broad signals coalesce at a higher temperature because they have a larger frequency difference than those coalescing at lower temperature (see ref 30a for a more detailed discussion on this point). Further evidence for this explanation is given by approximate calculations of the free activation enthalpies leading to almost identical values at 26 and 44 °C. (16.6 and 16.8 kcal/mol, respectively).

### Mechanistic Discussion

**Analysis Strategy.** Our analysis is based on the following strategy. It appears from our results that all four *cis* diastereomeric pairs of enantiomers<sup>3</sup> of **1** are observed in equilibrium populations of the same order of magnitude and have therefore nearly identical energies. The chemical background hereof is that the distortion<sup>34</sup> induced by replacing the symmetric acetylacetonate by the dissymmetric benzoylacetonate is small, as appears clearly from the fact that the coalescence occurs in the same temperature range for (C<sub>6</sub>H<sub>5</sub>)ClSn(acac)<sub>2</sub><sup>21</sup> as for (C<sub>6</sub>H<sub>5</sub>)ClSn(bzac)<sub>2</sub>,<sup>4</sup> at comparable static magnetic fields. In such a situation the hypothesis of noninterdigitating modes holds:<sup>30a,b,33a-c</sup> if a mode proceeds with a given rate constant in a given isomer, it does also proceed with a rate constant of the same order of magnitude in all the other isomers. Practically, this means that line shape modifications in a 1D spectrum, due to this mode applied to all isomers, are observed within a same coalescence region. For a slow exchange 2D spectrum this means that *all* the cross peaks arising from this mode, applied to *all* isomers are observed at a same temperature. Therefore, in the following mechanistic discussion we are allowed to examine to which set of modes a given mechanism does belong, independently of the isomer to which it is applied. Moreover, we look at these mechanisms in a somewhat different spirit as in previous work, since we have to interpret our results, not in terms of a single mode but rather of a triplet of modes.<sup>7,8</sup>

In the following we do not consider the associative mechanism, observed for (CH<sub>3</sub>)ClGe(acac)<sub>2</sub>,<sup>13</sup> since our spectra did not display

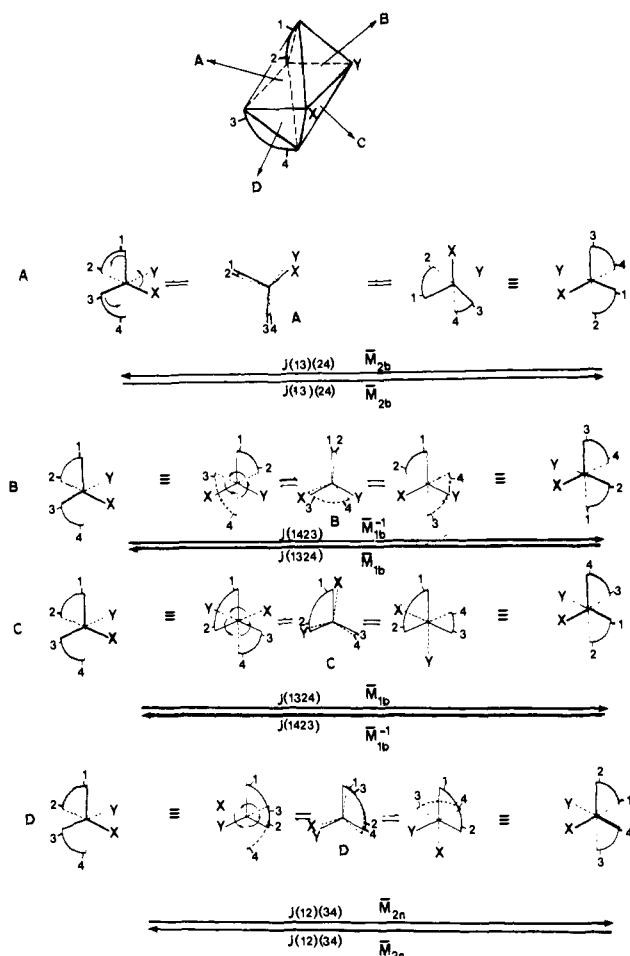


Figure 6. Four possible Bailar twists of *cis* bis chelate complexes M(AB)<sub>2</sub>XY.

any concentration effect. Neither do we discuss intermolecular ligand exchange since our spectra showed these to be unexistent or slow on the time scale at which **1** rearranges. It is also important for the discussion to remember that inversion of chirality cannot be observed here, i.e., that the modes  $M_k$  and  $\bar{M}_k$  are indistinguishable.<sup>3</sup>

**Bailar Twists.** Among the eight pathways of the Bailar twist<sup>6,27a</sup> that can be performed on an ideal octahedron<sup>35</sup> only four transform a *cis* bis chelate isomer to another *cis* one.<sup>35b-d</sup> These twists proceed about the four torsion axes (the imaginary C<sub>3</sub> axes<sup>6</sup> of the pseudo-octahedron) A, B, C, and D represented at the top of Figure 6. The stereochemical result of performing the corresponding twists A, B, C, and D is represented in Figure 6.

The permutation and mode symbolisms used are those of the preceding paper of this issue.<sup>3</sup> The twists A and D belong to the self-inverse modes  $\bar{M}_{2b}$  and  $\bar{M}_{2n}$ , respectively (see Table I of ref 3) while B and C do belong to the pair of non-self-inverse modes  $\bar{M}_{1b}$  +  $\bar{M}_{1b}^{-1}$ . This means that twist B is the reverse of twist C, and conversely, so that they must be considered together.<sup>3</sup> If Bailar twists do proceed in **1**, then only three among the four possible ones do actually occur, since our NMR results are compatible only with triplets of modes and not with quartets of modes. Since B and C must proceed together, only two triplets of twists are conceivable: A, B, and C and B, C, and D. The triplet A, B, and C has the permutational character of the triplet of modes  $\bar{M}_{1b}$  +  $\bar{M}_{1b}^{-1}$  +  $\bar{M}_{2b}$  while the triplet B, C, and D has that of  $\bar{M}_{1b}$  +  $\bar{M}_{1b}^{-1}$  +  $\bar{M}_{2n}$ .

Examination of Table IV of ref 3 reveals that the former is compatible with our NMR results (pattern 3B) while the latter

(33) (a) Finocchiaro, P.; Gust, D.; Mislou, K. *J. Am. Chem. Soc.* **1974**, *96*, 3205. (b) Finocchiaro, P.; Hounshell, W. D.; Mislou, K. *J. Am. Chem. Soc.* **1976**, *98*, 4952. (c) Mislou, K. *Acc. Chem. Res.* **1976**, *9*, 26 and references cited therein. (d) Brocas, J.; Gielen, M.; Willem, R. "The Permutational Approach to Dynamic Stereochemistry"; McGraw-Hill: New York, 1983; pp 399-400, p 503, and references cited therein.

(34) (a) Reference 33d, sections 4-3, 4-4-4, 9-8, 10-3, and 10-4. (b) Brocas, J.; Willem, R.; Fastenakel, D.; Buschen, J. *Bull. Soc. Chim. Belg.* **1975**, *84*, 483. (c) Brocas, J.; Willem, R.; Buschen, J.; Fastenakel, D. *Ibid.* **1979**, *88*, 415. (d) Nourse, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 2063.

(35) (a) Gielen, M.; Van Lautem, N. *Bull. Soc. Chim. Belg.* **1970**, *79*, 679. (b) Gielen, M. *Meded. Vl. Chem. Veren.* **1969**, *31*, 201. (c) Musher, J. I. *Inorg. Chem.* **1972**, *11*, 2335. (d) Musher, J. I.; Agosta, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 1320.

is excluded (pattern 3A). Therefore, if Bailar twists do indeed proceed, twist *D* is rigorously excluded while the three others must occur together. To our knowledge it is the first time that it is possible to conclude with such a degree of precision which twists do proceed. In previous works, the twists *A* and *D* could be distinguished from the set *B* + *C*, but no distinction between *A* and *D* was possible,<sup>7b,9</sup> since in the  $M(AA)_2X_2$  or  $M(AB)_2X_2$  systems studied they belong to the same mode  $\bar{M}_2$ . In these works<sup>7b,9</sup> it was demonstrated that there is chirality inversion, and, in some cases, mixing up of mode  $\bar{M}_1$  (twists *B* and *C*) with mode  $\bar{M}_2$  (twist *A* or *D* or both, see Table I of ref 3). While system **1** fails to demonstrate the inversion of chirality, it does allow one to distinguish twist *A* from *D*.

It is important to outline that this possibility is due to the conjunction of three circumstances, namely, (1) the fact that twist *A* proceeds not alone but in a triplet of twists; (2) the use of a  $M(AB)_2XY$  system; (3) the use of 2D slow exchange spectroscopy. Indeed, if point 1 were not satisfied, i.e., if twist *A* proceeded alone, it would be undistinguishable of *D* since as shown in Table III of ref 3 the modes  $\bar{M}_{2b}$  and  $\bar{M}_{2n}$  are not distinguishable in the absence of signal assignment, an experimental situation met here. Point 2 is demonstrated for  $M(AA)_2X_2$  and  $M(AB)_2X_2$  systems from the fact that twists *A* and *D* do belong to the same mode, as shown in Table I of ref 3. For  $M(AA)_2XY$  systems, the situation is a little bit more complicated. NMR exchange patterns of  $M(AA)_2XY$  systems have been studied by Bickley and Serpone.<sup>5a,b,e</sup> Table I of ref 5e shows that the single modes  $\bar{M}_{2n}$  ( $=A_5'$ ) and  $\bar{M}_{2b}$  ( $=A_7'$ ) are NMR distinguishable in a fast exchange 1D spectrum, even in the absence of signal assignment. This is in contrast to  $M(AB)_2XY$  systems. However, in the case where  $\bar{M}_{2n}$  or  $\bar{M}_{2b}$  is one component of a triplet of modes involving  $\bar{M}_{1b} + \bar{M}_{1b}^{-1}$ , the triplets  $\bar{M}_{1b} + \bar{M}_{1b}^{-1} + \bar{M}_{2b}$  and  $\bar{M}_{1b} + \bar{M}_{1b}^{-1} + \bar{M}_{2n}$  are NMR indistinguishable in a fast exchange 1D NMR spectrum, at least, in the absence of signal assignment. This is again in contrast to  $M(AB)_2XY$  systems. Point 3 is evident since only with 2D slow exchange spectroscopy is it possible to find the number of modes determining a process, since residual diastereotopism is not characteristic for the number of modes (see Table IV of ref 3). It is amazing to stress that in a  $M(AA)_2XY$  system,  $\bar{M}_{1b} + \bar{M}_{1b}^{-1} + \bar{M}_{2b}$  will give the same 2D spectral exchange pattern as  $\bar{M}_{1b} + \bar{M}_{1b}^{-1}$  (cross peaks at the same entries), but a different one for  $\bar{M}_{1b} + \bar{M}_{1b}^{-1} + \bar{M}_{2n}$ . This shows that in the field of *cis* bis chelates, the number of cross peaks is characteristic for the number of modes only in the case of  $M(AB)_2XY$  systems.

Our conclusion is therefore that if our results are to be explained in terms of Bailar twists, only three among the four possible ones do proceed (*A*, *B*, and *C*). Moreover, the fact that these three twists occur together allow us to distinguish two Bailar twists (*A* and *D*) which were not distinguished up to now.

We look now to determine whether there are mechanistic alternatives to the Bailar twists which are compatible with our NMR results.

**Ray-Dutt Twists.** In an idealized octahedron eight Ray-Dutt twists<sup>27b,35a</sup> can be conceived, belonging to the same mode as the Bailar twist.<sup>35a</sup> However, in the literature on tris chelate complexes it is a usual restriction to consider only those three possible Ray-Dutt twists in which two bidentate ligands move in their own plane, while the third remains immobile.<sup>6</sup> A fourth Ray-Dutt twist, converting a tris chelate complex into itself, but in which the gliding planes do not correspond to planes of the bidentate ligands is usually not considered, although it is conceivable.

For bis chelate complexes  $M(AB)_2XY$  we can consider *X* and *Y* together as a "pseudobidentate" ligand playing the role of the third bidentate ligand of tris chelate complexes.

If we adopt this point of view, the three usual Ray-Dutt twists have the same stereochemical character as the Bailar twists *B*, *C*, and *D* (see Figure 7), while the fourth one corresponds to the Bailar twist *A*.

If this usual restriction of the tris chelate literature<sup>6b,c</sup> is not taken into account, then the argumentation presented above for the Bailar twists applies equally well to Ray-Dutt twists. If on the contrary this usual restriction is adopted, the three remaining

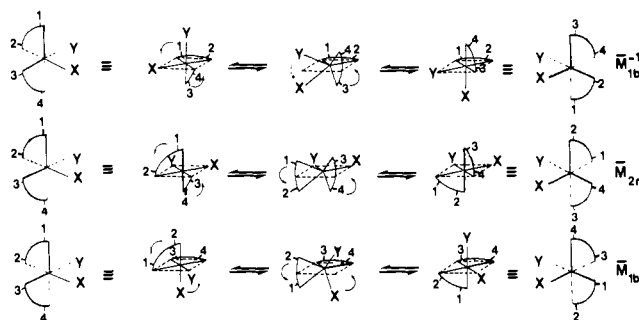


Figure 7. Three possible Ray-Dutt twists and their permutational character.

Ray-Dutt twists belong to the triplet of modes  $\bar{M}_{1b} + \bar{M}_{1b}^{-1} + \bar{M}_{2n}$  (see Figure 7), which has been shown to be in contradiction to our results. We have therefore to exclude the Ray-Dutt twists of Figure 7 as possible interpretation to our experimental results.

**Square-Pyramidal Intermediates.** We discuss the possibility that bond rupture mechanisms occur through a square-pyramidal axial intermediate<sup>5b,6,9</sup> (SP-AX), in a similar way as in Figure 8 of ref 9, taking properly into account microreversibility requirements. As previously we analyze only primary processes.<sup>9,36</sup> Taking into account the  $C_2$  symmetry of *cis*- $M(AA)_2X_2$  and the  $C_s$  symmetry of the corresponding SP-AX intermediate, Fay and Lindmark<sup>9</sup> showed that the four possible bond cleavages through the SP-AX intermediate are subdivided into the two symmetry equivalent a-cleavages (axial cleavage) and the two symmetry equivalent b-cleavages (equatorial cleavage). They pointed out that if only axial cleavage or equatorial cleavage does occur, the permutational character of the rearrangements is given by the combination of modes  $M_0 + \bar{M}_1$  (ref 3) ( $A_1 + A_5$  in their symbolism<sup>9</sup>). In contrast to this, they showed that if axial and equatorial cleavages, although symmetry unequivalent, do proceed with similar rate constants the permutational character of the rearrangements is  $M_0 + M_1 + \bar{M}_1 + \bar{M}_2$  ( $A_1 + A_2 + A_5 + A_6$  in their symbolism<sup>9</sup>). Their analysis takes into account the fact that if it is assumed that two symmetry unequivalent pathways *x* and *y* from the *cis* complex to SP-AX have identical or nearly identical rate constants, then the four possible sequences of pathways *cis* → SP-AX → *cis*, namely  $\{x, x^{-1}\}$ ,  $\{x, y^{-1}\}$ ,  $\{y, x^{-1}\}$ , and  $\{y, y^{-1}\}$  have similar rate constants.

In  $M(AA)_2XY$  and  $M(AB)_2XY$  systems all four possible bond cleavages are symmetry unequivalent. Therefore, it is conceivable either, that only one of the four bond cleavages does occur or that two, three or all four of them proceed with similar rate constants. More precisely, if *n* (*n* = 1, 2, 3, or 4) bond cleavages do occur with identical rate constants, then *n*<sup>2</sup> sequences of the type *cis* → SP-AX → *cis* must have identical rate constants. We have looked systematically at the permutational character of all these possible sequences. The results are presented in Table I. Herein we indicate which combinations of modes, with their respective weights, result from sequences involving cleavage of 1, 2, 3, or 4 bonds, as a function of the bond(s) cleaved. Note that since *n*<sup>2</sup> sequences are possible when *n* bonds are cleaved the sum of the weights in the combinations must be equal to *n*<sup>2</sup>. Note also that only 6 from the 16 modes are represented in the sequences. Finally, the trivial identity mode appears in all sequences with a weight equal to *n*, corresponding to the *n*{pathway-microreverse pathway} sequences having the identity as net permutational character. Table I shows that according to the bonds cleaved, 0, 4, 8, 16, or 20 pairs of cross peaks can be expected in the slow exchange 2D spectrum (see Tables III and IV of ref 3), but never 12. Since 12 pairs of cross peaks were observed, we have to exclude the possibility that **1** rearranges with bond cleavages through a SP-AX intermediate. It is the first time that this mechanism can be differentiated from twist mechanisms in such an unambiguous way on a permutational base alone. Indeed in a 1D NMR experiment these mechanisms give rise to theoretically or experi-

**Table I.** Combinations of Modes of *cis*-M(AB)<sub>2</sub>XY when 1, 2, 3, or 4 Bond Cleavages Are Possible in a Rearrangement of the Type *cis* → SP-AX → Cis<sup>a</sup>

no. of bond cleavages	bond cleaved				weight of the modes						
	1	2	3	4	$\bar{M}_{0n}$	$\bar{M}_{1x}$	$\bar{M}_{1y}$	$\bar{M}_{1b}$	$\bar{M}_{1b}^{-1}$	$\bar{M}_{2b}$	NPCP
1	x				1						0
		x			1						0
			x		1						0
				x	1						0
2	x	x			2	2					4
	x		x		2					2	4
	x			x	2			1	1		8
		x	x		2			1	1		8
			x	x	2		2			2	4
				x	2						4
3	x	x	x		3	2		1	1	2	16
	x	x		x	3	2		1	1	2	16
	x		x	x	3		2	1	1	2	16
		x	x	x	3		2	1	1	2	16
4	x	x	x	x	4	2	2	2	2	4	20

<sup>a</sup>The bonds are characterized with the label of the closest bridgehead (see Figure 1 of ref 3). 1 = axial cleavage on the bidentate trans to X; 2 = equatorial cleavage on the same bidentate; 3 = equatorial cleavage on the bidentate trans to Y; 4 = axial cleavage on the same bidentate. The bonds cleaved are indicated with crosses. The number in the mode entries are their weights in the resulting combination. NPCP = number of pairs of cross peaks; see ref 3, Table IV.

mentally indistinguishable exchange patterns. The SP-AX mechanism has been excluded up to now only on qualitative, albeit convincing, energetic grounds. It is only because 2D NMR allows us to count the number of combinations that we can distinguish these two types of mechanisms.

**Trigonal-Bipyramidal Intermediates.** It is easy to show, using topological methods previously described,<sup>37</sup> that all the reasonable trigonal-bipyramidal structures conceivable as intermediates for the rearrangements of *cis* bis chelate complexes are those represented in Figure 8. These intermediates were already discussed in the context of the dynamic stereochemistry of Ti(diketonate)<sub>2</sub>(OR)<sub>2</sub> complexes.<sup>9</sup> The symbols AX or EQ indicate that the dangling ligand occupies the axial or equatorial position, respectively, while X or Y indicates in addition, where necessary that the monodentate X or Y occupies an axial position. The mechanisms in Figure 8, presented in the literature<sup>5,6,9</sup> as possible pathways for this type of compounds, do all satisfy the requirement of least motion on the pathway from the *cis* bis chelate complex to the TBP intermediate and conversely. The numerous alternatives,<sup>46</sup> which do not satisfy this condition, are considered unlikely. For this reason, the intermediate in which both X and Y occupy axial positions is excluded, since it can be generated through least motions only from a not experimentally observed *trans* bis chelate. On the other hand, ring constraints exclude those intermediates in which rings span *trans* positions as in the six-coordinate complex itself. Together with these mechanisms, the mode to which they belong is indicated. Note that the two TBP AX mechanisms are the reverses of each other ( $\bar{M}_{0n}$ ). The reverses of the TBP EQ Y and TBP EQ X mechanisms represented in Figure 8 are those in which bonds 1 and 4 are cleaved, respectively, giving rise to the same permutational character ( $\bar{M}_{1x}$  and  $\bar{M}_{1y}$ , respectively). The first evident observation is that since our results must be explained in terms of triplets of modes, none of the six mechanisms of Figure 8, considered separately is compatible with our results. Therefore, only combinations of mechanisms can explain our results. The only ones explaining our results must contain  $\bar{M}_{0n}$ , together with  $\bar{M}_{1x}$  and/or  $\bar{M}_{1y}$  and/or  $\bar{M}_{1b}$  (see Figure 8). These are the first alternatives to the three twist mechanisms A, B, and C which are allowed by our results. We have no permutational evidence to exclude them, but we present here some arguments making these combinations energetically unacceptable. In order for the TBP mechanisms to have similar rates, the intermediates must have similar energies. This is certainly not the case for **1**, considering the orientation rules of substituents predicted theoretically some years ago<sup>38</sup> and dem-

onstrated experimentally for five-coordinate tin compounds.<sup>39</sup> Indeed, it is sure<sup>39</sup> that those intermediates with Y = Ph in apical position are much less stable than those having X = Cl in apical position. Therefore the necessary condition that  $\bar{M}_{1x}$  and  $\bar{M}_{1y}$  do proceed with similar rates is very unlikely to be realized.

A sequence six-coordinate bis chelate → nonrigid TBP → bis chelate is expressible as a combination of modes. Some of these sequences lead to a triplet of modes of the observed type 3B. We found, however, that this is actually the case of TBP AX intermediates rearranging only by simultaneous opening the bidentate ligand and reclosing the dangling ligand, a process which can hardly be more rapid than opening and closing the *same* bidentate ligand of the six-coordinate bis chelate.

Rapid rearrangements between different intermediates of Figure 8 through the most likely Berry mechanisms can be excluded. Indeed, the Berry mechanism can only be expected to be rapid on the measuring time scale when it converts structures having comparable energies. Therefore this situation is only plausible for rearrangements between TBP AX and TBP EQ X. Indeed, for any other pair of TBP's the structures are not characterized by similar energies or are not directly related by the Berry mechanism. However, in the case mentioned above, the permutational character resulting involves more than three modes.

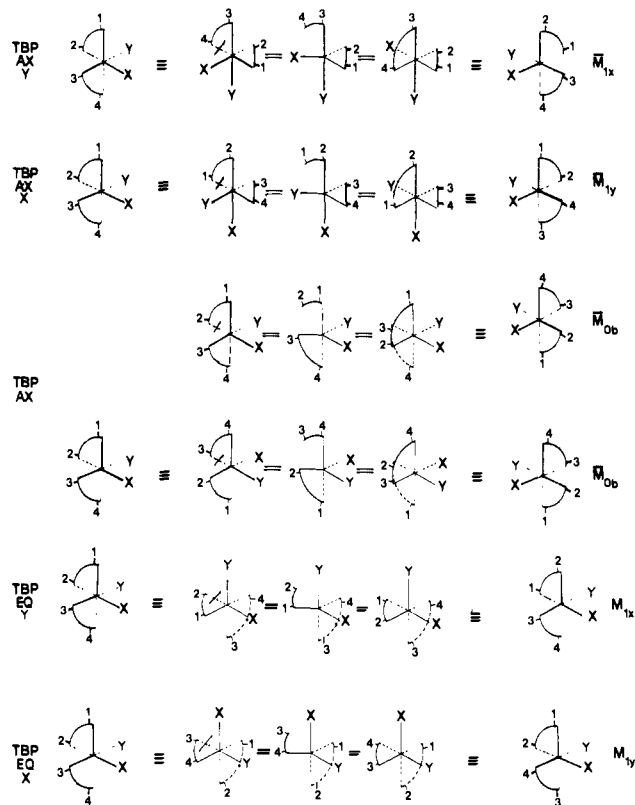
Our conclusion is therefore that unless there is an unlikely mixing of processes involving intermediates which are expected to have very different energies, or an unlikely nonrigid intermediate is admitted, rearrangements of **1** through trigonal-bipyramidal intermediates are excluded.

**Cis ⇌ Trans ⇌ Cis Isomerizations.** We did also envisage the possibility that if the *trans* isomers are not directly observed, the *cis* structures rearrange through a short-lived *trans* intermediate. We examined in a very systematic way all the possible rearrangements of the type  $\Delta$  *cis* ⇌ *trans* ⇌  $\Delta$  *cis* and  $\Lambda(\Delta)$  *cis* ⇌ *trans* ⇌  $\Lambda(\Delta)$  *cis* using a mathematical technique described previously.<sup>40,42,43</sup> Only single modes result, incompatible with

(37) (a) Reference 33d, pp 652–680. (b) Reference 35b. (c) Gielen, M.; Willem, R. *Phosphorus Sulfur* **1977**, *3*, 339. (d) Gielen, M.; Depasse-Delit, C.; Nasielski, J. *Bull. Soc. Chim. Belg.* **1969**, *78*, 357.

(38) (a) Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* **1963**, *2*, 613. (b) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047. (c) Reference 33d, section 13-2-2 and references cited therein.

(39) (a) Mügge, C.; Jurkschat, K.; Tzschach, A.; Zschunke, A. *J. Organomet. Chem.* **1979**, *164*, 135. (b) Korecz, L.; Saghier, A. A.; Burger, K.; Tzschach, A.; Jurkschat, K. *Inorg. Chim. Acta* **1982**, *58*, 243. (c) Jurkschat, K.; Mügge, C.; Tzschach, A.; Zschunke, A. *Z. Anorg. Allg. Chem.* **1980**, *463*, 123. (d) Tzschach, A.; Jurkschat, K.; Mügge, C. *Ibid.* **1982**, *492*, 135. (e) Tzschach, A.; Jurkschat, K.; Zschunke, A.; Mügge, C. *Z. Anorg. Allg. Chem.* **1982**, *488*, 45. (f) Jurkschat, K.; Mügge, C.; Tzschach, A.; Zschunke, A.; Engelhardt, G.; Lipmaa, E.; Mägi, M.; Larin, M. F.; Pestunovich, V. A.; Voronkov, M. G. *J. Organomet. Chem.* **1979**, *171*, 301. (g) Tzschach, A.; Jurkschat, K.; Zschunke, A.; Mügge, C. *J. Organomet. Chem.* **1980**, *193*, 299. (h) Zschunke, A.; Mügge, C.; Scheer, M.; Jurkschat, K.; Tzschach, A. *J. Crystallogr. Spectrosc. Res.* **1983**, *13*, 201.



**Figure 8.** Mechanisms involving several trigonal-bipyramidal intermediates and their permutational character. EQ and AX characterizes equatorial or axial positions of the dangling ligand while Y and X indicate that these monodentate ligands occupy an axial position, where necessary.

our results. We performed an analogous analysis, assuming a nonrigid trans intermediate.<sup>44</sup> According to the mode of rearrangement considered at the level of the trans intermediate it is possible to demonstrate that either the triplet  $\bar{M}_{0b} + \bar{M}_{2b} + \bar{M}_{2n}$ , or a combination of all the modes of the cis structure results, both possibilities being in contradistinction to our results. Therefore, although rearrangements involving a short-lived trans intermediate have been shown to be possible for cis six-coordinate transition metal hydrides,<sup>45</sup> this possibility must be rigorously excluded for compound **1**.

(40) Reference 33d, sections 11-5-3-4 and references cited therein.

(41) (a) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. (b) Reference 33d, Section 13-2-2 and references cited therein.

(42) The general approach consists in examining all the possible sequences of modes-microreverse modes of the type  $M^{CT}(y^{-1})M^{TC}(y)$  where  $M^{TC}(y)$  represents a rearrangement mode from cis to trans and  $M^{CT}(y^{-1})$  is the microreverse of  $M^{TC}(y)$ . For rearrangements proceeding with chirality change all the sequences of the type  $M^{CT}(y^{-1}\sigma)M^{TC}(y)$  must be studied, where  $\sigma$  represents an improper symmetry operation of the trans skeleton. Such a sequence of modes results in linear combinations of modes of rearrangements of the cis compound. It suffices then to compare these linear combinations to those which are allowed by the experimental NMR results. For more details about this procedure see reference 40 and 43.

(43) (a) Reference 33d sections 10-2, 12-6, and 13-2-3; (b) Klemperer, W. G. *J. Am. Chem. Soc.* **1973**, *95*, 2105. (c) Hutchings, M. G.; Johnson, J. B.; Klemperer, W. G.; Knight, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 7126. (d) Willem, R. *J. Chem. Soc., Dalton Trans.* **1979**, 33.

(44) The analysis is similar as in ref 42, except that the symmetry group of the trans intermediate must be extended to a group containing all the permutations describing the considered rearrangements of the intermediate. This is merely a kind of Longuet-Higgins group, i.e., a symmetry group of nonrigid molecule, from which the inversion about the mass center has been removed, see ref 33d, sections 8-1-5, 9-5-3, 11-5-3-4, and references cited therein.

(45) (a) Meakin, P.; Muetterties, E. L.; Tebbe, F. N.; Jesson, J. P. *J. Am. Chem. Soc.* **1971**, *93*, 4701. (b) For a further discussion about this problem, see ref 33d, section 13-2-1-2.

(46) These are in fact all the possible polytopal modes of rearrangements from the six-coordinate cis bis chelate to each of the proposed trigonal bipyramidal intermediate. For a definition of polytopal mode of rearrangements, see ref 33d, section 4-4-3 and Chapter 10.

## Conclusion

The permutational analysis of our 2D NMR results leads to the conclusion that only the twists of the type *A*, *B*, and *C* explain our results: square-pyramidal intermediates and cis-trans isomerizations are excluded. Trigonal-bipyramidal intermediates are only compatible with the experimental results under unrealistic energetic conditions. Twist mechanisms did also appear to be the most likely explanation to the results obtained by other researchers for  $M(AA)_2X_2$ ,  $M(AB)_2X_2$ , and  $M(AA)_2XY$  systems.

However, only seldom could up to now some precise information be obtained to distinguish between these twists.<sup>7p,9</sup> It has been the main merit of 2D NMR in this work to offer the new possibility of stating more precisely which Bailar twists do proceed and which do not. Although transition state *D* is the only one in which both bidentates are eclipsed, we have, however, no clear mechanistic explanation justifying why twist *D* is much slower than the three other twists.

As stated, this type of refined mechanistic analysis originates from the use of slow exchange 2D NMR spectroscopy. It would, however, be audacious to imagine that 2D NMR will replace completely the more traditional 1D NMR line shape analysis or its analysis of residual diastereotopism. For instance, the static facets of the stereochemistry of **1** were essentially elucidated in this work with 1D NMR spectra.

Moreover, for the moment 2D NMR does not allow one to determine activation parameters. In addition, the presence of artifacts or of cross peaks arising from two-step pathways when mixing times are too long<sup>32</sup> may lead to erroneous interpretations. Finally, 2D NMR does not solve systematically the often crucial problem of signal assignment. We believe that our work shows that 2D NMR must be seen as a complementary tool to 1D NMR in solving stereochemical problems.

## Experimental Section

**Synthesis of 1.** The synthesis of **1** was performed at ca. 40 °C by reacting the sodium salt of benzoylacetone with a commercial sample of trichlorophenyltin. Na (1.44 g, 62 mmol) was dissolved in 30 mL of methanol and then 10 g (62 mmol) of benzoylacetone was added with stirring during 1 h. The sodium salt of benzoylacetone formed almost immediately and was obtained as a white powder by removal of the solvent at reduced pressure. The white solid was then washed with ether in order to remove unreacted benzoylacetone. The sodium salt (8.6 g, 52 mmol) of benzoylacetone was added to a solution of  $C_6H_5SnCl_3$  (6 g, 20 mmol) in 150 mL of dry dichloromethane, and the mixture was allowed to reflux for 1 h. After cooling, the unreacted material was filtered off and the desired product, which was soluble in dichloromethane, was then precipitated with petroleum ether. Several recrystallizations from benzene/petroleum ether gave white crystals (mp 155–157 °C).

NMR characteristics, at 10 °C, in  $CDCl_3$ , with  $Me_4Si$  as internal standard, at 270 MHz are as follows: 2.349, 2.316, 2.299, 2.296, 2.210, 2.183, 2.168, 2.158 ppm, which all undergo preexchange broadening simultaneously, and then coalescence, at higher temperatures. Although elemental analyses were satisfactory,<sup>4</sup> we found smaller signals from  $Cl_2Sn(bzac)_2$ <sup>3c</sup> at 2.413, 2.395, 2.273, 2.250 ppm and an unidentified singlet at 2.214 ppm, probably due to  $Ph_2Sn(bzac)_2$  (see text) with fraction about 10%. We did not succeed in eliminating them by further purifications, crystallization or sublimation. One of the samples isolated contained a small amount of free benzoylacetone, with resonance at 2.180 ppm.<sup>11</sup>

**NMR Spectra.** High-resolution 270-MHz  $^1H$  NMR spectra were obtained on a Bruker HX 270 spectrometer, equipped with an Aspect 2000 computer and a B-VT 1000 Temperature Controller. The program for Lorentz-Gauss line transformation<sup>30</sup> delivered by Bruker was modified.<sup>30e</sup> For the 2D experiments, the EX SY program provided by Bruker was used. The mixing times<sup>32</sup> for these experiments ranged typically between 10 and 40 ms.

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**Registry No.** **1**, 71317-83-4; Na, 7440-23-5;  $C_6H_5SnCl_3$ , 1124-19-2; Hbzac, 93-91-4; Na(bzac), 17664-05-0.