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# Kinetic Analysis of the Configurational Rearrangements in and the Stereochemistry of Some Organotin(IV) β-Ketoenolate Complexes[1]

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The stereochemistry of $RClSn(acac)_2$ complexes ($R = C_6H_5$, $CH_3$; acac = $CH_3COCHCOCH_3^-$) has been investigated by dynamic nmr methods. These complexes are predominantly cis in chloroform-*d* and bromoform solutions with a small amount of the trans form present; when R is $C_6H_5$, the complex is ~95% cis and ~5% trans. Attempts to assess the structure of $(CH_3)_2Sn(acac)_2$ in solution by variable-temperature nmr techniques proved unsuccessful. Kinetics of configurational rearrangements which exchange acac ring protons between the two nonequivalent sites in the methylchloro- and phenylchlorotin(IV) acetylacetonate complexes, along with exchange of methyl groups in diphenyltin(IV) acetylacetonate, have been determined by nmr line broadening in dichloromethane, chloroform-*d*, and bromoform solutions. First-order rate constants at 25°, activation energies, and entropies of activation for the exchange process are respectively as follows: for $(C_6H_5)_2Sn(acac)_2$, 369 ± 58 ($CDCl_3$) and 281 ± 37 $sec^{-1}$ ($CH_2Cl_2$), 8.1 ± 0.3 ($CDCl_3$) and 7.4 ± 0.3 kcal/mol ($CH_2Cl_2$), −21.7 ± 1.4 ($CDCl_3$) and −24.5 ± 1.2 eu ($CH_2Cl_2$); for $(CH_3)ClSn(acac)_2$ in $CDCl_3$, 36 ± 3 $sec^{-1}$, 14.6 ± 1.1 kcal/mol, −4.3 ± 3.7 eu; for $(C_6H_5)ClSn(acac)_2$, 4.1 ± 0.9 ($CDCl_3$) and 2.9 ± 0.4 $sec^{-1}$ ($CHBr_3$), 12.7 ± 2.0 ($CDCl_3$) and 14.7 ± 0.8 kcal/mol ($CHBr_3$), and −15 ± 6 ($CDCl_3$), and −9.1 ± 2.4 eu ($CHBr_3$). Substitution of chloride in $Cl_2Sn(acac)_2$ by phenyl or methyl groups increases the lability in the order $Cl_2Sn < (C_6H_5)ClSn < (CH_3)ClSn < (C_6H_5)_2Sn$.

## Introduction

Notwithstanding the numerous studies reported on β-ketoenolate complexes of transition and posttransition metals,[2-10] relatively little attention has been paid to organometallic β-ketoenolate complexes of group IV (Si, Ge, Sn) elements with regard to stereochemistry and, to an even lesser extent, configurational rearrangements in the chelate rings. A detailed nmr and infrared study[11] on $X_2Sn(acac)_2$ (X = F, Cl, Br, or I; acac = anion of acetylacetone) complexes shows that these possess the cis structure in solution and in the solid state and that stereochemical nonrigidity follows the order $F > I > Br \geq Cl$. A single-crystal X-ray diffraction study[12] of $Cl_2Sn(acac)_2$ also reveals a cis stereochemistry in the solid state.

It is now well established that dialkyl- and diaryltin(IV) form six-coordinate,[13-18] monomeric[18-21] complexes with β-ketoenols,[14,15,18,20] 8-hydroxyquinoline,[13,16-19] and tropolone.[21] Failure to resolve enantiomers of $(C_6H_5)_2Sn(acac)_2$ over D-lactose by column chromatography,[18] nmr and infrared data,[15] and a small dipole moment[18] (3.78 D in $C_6H_6$ and 4.02 D in $C_6H_{12}$) led Nelson and Martin[18] and McGrady and Tobias[15] to deduce a trans stereochemistry in solution for this complex. Recent Mossbauer studies,[22] however, indicate that diphenyl bis(acetylacetonate) adopts the cis structure in the solid state. In agreement with this, polarization measurements,[23] variable-temperature nmr studies,[24] and dielectric relaxation studies[25] demonstrate that the diphenyltin complex exists in the cis form in solution, although the latter studies did not preclude a mixture of cis and trans isomers with the former predominating. Infrared,[15,26] Raman,[15,26,27] nmr,[15] Mossbauer,[22] and X-ray diffraction[28] studies on $(CH_3)_2Sn(acac)_2$ reveal that this complex adopts the trans structure in solution and in the solid state. Polarization[23] and dielectric loss[29] measurements suggest a cis structure.

Haloalkyltin(IV) acetylacetonates, $RXSn(acac)_2$ (R = alkyl; X = Cl, Br, or I) were assigned a trans stereochemistry by Kawasaki and coworkers[30] on the basis of nmr evidence, presumably from room-temperature spectra. A later report[31] on $RXSn(acac)_2$ complexes explains the temperature dependence of the nmr spectrum of $(CH_3)ClSn(acac)_2$ in terms of a cis $\rightleftarrows$ trans isomerization reaction. Nmr studies[32] on $(C_6H_5)XSn(acac)_2$ (X = Cl or Br) complexes in chloroform-*d* and bromoform revealed four methyl and two acetylacetonate ring proton (−CH=) nmr resonance signals; these were suggested as arising from a linear $C_6H_5$-Sn-X stereochemis-

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try and from a distorted acetylacetonate ring structure, for example, a structure containing "somewhat localized double bonds." Such a distorted structure has also been proposed[30,32-34] for $X_2Sn(acac)_2$ (X = Cl, Br, or I) chelates but has since been shown[11] to be incorrect. Furthermore, the coalescence phenomena of the -CH= proton resonances in the limited variable-temperature nmr data available on the phenylchlorotin(IV) acetylacetonate complex (in $CHCl_3$ and $CHBr_3$) were misinterpreted[32] in terms of hindered internal rotation of the phenyl group around the Sn-C bond ($E_a$ = *ca.* 3 kcal/mol).

This work reports our findings on the structure and on the stereochemical lability of $(C_6H_5)_2Sn(acac)_2$ and $RClSn(acac)_2$ (R = $CH_3$ or $C_6H_5$).

## Experimental Section

**Materials.** Diphenyltin dichloride, dimethyltin dichloride, phenyltin trichloride, and methyltin trichloride were purchased from Alfa Inorganics and used as received. Fisher reagent grade 2,4-pentanedione was also used without further purification. Sodium and/or thallium salts of 2,4-pentanedione were prepared by standard procedures[35] by allowing sodium metal or thallium carbonate to react with acetylacetone in 95% alcohol. Choroform-*d* was prepared by a modified procedure[36] of that of Paulsen and Cooke.[37] Bromoform (Canlab) was purified by distillation over molecular sieves (Type 4A) just prior to use. Hexane and dichloromethane were refluxed over calcium hydride and distilled therefrom prior to use.

**Diphenylbis(2,4-pentanedionato)tin(IV).** This compound was prepared using established procedures.[15,20,38] Chemical shifts (9.8 g/100 ml; $CDCl_3$-TMS; ~37°): −5.41 ppm (-CH=) and −1.98 ($CH_3$).

**Dimethylbis(2,4-pentanedionato)tin(IV).** This compound was synthesized by a method reported earlier.[26,38] Chemical shifts (10.3 g/100 ml; $CDCl_3$-TMS; ~37°): −5.32 ppm (-CH=), lit.[15] −5.27 ppm; −1.96 ppm ($CH_3$); −0.59 ppm (*Sn*-$CH_3$), lit.[15] −0.49 ppm. $J(^{117}Sn-CH_3)$ = 96.8 Hz, lit.[15] 95.0 Hz; $J(^{119}Sn-CH_3)$ = 101.6 Hz, lit.[15] 99.3 Hz.

**Phenylchlorobis(2,4-pentanedionato)tin(IV).** A 72% yield (1.84 g) of this product was obtained from the reaction of 1.81 g (5.99 mmol) of phenyltin trichloride with 1.61 g (13.2 mmol) of sodium acetylacetonate in 75 ml of dichloromethane. The reaction mixture was refluxed for *ca.* 3 hr and filtered hot. The filtrate was concentrated to about 30 ml under a nitrogen stream; dry hexane was then added until the first signs of turbidity. Cooling in a freezer (−4°) gave the desired white crystalline compound which was filtered and recrystallized from dry dichloromethane–hexane solutions; mp 149–150°, lit.[20] mp 149–152°. Chemical shifts in $CDCl_3$-TMS (8.8 g/100 ml; ~37°): −2.07 ppm ($CH_3$) and −5.50 ppm (-CH=).

*Anal.* Calcd for $C_{16}H_{19}O_4ClSn$: C, 44.75; H, 4.46; Cl, 8.25; Sn, 27.64. Found: C, 44.60; H, 4.47; Cl, 8.42; Sn, 27.56.

**Methylchlorobis(2,4-pentanedionato)tin(IV).** To sodium acetylacetonate (2.87 g, 23.5 mmol) was added 2.58 g (10.7 mmol) of methyltin trichloride in 75 ml of dichloromethane. The mixture was refluxed for approximately 4 hr and then filtered hot. Concentrating the filtrate to about half its volume and adding dry hexane yielded a white product. Recrystallization from dichloromethane–hexane solutions gave 1.0 g (25% of theoretical); mp 135–137°, lit.[20] mp 135–136°. The purity of this product was further verified by nmr and infrared spectra. Substitution of thallous acetylacetonate for sodium acetylacetonate yielded 72% of the product. Chemical shifts in $CDCl_3$-TMS (15.8 g/100 ml; ~28°): −0.86 ppm (*Sn*-$CH_3$), −2.04 ppm (acac $CH_3$), −5.51 ppm (acac -CH=). $J(^{117}Sn-CH_3)$ = 119.7 Hz; $J(^{119}Sn-CH_3)$ = 125.2 Hz.

**Preparation of Solutions.** In view of the possible hydrolysis[15,39] of these organotin complexes, solutions were prepared and subsequently handled under anhydrous conditions in a dry nitrogen atmosphere in a glove bag. Nmr samples were degassed and the tube was flame-sealed *in vacuo*. When these nmr samples were further required, they were stored in liquid nitrogen.

**Measurement of Nmr Spectra.** Proton chemical shifts (±0.01 ppm) and coupling constants (±0.3 Hz) were obtained with a Varian Associates A-60A high-resolution nmr spectrometer operating at 60.00 MHz. Sweep widths were calibrated using a $CHCl_3$–TMS standard or by the audio side band technique. Variable-temperature nmr spectra were run in the frequency-sweep mode on a Varian HA-100 high-resolution spectrometer operating at 100.00 MHz and equipped with a V-6040 variable-temperature controller and a V-4343 variable-temperature probe.

Probe temperatures were measured from chemical shift differences between nonequivalent protons of methanol (−85 to +40°) or 1,2-ethanediol (40–80°) using a modified version[40] of Van Geet[41] equations, unless otherwise noted, in the appropriate temperature ranges. A discrepancy of ~4° is evident between the Varian and the Van Geet temperatures in the low-temperature region. Such discrepancy may lead to some small but significant errors in the activation parameters; for example, from 0.4 to 1.6 kcal/mol in $E_a$ and from 1 to 5 eu in $\Delta S^{\ddagger}$.[11,42]

Various possible experimental errors can affect the nmr line shapes with consequences in the accuracy of the results. These have been discussed by several workers, notably by Allerhand and coworkers.[43] Instrument instability, calibration error, and spectral distortions are, among others, the chief sources of errors. At least 7 min was allowed at each temperature to ensure temperature equilibration. To maintain temperature stability, minimum adjustments in gas-flow rate and spinning rate were made when deemed necessary. At each new temperature and between scans, the field homogeneity was maximized to offset deterioration caused by change in temperature and by instrumental instability. Instability errors resulting from changes in sweep rate and frequency and from static magnetic fields during scans were minimized by averaging a minimum of five spectra at each temperature. Possible spectral distortions from excessive use of electronic filtering, saturation effects, and mismatch of sweep and recorder response were minimized by employing (a) a radiofrequency amplitude below saturation level, (b) slow sweep rates (0.2 or 0.1 Hz/sec), and (c) the least amount of electronic filtering. Because of the low solubility of some of the organotin complexes and the necessity of using the less abundant -CH= protons, it was necessary at times to increase slightly electronic filtering to improve the signal to noise ratio.

**Determination of Mean Lifetimes.** Lifetimes were extracted from nmr spectra recorded in the appropriate solvent over the indicated temperature range: $(C_6H_5)_2Sn(acac)_2$, −12.7 to −53.7° ($CDCl_3$), +3.0 to −56.8° ($CH_2Cl_2$); $(CH_3)ClSn(acac)_2$, −0.5 to +29.5° ($CDCl_3$); $(C_6H_5)ClSn(acac)_2$, 17.5 to 58.7° ($CDCl_3$), 26.6 to 80.7° ($CHBr_3$). The following characteristic line shape parameters were selected from nmr spectra: $R$, the ratio of maximum intensity to minimum central intensity at $(\nu_a + \nu_b)/2$; $\delta\nu_e$, the chemical shift separation during exchange; $W_{1/4}$, $W_{1/2}$, and $W_{3/4}$, the full line widths at one-fourth, one-half, and three-fourths of maximum amplitude. Average values of these parameters for five spectral scans are summarized in Table I. Mean lifetimes, $\tau$ (Table I), for exchange of methyl groups in $(C_6H_5)_2Sn(acac)_2$ and acetylacetonate ring protons in $(CH_3)ClSn(acac)_2$ and $(C_6H_5)ClSn(acac)_2$ were obtained by comparing experimental line shape parameters with those from calculated spectra using the Gutowsky–Holm[44] total line shape equation. The calculated spectra were computed at intervals of 0.005 Hz for a range of about 240 values of $\tau$. Input parameters used in the computation were as follows: $\delta\nu_0$, chemical shift differences between the two resonance signals in the absence of exchange; a value for the population at both sites, $P_a = P_b = 0.5$; and a value for $T_2$, the transverse relaxation time. Except for $(C_6H_5)_2Sn(acac)_2$ in $CH_2Cl_2$, $\delta\nu_0$ is temperature dependent; $T_2$ was in all cases temperature dependent as evidenced from viscosity broadening in the region of slow exchange [*e.g.*, $W_{1/2}$ is 1.39 Hz at −20.2° and 1.56 Hz at −44.5° for

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**Table I.** Spectral Parameters and Lifetimes for Exchange of Acetylacetonate $CH_3$ Group or -CH=Protons in $(C_6H_5)_2Sn(acac)_2$ and $RClSn(acac)_2$ ($R = CH_3, C_6H_5$) in Various Solvents

$(C_6H_5)_2Sn(acac)_2$ in $CDCl_3$

| Temp., °C | R LF | R HF | $\delta\nu_e$, Hz | Linewidths, Hz $W_{1/4}$ | $W_{1/2}$ LF | $W_{1/2}$ HF | $W_{3/4}$ LF | $W_{3/4}$ HF | $\tau \times 10^2$ sec |
|---|---|---|---|---|---|---|---|---|---|
| -53.7 | 2.34 | 2.43 | 5.56[a] | - | 3.18 | 3.18 | 1.69 | 1.69 | 18.4 ± 1.4[b] |
| -50.6 | 2.11 | 2.08 | 5.58[a] | - | 3.89 | 3.88 | 1.92 | 1.92 | 15.1 ± 1.4 |
| -48.4 | 1.73 | 1.78 | 5.59[a] | - | - | - | 2.15 | 2.22 | 11.8 ± 0.9 |
| -46.8 | 1.53 | 1.55 | 5.43[a] | - | - | - | 2.60 | 2.75 | 9.87 ± 0.79 |
| -43.3 | 1.18 | 1.19 | 4.66[a] | - | - | - | - | - | 7.38 ± 0.07 |
| -42.4 | 1.05 | 1.17 | 4.46[a] | - | - | - | - | - | 6.60 ± 0.86 |
| -39.4 | - | - | 2.53 | - | - | - | - | - | 5.61 |
| -38.0($T_c$) | - | | - | a | a | | 5.69 | | 5.86 |
| -33.4 | - | | - | a | 5.84 | | 3.57 | | 3.90 ± 0.23 |
| -27.6 | - | | - | 6.54 | 3.85 | | 2.24 | | 2.53 ± 0.09 |
| -22.1 | - | | - | 5.05 | 2.90 | | 1.66 | | 1.75 ± 0.05 |
| -12.7 | - | | - | 3.55 | 2.06 | | 1.14 | | 0.99 ± 0.05 |

$(C_6H_5)_2Sn(acac)_2$ in $CH_2Cl_2$

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| -56.8 | 3.37 | 3.34 | 6.11[a] | - | 2.75 | 2.40 | 1.39 | 1.25 | 20.3 ± 3.3[b] |
| -53.8 | 3.12 | 3.26 | 6.32[a] | - | 3.00 | 2.68 | 1.54 | 1.51 | 16.0 ± 1.7 |
| -51.7 | 2.99 | 2.96 | 6.31[a] | - | 2.97 | 2.65 | 1.48 | 1.39 | 15.7 ± 1.3 |
| -48.8 | 2.36 | 2.30 | 6.42[a] | - | 3.70 | 3.60 | 1.93 | 1.83 | 11.3 0.9 |
| -48.4 | 2.02 | 1.99 | 6.40[a] | - | 4.27 | 4.29 | 2.10 | 1.86 | 10.4 1.0 |
| -46.8 | 1.69 | 1.78 | 6.33[a] | - | - | - | 2.83 | 2.36 | 8.02 0.81 |
| -45.0 | 1.82 | 1.79 | 6.30[a] | - | - | - | 2.74 | 2.27 | 8.20 ± 0.90 |
| -42.3 | 1.47 | 1.51 | 5.77[a] | - | - | - | 3.09 | 2.92 | 6.94 0.34 |
| -38.6 | 1.14 | - | 4.90 | - | - | - | - | - | 5.82 ± 0.77 |
| -37.4($T_c$) | - | | - | a | a | | 6.27 | | 4.53 |
| -35.1 | - | | - | a | 7.70 | | 5.21 | | 3.99 0.35 |
| -30.5 | - | | - | 8.73 | 5.46 | | 3.25 | | 2.84 ± 0.19 |
| -24.8 | - | | - | 6.40 | 3.82 | | 2.13 | | 1.92 0.06 |
| -17.5 | - | | - | 5.20 | 2.87 | | 1.51 | | 1.40 0.11 |
| -9.5 | - | | - | 3.83 | 2.18 | | 1.22 | | 0.99 ± 0.04 |
| -6.0 | - | | - | 3.55 | 1.88 | | 0.95 | | 0.78 ± 0.15 |
| 3.0 | - | | - | 2.79 | 1.48 | | 0.74 | | 0.50 ± 0.13 |

$(CH_3)ClSn(acac)_2$ in $CDCl_3$

| Temp., °C | R LF | R HF | $\delta\nu_e$, Hz | Linewidths $W_{1/4}$ LF | $W_{1/4}$ HF | $W_{1/2}$ LF | $W_{1/2}$ HF | $W_{3/4}$ LF | $W_{3/4}$ HF | $\tau \times 10^2$ sec |
|---|---|---|---|---|---|---|---|---|---|---|
| -0.5 | 5.29 | 5.58 | 8.51[a] | 4.76[a] | 4.03[a] | 2.31 | 2.10 | 1.21 | 1.20 | 14.6 ± 1.1[b] |
| 4.5 | 2.98 | 3.06 | 8.01[a] | - | - | 3.47 | 3.18 | 1.86 | 1.82 | 8.25 ± 0.36 |
| 7.5 | 2.00 | 2.14 | 7.44 | - | - | 4.85 | 4.25 | 2.55 | 2.29 | 6.59 ± 0.54 |
| 11.5 | 1.22 | 1.29 | 6.04 | - | - | - | - | - | - | 4.39 ± 0.18 |
| 13.5 | 1.03 | 1.06 | 3.74 | - | - | - | - | - | - | 3.42 ± 0.07 |
| 16.0 | - | | - | 12.59[a] | | 9.12 | | 6.65 | | 3.12 ± 0.12 |
| 21.5 | - | | - | 9.03[a] | | 5.30 | | 3.06 | | 1.88 ± 0.04 |
| 26.5 | - | | - | 6.58[a] | | 3.75 | | 2.14 | | 1.40 ± 0.02 |
| 29.5 | - | | - | 4.74[a] | | 2.57 | | 1.38 | | 0.86 ± 0.06 |

$T_c = 17.0°$

$(C_6H_5)ClSn(acac)_2$ in $CDCl_3$

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 17.5 | 13.78 | 13.69 | 10.07[a] | 3.35[a] | 3.07[a] | - | 1.54 | - | 0.88 | 24.3 ± 2.3[b] |
| 28.5 | 4.00 | 4.03 | 9.71[a] | - | - | 3.19 | 3.12 | 1.54 | 1.69 | 8.27 ± 0.57 |
| 37.3 | 1.29 | 1.35 | 8.31 | - | - | - | - | - | - | 4.17 ± 0.67 |
| 44.2 | 1.34 | 1.36 | 8.22 | - | - | - | - | - | - | 4.23 ± 0.62 |
| 44.4 | 1.20 | 1.29 | 7.01 | - | - | - | - | - | - | 3.52 ± 0.13 |
| 46.0($T_c$) | - | | - | 16.11[a] | | 11.64 | | 8.64 | | 2.90 ± 0.31 |
| 48.5 | - | | - | 15.25[a] | | 10.42 | | 6.14 | | 2.30 ± 0.26 |
| 50.2 | - | | - | 15.04[a] | | 10.46 | | 7.55 | | 2.46 ± 0.07 |
| 58.7 | - | | - | 9.17[a] | | 5.25 | | 3.16 | | 1.36 ± 0.02 |

$(C_6H_5)ClSn(acac)_2$ in $CHBr_3$

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 26.6 | 9.09 | 9.78 | 12.30[a] | 4.80[a] | 4.39[a] | 2.18 | 2.24 | 1.11[c] | 1.14[c] | 16.1 ± 2.2[b] |
| 29.2 | 5.98 | 6.42 | 11.98 | 5.93[a] | 5.40[a] | 2.87 | 2.83 | 1.46 | 1.52 | 10.5 ± 1.1 |
| 41.7 | 2.63 | 3.00 | 11.30 | - | - | 4.94 | 4.81 | 2.69 | 2.58 | 5.17 ± 0.21 |
| 44.9 | 1.41 | 1.51 | 9.39 | - | - | - | - | 4.93 | 4.55 | 3.12 ± 0.07 |
| 50.6 | 1.31 | 1.28 | 8.08 | - | - | - | - | - | - | 2.72 ± 0.12 |
| 52.2 | - | - | 4.70 | - | - | - | - | - | - | 2.13 |
| 53.1($T_c$) | - | | - | 16.98[a] | | 12.92 | | 9.45 | | 1.91 ± 0.03 |
| 57.7 | - | | - | 14.74[a] | | 8.90 | | 5.49 | | 1.36 ± 0.00 |
| 63.8 | - | | - | 10.24[a] | | 5.97 | | 3.38 | | 0.95 ± 0.02 |
| 66.8 | - | | - | 8.74[a] | | 4.83 | | 2.81 | | 0.79 ± 0.00 |
| 73.4 | - | | - | 6.27[a] | | 3.58 | | 1.95 | | 0.55 ± 0.03 |
| 80.7 | - | | - | 4.84[a] | | 2.61 | | 1.33 | | 0.35 ± 0.05 |

[a] Not used to obtain $\tau$. [b] One standard deviation. [c] Small error in $W_{3/4}$ leads to large error in $\tau$.

$(CH_3)ClSn(acac)_2$ in $CDCl_3$ solutions; for $(C_6H_5)ClSn(acac)_2$ in $CDCl_3$, $W_{1/2}$ is 1.08 Hz (−16.3°) and 1.27 Hz (−42.6°)] and from differences in $W_{1/2}$ in the slow- and in the fast-exchange regions [*e.g.*, $W_{1/2}$ is 0.8 Hz at 35° but 2.50 Hz at *ca.* −70° for $(C_6H_5)_2Sn(acac)_2$ in $CH_2Cl_2$].

Values of $\delta\nu$ at temperatures in the region of exchange were obtained from linear least-squares extrapolation of the temperature dependence in the slow-exchange region. Following the method established by Fay and Lowry,[45] values of the transverse relaxation times, $T_{2a} = T_{2b}$, were established from line widths of the acetylacetonate methyl resonance of $(CH_3)_2Sn(acac)_2$ in the appropriate solvents and at the appropriate temperature for $(C_6H_5)_2Sn(acac)_2$ and from the acetylacetonate ring proton resonance of $(CH_3)_2Sn(acac)_2$ for $(CH_3)ClSn(acac)_2$ and $(C_6H_5)ClSn(acac)_2$ in $CDCl_3$. For the methylchloro complex in $CHBr_3$ solution, $T_2$ values were obtained from the acetylacetonate methyl resonance of the dimethyl complex,[46] also in bromoform. The low solubility of the dimethyltin complex in bromoform precluded attempts to obtain reliable -CH= line widths.

Below coalescence, mean lifetimes were extracted, in general, by comparing experimental and calculated spectra as to values of $R$, $\delta\nu_e$, $W_{1/4}$, $W_{1/2}$, and $W_{3/4}$. At and above coalescence, $\tau$ values were obtained by comparing values of $W_{1/4}$, $W_{1/2}$, and $W_{3/4}$. Residence times given in Table I represent the average $\tau$ values in which $\delta\nu_e$ was given a weighting factor of 2. Also, values of $\delta\nu_e$ which fall on or close to the least-squares straight-line plots of $\delta\nu$ *vs.* temperature were not used as they yielded anomalous values of $\tau$. In addition, in the case of the phenylchloro- and methylchlorotin complexes, values of $W_{1/4}$ were not compared because of Sn-$H_\gamma$ spin-spin coupling[47] which may broaden the line shape in this region.

The order of the kinetics of configurational rearrangements in the complexes reported here was checked by assessing the mean residence times at five different concentrations in the range 0.04–0.12 $M$ for $(C_6H_5)_2Sn(acac)_2$ and 0.16–0.52 $M$ for $(CH_3)ClSn(acac)_2$ in $CDCl_3$ solutions, at a temperature below and above coalescence; for $(C_6H_5)ClSn(acac)_2$ in $CHBr_3$ solutions, two concentrations were used to obtain lifetimes at several temperatures in the range 23–72°.

Arrhenius activation energy, $E_a$, and frequency factors, $A$, were obtained in the usual way from the slope and intercept, respectively, of the least-squares straight-line plots of log $k$ *vs.* $1/T$ (see Figures 3 and 4 later in this paper), where $k = 1/\tau_a$ is the first-order rate constant for exchange. Activation entropies, $\Delta S^{\ddagger}$, were obtained from the relation $\Delta S^{\ddagger} = R[\ln A - \ln RT/Nh] - R$.

## Results and Discussion

**Stereochemistry and Bonding.** There is no longer any doubt as to the stereochemistry of $(CH_3)_2Sn(acac)_2$ in the

(45) R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **6**, 1512 (1967).

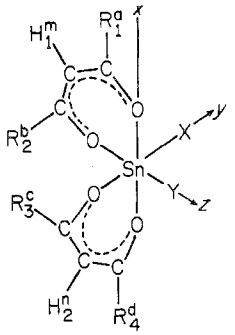
(46) Use of line widths from acetylacetonate $CH_3$ resonances to estimate $T_2$ values yields mean lifetimes and activation parameters for exchange of -CH= groups in $(CH_3)ClSn(acac)_2$ in $CDCl_3$ equal to those obtained from using -CH= proton resonances to compute $T_2$.

(47) Y. Kawasaki, *J. Inorg. Nucl. Chem.*, **29**, 840 (1967).

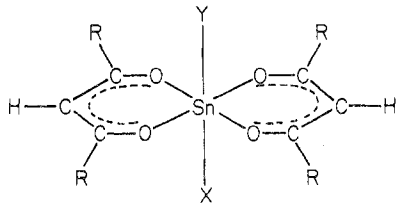
solid state (trans) and of $(C_6H_5)_2Sn(acac)_2$ in solution (cis) and in the solid state (cis). Unfortunately, the structure of the dimethyltin complex in solution is still open to question. The large value of the dipole moment (static) of 2.95 D for $(CH_3)_2Sn(acac)_2$ was suggested[23] as describing a structure basically of the cis type in which the C-Sn-C bond angle may have a value in the 90–110° range. Raman studies[27] in solution and in the solid state, however, rule out a cis structure in solution, and a trans → cis isomerization upon passing from the solid state to solution. The observed moment may arise[27] entirely from atomic polarization in which the C-C-C moieties of the two acetylacetonate rings undergo dynamic "flapping" to give a cisoid arrangement of the rings about the $SnO_4$ plane in the overall trans molecular structure of the complex. Yet dielectric loss measurements[29] indicate that although the atomic polarization contribution to the dipole moment is high (115 $cm^3$) there is a significant contribution from the orientation polarization (63 $cm^3$) with implications that the molecule is definitely polar and cis in solution. A distorted cis (or trans) structure, where 90° < C-Sn-C angle < 180°, as well as the existence of cis-trans equilibria, is not precluded by polarization and dielectric loss measurements. Regularities observed in $\mu_{static}$ would indicate[29] that the trans form is either absent or always present in the same proportions along with the cis form. Such a possibility appears to be ruled out by the nearly identical values[27] of the polarizability tensor for the symmetric $SnC_2$ stretching vibration at 510 $cm^{-1}$ in the solution and solid-state Raman spectra of the dimethyltin complex.

Our attempts at determining the stereochemical nature of $(CH_3)_2Sn(acac)_2$ in solution by the variable-temperature nmr technique proved unsuccessful. Only a single, relatively sharp acac methyl proton resonance ($W_{1/2}$ = 3.13 Hz at −77°; 0.97 Hz at 26°; in $CDCl_3$-$CCl_4$ solutions), a single acetylacetonate ring proton signal, and a single *Sn*-$CH_3$ resonance were observed. These observations are inconsistent neither with a trans structure in solution nor with a cis structure, but only a time-averaged methyl resonance is observed owing to a rapid intra- or intermolecular exchange process.[2]

Variable-temperature nmr spectra of methylchloro- and phenylchlorotin acetylacetonate complexes are presented in Figures 1 and 2, respectively. The geometries and expected signal multiplicities for these two compounds are shown in I and II (the letters a, b, c, and d define the nonequivalent




I
cis-Λ ($C_1$)
4 R, 2 ring H




II
trans ($C_{2v}$)
1 R, 1 ring H

methyl sites; m and n denote the nonequivalent -CH= sites).

Observation of four methyl resonances in the variable-temperature spectra is consistent with these complexes existing in solution in the cis configuration, at least at low temperatures. In an earlier report,[32] the methyl quartet and ring proton doublet in the spectrum of $(C_6H_5)XSn(acac)_2$

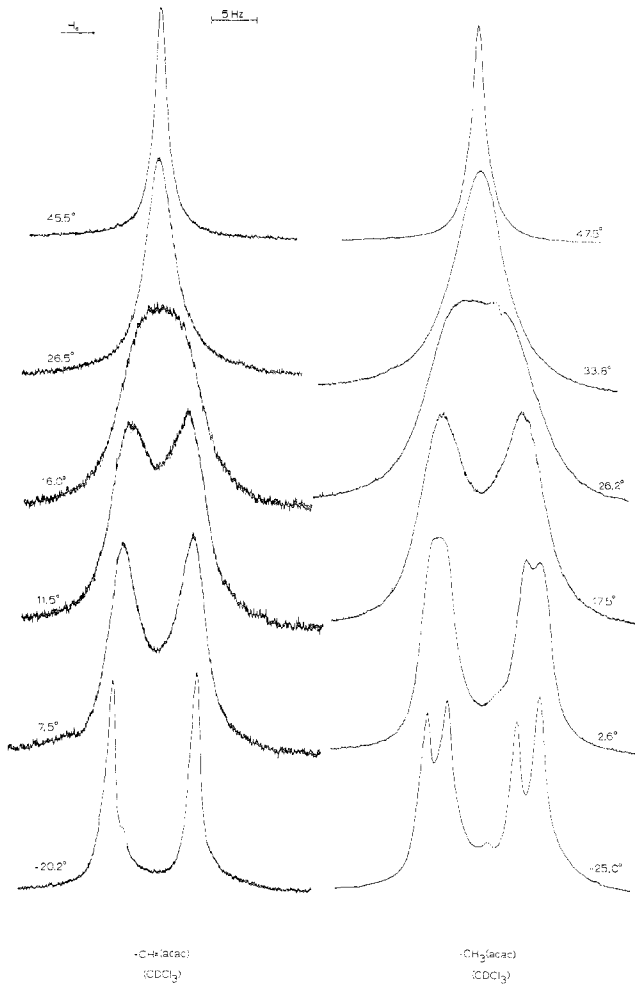



**Figure 1.** Nmr spectra for the acetylacetonate ring proton region and methyl region as a function of temperature for *cis*-$(CH_3)ClSn(acac)_2$ in chloroform-*d*. -CH= and $CH_3$ regions were recorded at different spectrum amplitudes. Dashed lines refer to resonances attributed to the trans isomer (see text).

(X = Cl or Br) were incorrectly attributed to a trans configuration. Observations analogous to those reported here for $(CH_3)ClSn(acac)_2$ and shown in Figure 1 were interpreted[31] in terms of (a) a cis configuration at −30°, (b) a trans structure at 20°, and (c) in the intermediate temperature range 0–15°, a cis ⇄ trans isomerization reaction (the -CH= proton region consisted of three resonance lines). In accord with this observation, we also note a distinct -CH= proton doublet and an additional weak signal at −20° (shown as a dashed line in Figure 1). A small resonance is also observed between the downfield and upfield doublets in the acetylacetonate methyl region. These two signals are ascribed to the existence of a small amount of the trans isomer, but obliteration of the -CH= resonance of the trans form with increase in temperature is probably a result of masking by the broadening of the more intense -CH= resonances of the cis isomer and not to a cis-trans equilibration reaction (*vide infra*). In the high-temperature region, signals from the cis and trans isomers appear to have identical chemical shifts.

Similarly, spectra of the phenylchlorotin complex reveal (Figure 2, dashed lines) an additional small -CH= signal (−5.65 ppm; $CDCl_3$; ~37°) and a slightly perceptible methyl resonance. Again we attribute these low-intensity signals to the trans structure. The possibility of impurities was eliminated because additions of 2,4-pentanedione, sodium acetylacetonate, and dichloromethane all reveal different

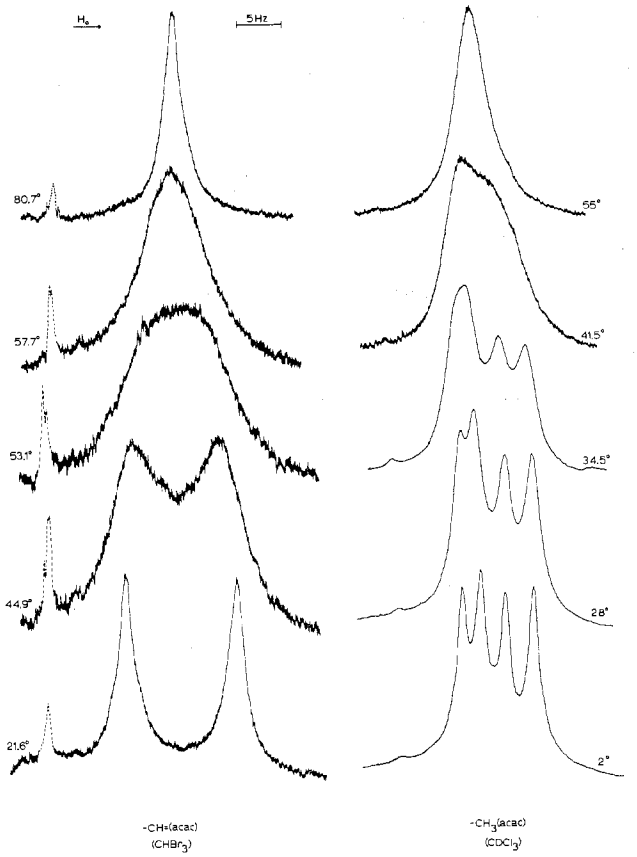



**Figure 2.** Nmr spectra for the acetylacetonate ring proton (in bromoform) and methyl region (in chloroform-*d*) as a function of temperature for *cis*-$(C_6H_5)ClSn(acac)_2$. Temperatures shown for the methyl spectra are based on the Varian graph. Dashed lines refer to resonances attributed to the trans isomer (see text). Ring proton and methyl spectral regions were recorded at different spectrum amplitudes.

chemical shifts from the $(C_6H_5)_2Sn(acac)_2$ complex. Integration of the -CH= resonances at four selected temperatures between the high- and low-temperature regions shows that the phenylchlorotin complex exists in solution as ~95% cis and ~5% trans. It is important to note that the signals due to the trans isomer (Figure 2) remain unchanged and thus no cis–trans equilibration occurs at least at temperatures below 81°.

Much has been said about the bonding scheme in six-coordinate tin(IV) complexes. On the basis of tin–methyl spin–spin coupling in *trans*-$(CH_3)_2Sn(acac)_2$, McGrady and Tobias[15] have proposed that the bonds in the C–Sn–C moiety are essentially $sp_z$ hybrids while the $5p_x$ and $5p_y$ orbitals are used to accommodate the four "highly ionic" tin–oxygen bonds in the equatorial plane. Schlemper[16,28] contends that the equatorial bonds to the acetylacetonate ligands are of the three-center four-electron type, using the tin $p_x$ and $p_y$ orbitals. Some admixture from $5d_{z^2}$ and $5d_{x^2-y^2}$ has also been suggested.[17,48] Using the Holmes–Kaesz[49] (H–K) correlation of amount of s character in an Sn–C bond with tin–proton coupling constants and the values of $J(^{117}Sn-CH_3)$ and $J(^{119}Sn-CH_3)$, 119.7 and 125.2 Hz, respectively, for $(CH_3)ClSn(acac)_2$ it would appear that the Sn–C bond has ~56% s character. The small, long-range Sn–$CH_3$ (acac) coupling constant of 2.2 Hz[47] also would indicate a certain degree of s character in the Sn–O bonds. Indeed, if the s character is maximized along the Sn–$CH_3$ bond in $(CH_3)ClSn(acac)_2$, a stronger tin–oxygen bond trans to Sn–$CH_3$ is predicted. No crystal structure of this compound has been reported. Also, it is not clear how much d-orbital involvement the H–K treatment can tolerate in a bonding scheme of Sn(IV) compounds, nor is a near lack of s character in the equatorial plane understood. The possible breakdown of the H–K correlation in six-coordinate tin complexes cannot be overlooked.

**Kinetics of Configurational Rearrangements.** Representative spectra of $(C_6H_5)_2Sn(acac)_2$ have been reported earlier;[24] those of $(CH_3)ClSn(acac)_2$ and $(C_6H_5)ClSn(acac)_2$ are illustrated in Figures 1 and 2, respectively. Broadening and collapse of the -CH= and $CH_3$ proton resonances into a single, sharp line in the high-temperature limit are ascribed to a configurational rearrangement process in the chelate rings which exchanges acetylacetonate ring protons and methyl groups between the two and four, respectively, nonequivalent sites in the cis $C_1$ isomer; in the diphenyltin complex, exchange of methyl groups occurs between the two nonequivalent sites of the $C_2$ isomer. To describe this exchange process, one first-order rate constant is required in the case of the $C_2$ isomer (methyl groups) and $C_1$ isomer (-CH= protons); three independent first-order rate constants will define the methyl group exchange process in the methylchloro- and phenylchlorotin complexes. Analysis of the latter four-site exchange is not only complicated *per se*, but to make matters worse the transverse relaxation times are temperature dependent. Mean resident times (Table I), $\tau = \tau_a\tau_b/(\tau_a + \tau_b)$, for the two-site exchange process were obtained by comparing experimental spectra with spectra computed by the Gutowsky–Holm[44] equation (see Experimental Section). Concentration dependence studies of the lifetimes show that the exchange process is independent of concentration and is first order. Arrhenius and Eyring activation parameters, along with values of $k$ at 25° and at the appropriate coalescence temperatures, $T_c$, are listed in Table II. Also included for comparison are values for the exchange process in $Cl_2Sn(acac)_2$.[11]

Values of the activation parameters of Table II for the organotin chelates are subject to some appreciable systematic errors owing to the temperature dependence of the transverse relaxation times throughout the temperature range at which kinetic data are reported. The effect of using a fixed value of $T_2$ obtained in the high-temperature limit was tested for $(C_6H_5)_2Sn(acac)_2$ in dichloromethane solutions. Results are analogous to those reported by Jones and Fay[11] for dihalotin acetylacetonate complexes. Fixed values of $T_2$ lead to significant large deviations above and below coalescence in the log $k$ *vs.* $1/T$ least-squares plot of Figure 3; the result of this is an error of about 1 kcal/mol in $E_a$ and 4 eu in $\Delta S^{\ddagger}$. Slightly larger deviations were obtained when $T_2$ values were abstracted from the line widths[45] of the isostructural $Cl_2Zr(acac)_2$ complex in dichloromethane: 1.4 kcal/mol in $E_a$ and 5.5 eu in $\Delta S^{\ddagger}$. Thus, $T_2$ values used in the calculated spectra were obtained at the appropriate temperature from the line widths of acetylacetonate proton resonances of $(CH_3)_2Sn(acac)_2$ (*vide supra*).[50] Errors in the activation parameters of Table II represent the random scatter of the

(48) J. A. S. Smith and E. J. Wilkins, *Chem. Commun.*, 381 (1965).

(49) J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 83, 3903 (1961).

(50) Though the structure of $(CH_3)_2Sn(acac)_2$ is still in doubt, it need not be isostrucural with complexes reported here in order to use its proton resonance line widths to estimate $T_2$ values. For example, acetylacetonate methyl proton resonances of $Rh(acac)_3$ and *cis*-$Cl_2Zr(acac)_2$ in dichloromethane, though not isostructural, have nearly identical temperature-dependent line widths.[45]

**Table II.** Arrhenius and Eyring Activation Parameters for Configurational Rearrangements in Organotin(IV) β-Ketoenolate Complexes

| Parameters | $(C_6H_5)_2Sn(acac)_2$ | | $(CH_3)ClSn(acac)_2$ | $(C_6H_5)ClSn(acac)_2$ | | $Cl_2Sn(acac)_2$[c] |
|---|---|---|---|---|---|---|
| | $CDCl_3$ | $CH_2Cl_2$ | $CDCl_3$ | $CDCl_3$ | $CHBr_3$ | 1,1,2,2-$C_2H_2Cl_4$ |
| $T_c$,[a] °C | −38.0 | −37.4 | 17.0 | 46.0 | 53.1 | 82 |
| $E_a$, kcal/mol | 8.1 ± 0.3[b] | 7.4 ± 0.3 | 14.6 ± 1.1 | 12.7 ± 2.0 | 14.7 ± 0.8 | 16.0 ± 0.4 |
| log $A$ | 8.49 ± 0.31 | 7.87 ± 0.26 | 12.29 ± 0.81 | 9.96 ± 1.38 | 11.25 ± 0.52 | 10.92 ± 0.23 |
| $\Delta H^{\ddagger}_{25}$, kcal/mol | 7.5 ± 0.3 | 6.8 ± 0.3 | 14.1 ± 1.1 | 12.2 ± 2.0 | 14.1 ± 0.8 | |
| $\Delta S^{\ddagger}_{25}$, eu | −21.7 ± 1.4 | −24.5 ± 1.2 | −4.3 ± 3.7 | −15 ± 6 | −9.1 ± 2.4 | −10.6 ± 1.0 |
| $\Delta G^{\ddagger}_{25}$, kcal/mol | 13.95 ± 0.09 | 14.11 ± 0.08 | 15.32 ± 0.05 | 16.61 ± 0.12 | 16.81 ± 0.07 | |
| $k_{25}$, sec$^{-1}$ | 369 ± 58 | 281 ± 37 | 36 ± 3 | 4.1 ± 0.9 | 2.9 ± 0.4 | 0.15 |
| $\Delta G^{\ddagger}_{T_c}$, kcal/mol | 12.60 ± 0.02 | 12.59 ± 0.02 | 15.29 ± 0.04 | 16.93 ± 0.08 | 17.06 ± 0.04 | |
| $k_{T_c}$, sec$^{-1}$ | 9.5 ± 0.3 | 10.3 ± 0.4 | 17 ± 1 | 17 ± 2 | 25.0 ± 1.4 | |

[a] ±1°. [b] Random errors estimated at the 95% confidence limit. [c] Reference 11.

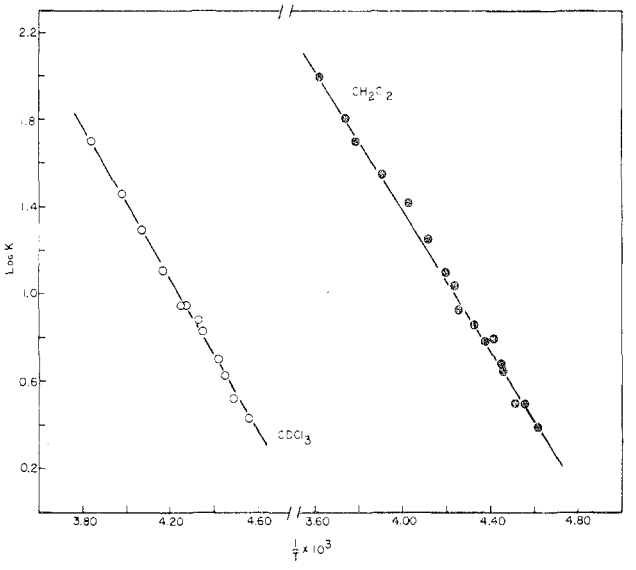



**Figure 3.** log $k$ *vs.* $1/T$ least-squares plots for acetylacetonate methyl group exchange in $(C_6H_5)_2Sn(acac)_2$. $k = 1/2\tau$ is the first-order rate constant for the configurational rearrangement process.

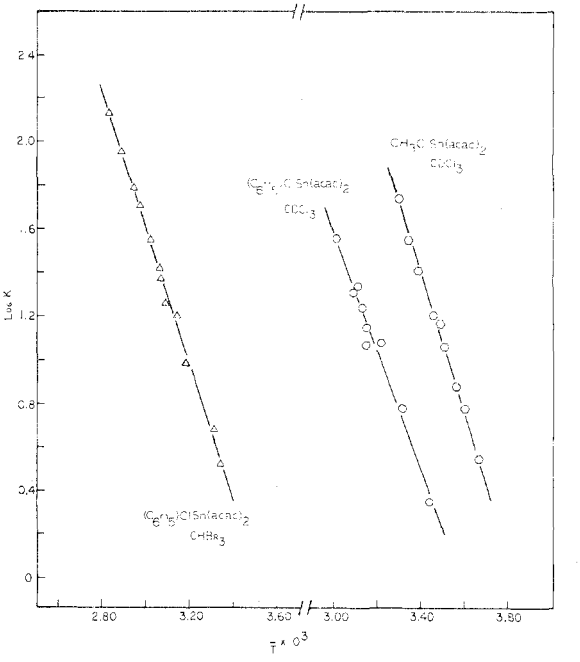



**Figure 4.** log $k$ *vs.* $1/T$ least-squares plots for acetylacetonate ring proton exchange in $RClSn(acac)_2$ (R = $CH_3$, $C_6H_5$). $k = 1/2\tau$ is the first-order rate constant for the exchange process.

data points in Figures 3 and 4. Also, a reasonable uncertainty in $T_2$ appears to lead to systematic errors of the order of ±1 kcal/mol in the activation energy and ±4 eu in the activation entropy.[11]

Several features may be noted in Table II. The rate of configurational rearrangements in the tin(IV) acetylacetonates decreases in the order $(C_6H_5)_2Sn > (CH_3)ClSn > (C_6H_5)ClSn > Cl_2Sn$. Interestingly, the rate of intermolecular exchange of acetylacetonate ligands in the systems $RR'Sn(acac)_2$-Hacac decreases in the order $(CH_3)_2Sn > (C_6H_5)_2Sn > (CH_3)ClSn > Cl_2Sn$.[51] Evidently, replacement of a chloride in $Cl_2Sn(acac)_2$ with a phenyl or a methyl group leads to a significant increase in the stereochemical lability of the acetylacetonate complexes. Substitution of the two chloro groups increases the lability further. It is not surprising then that, in view of the greater labilizing effect of methyl groups *vis a vis* phenyl groups on coordinated acetylacetonate ligands, our efforts to observe coalescence behavior in the $(CH_3)_2Sn(acac)_2$ complex proved unsuccessful. Although the activation energy is, within experimental error, nearly independent of methyl and phenyl groups in $RClSn(acac)_2$, the activation energy of the diphenyltin complex is substantially lower by *ca.* 5–6 kcal/mol; entropies of activation are also lower. In addition, activation parameters of $(C_6H_5)_2Sn(acac)_2$ appear to be nearly independent of solvent; $E_a$ for the phenylchlorotin complex in bromoform is 2 kcal/mol higher than in chloroform-*d*, but owing to the experimental uncertainty in the latter solvent any discussion of possible solvent effects is tenuous. An added observation is that at coalescence, $RClSn(acac)_2$ complexes are slightly more nonrigid than the diphenyltin complex. The activation energy reported here for $(C_6H_5)ClSn(acac)_2$ does not agree with the low value of 3 kcal/mol reported by Kawasaki and Tanaka.[32]

Recently, we[38] reported a study on intermolecular acetylacetonate ligand exchange between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ complexes in which the rate of exchange was first order in $[(C_6H_5)_2Sn(acac)_2]$. The rate-determining step was identified as rupture of one Sn–O bond in the diphenyltin complex; $E_a = 7.5 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger} = -33 \pm 5$ eu, and $k_{25} = 3.8$ sec$^{-1}$ ($CDCl_3$ solutions). The activation energy for exchange of methyl groups in $(C_6H_5)_2Sn(acac)_2$ in chloroform-*d* solutions (Table II) is 8.1 ± 0.3 kcal/mol, $\Delta S^{\ddagger}$ is −21.7 ± 1.4 eu, and $k_{25}$ is 369 sec$^{-1}$. The activation energy for the two processes is nearly identical, within experimental error, but the rate of the intramolecular process is *ca.* 100-fold faster, attributable to differences in the entropy of activation.

**Methyl Proton Nmr Region.** A feature of possible mechanistic significance concerns the four methyl proton signals in Figures 1 and 2. The components of the lower field and higher field doublets in the $(CH_3)ClSn(acac)_2$ spectra (Figure 1) broaden and collapse simultaneously with increasing tem-

(51) G. E. Glass and R. S. Tobias, *J. Organometal. Chem.*, **15**, 481 (1968).

perature to yield one broad line at 21.5°. A further increase in temperature produces a single, sharp line in the high-temperature limit. The methyl proton resonances in the $(C_6H_5)ClSn(acac)_2$ spectra (Figure 2) appear to undergo the same coalescence pattern. It is also noted that the -CH= proton signals undergo broadening and coalescence in the same temperature range as the methyl resonances, so that whatever the mechanism responsible for the nmr coalescence behavior, both the ring protons and the methyl groups are exchanged between their respective nonequivalent sites by the same physical process.

The magnitude of $Sn\text{-}CH_3$ proton coupling to the low-field component of the two methyl signals in *cis*-$X_2Sn(acac)_2$ (X = Cl, Br, or I) has been observed to be larger than that to the upfield component.[11,52] This has led to the assignment of the lower field resonance to the *unique pair* of $CH_3$ groups in the nonequivalent site trans to the halo groups. Also, the low-field and high-field methyl resonances of $Cl_2Sn(acac)_2$ are shifted upfield by 0.62 and 0.54 ppm,[52] respectively, on going from chloroform-*d* to benzene solvent. A solvation model with benzene molecules in tangential contact with the surface of the complex[53] and clustered about the $C_2$ axis of $X_2Sn(acac)_2$ predicts that methyl groups trans to X groups will exhibit the larger upfield shift. Hence, the lower field methyl signal has been associated with acetylacetonate methyl groups trans to X groups.[52] Moreover, the methyl groups trans to the methoxy groups in dimethoxybis(*N,N,N',N'*-tetramethylmalonamidato)titanium(IV) were assigned to the lower field resonance by Weingarten and coworkers[54] on the basis of the more rapid loss of rotation of the $N(CH_3)_2$ group trans to the monodentate methoxy ligands. We have not been successful in estimating the magnitudes of $J(Sn\text{-}CH_3)$ involving the four nonequivalent methyls owing to the broadness of the resonances and to the expected low values of $J$ (~2-3 Hz[47]). However, at 11.7° the solvent shift on passing from chloroform-*d* to benzene, $\Delta_{C_6H_6}^{CDCl_3}$, is 0.50 ppm for the low-field doublet (unresolved at 500 Hz sweep width) in the $(C_6H_5)ClSn(acac)_2$ spectra while that of the higher field doublet is 0.41 and 0.46 ppm, respectively, for the downfield and upfield component. In the methylchlorotin spectra at 13.8°, $\Delta_{C_6H_6}^{CDCl_3}$ of the low-field doublet (unresolved at this temperature; 500-Hz sweep width) is 0.43 ppm, that of the upfield doublet is 0.36 ppm.[55] Accordingly, we assign the low-field doublet (Figures 1 and 2) to the unique acetylacetonate methyl groups trans to, and equatorial with, the monodentate ligands in the phenylchloro- and methylchlorotin complexes. Coalescence of the four methyl signals to a single resonance in the spectra of both complexes is attributed to a configurational rearrangement process which time-averages the methyl proton environments among the four nonequivalent sites of the cis isomers.[56]

A permutational and mechanistic analysis of the configurational rearrangements in these $XYSn(AA)_2$-type complexes appears in the following publication.[57]

**Acknowledgment.** Support of this work by the National Research Council of Canada is gratefully acknowledged.

**Registry No.** $(C_6H_5)_2Sn(acac)_2$, 20179-85-5; $(CH_3)ClSn(acac)_2$, 52730-55-9; $(C_6H_5)ClSn(acac)_2$, 52730-56-0.

(52) J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc. A*, 1749 (1966).

(53) A. Mackor and H. A. Meinema, *Recl. Trav. Chim. Pays-Bas*, 91, 911 (1972).

(54) H. Weingarten, M. G. Miles, and N. K. Edelmann, *Inorg. Chem.*, 8, 879 (1968).

(55) Interestingly, the tin methyl proton signal suffers a paramagnetic downfield shift by 0.19 ppm on going from chloroform-*d* to benzene.

(56) Line shapes for the four-site methyl proton spectra of $(CH_3)ClSn(acac)_2$ in $CDCl_3$ were computer-fitted in the range 17.5–47.5° using a random scrambling matrix as part of the input in the computer program DNMR3 (QCPE, Indiana University). Chemical shifts in the absence of exchange were estimated from an extrapolation of the shifts at the slow-exchange region. A linear least-squares plot of log $k$ *vs.* $1/T$ for the best spectral fit yielded the following activation parameters: $E_a = 12.0 \pm 1.0$ kcal/mol, $\log A = 10.2 \pm 0.7$, $\Delta H^{\ddagger}_{25} = 11.4 \pm 1.0$ kcal/mol, $\Delta S^{\ddagger}_{25} = -13.8 \pm 3.4$ eu, $\Delta G^{\ddagger}_{25} = 15.55 \pm 0.03$ kcal/mol, $k_{25} = 25$ sec$^{-1}$. Only the overall rate constant for exchange between the four sites is reported—rate constants for exchange between any two sites were not accessible with the method of computer fitting we employed. Differences between the above values and those presented in Table II are probably the result of using different $T_2$ values and of the rather poor fit in the region of the signals below one-fourth of the maximum height. Within these limitations the values are in reasonable agreement.

(57) D. G. Bickley and N. Serpone, *Inorg. Chem.*, 13, 2908 (1974).