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STEREOCHEMISTRY OF, AND KINETICS OF ENVIRONMENTAL AVERAGING PROCESSES IN SOME ORGANOGermanium(IV) AND ORGANOSILICON(IV) CHELATES*

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Summary

The stereochemistry of $(C_6H_5)ClM(acac)_2$ ($M = Ge, Si$; $acac = CH_3COCHCOCH_3^-$), $(C_6H_5)_2Ge(acac)_2$, and $(CH_3)ClSi(acac)_2$ complexes has been investigated in $CDCl_3/CCl_4$ solutions by dynamic proton magnetic resonance spectroscopy. The phenylchloro complexes adopt predominantly a *cis* (C_6H_5, Cl) structure in solution with a small amount of the *trans* (C_6H_5, Cl) form ($\leq 5\%$); while methylchlorosilicon acetylacetonate is *cis* (CH_3, Cl) in solution. The structure of the diphenylgermanium complex cannot be unequivocally assigned. Environmental averaging of the acetylacetonate ring protons ($-CH=$) in the C_1 -type *cis*-phenylchloro complexes has also been studied by total lineshape line-broadening techniques in $CDCl_3/CCl_4$ solutions in the temperature range: $(C_6H_5)ClGe(acac)_2$, $13.2-62.2^\circ$; and $(C_6H_5)ClSi(acac)_2$, -69.6 to -49.3° . Activation parameters are: for $(C_6H_5)ClGe(acac)_2$, $E_a = 12.8 \pm 1.2$ kcal/mol, $\Delta S^\ddagger = -13 \pm 4$ eu, $k_{298} = 9.4$ sec $^{-1}$; and for $(C_6H_5)ClSi(acac)_2$, $E_a = 6.4 \pm 1.0$ kcal/mol, $\Delta S^\ddagger = -22 \pm 5$ eu, and $k_{298} = 4.2 \times 10^3$ sec $^{-1}$. It is argued, on the basis of the order of lability ($PhClSi \gg PhClGe > PhClSn$), that the exchange phenomena probably proceed via a twist mechanism if environmental averaging occurs by a sole reaction pathway.

Introduction

Organosilicon(IV) derivatives with β -ketoenols, $RCISi(acac)_2$ ($R = CH_3, C_6H_5$; $acac = CH_3COCHCOCH_3^-$) were first reported by West [2]. Infrared

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spectroscopic evidence indicated that the complexes were six-coordinate; $(\text{CH}_3)_2\text{Si}(\text{acac})_2$ and $\text{R}_3\text{Si}(\text{acac})$ compounds were shown to exist as four-coordinate species with unidentate acetylacetonate ligands. Stereochemical lability on the latter triorganosilicon acetylacetonates were recently reported [3]. The monochloroorganosilicon(IV) derivatives above were suggested to exist in either the *cis* (R, Cl) and/or *trans* (R, Cl) stereochemistry, but have not been the subject of further study. We note, however, that $\text{X}_2\text{Si}(\text{acac})_2$ complexes, where $\text{X} = \text{Cl}^-$ and CH_3COO^- , have been investigated; $\text{Cl}_2\text{Si}(\text{acac})_2$ possesses the *trans* (Cl, Cl) structure [4] (low temperature NMR spectra), while $(\text{CH}_3\text{COO})_2\text{Si}(\text{acac})_2$ exists predominantly in the *trans* form in the solid state and in freshly prepared solution but isomerizes in solution to the *cis* structure to yield an equilibrium mixture ($[\textit{cis}]/[\textit{trans}] = 1.6$) [5-7]. More recently, it was reported that reaction of CH_3SiCl_3 or $\text{C}_6\text{H}_5\text{SiCl}_3$ with dibenzoylmethane (Hbzbz) yields the five-coordinate $[\text{RSi}(\text{bzbz})_2]^+\text{Cl}^-$ complex [8].

Organogermanium(IV) complexes with β -diketones have received even less attention [9, 10]. Mehrotra and Mathur [11] reported the synthesis of the monomeric, six-coordinate $(\text{C}_6\text{H}_5)_2\text{Ge}(\text{acac})_2$ complex and of $(\text{t-C}_4\text{H}_9)_3\text{Ge}(\text{acac})$, suggested as being five-coordinate. The stereochemistry and stereochemical lability of several dihalo six-coordinate germanium(IV) complexes with β -diketones have also been studied [12, 13]; these adopt predominantly the *cis* structure with some *trans* form present (ca. 15-20%) [12].

The purpose of the present investigation is twofold (1) to elucidate the stereochemistry in solution of $\text{RClSi}(\text{acac})_2$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$), $(\text{C}_6\text{H}_5)\text{ClGe}(\text{acac})_2$, and $(\text{C}_6\text{H}_5)_2\text{Ge}(\text{acac})_2$ by variable temperature ^1H NMR spectroscopy, and (2) to study the kinetics of the configurational rearrangement phenomena in the monochloroorganometal complexes in $\text{CDCl}_3/\text{CCl}_4$ solutions. The particular case of the rearrangements in $(\text{CH}_3)\text{ClGe}(\text{acac})_2$ will be the subject of a later report [14].

Experimental

Materials and solvents. Diphenyldichlorogermane, phenyltrichlorosilane, methyltrichlorosilane, and thallos carbonate were purchased from Alfa Inorganics and used without further purification. Tetraphenylgermane and tetrachlorogermane were also used as received from the supplier (Research Organic/Inorganic Chemical Corp.). Acetylacetone (2,4-pentanedione) was Fisher Certified Reagent. Reagent grade hexane and carbon tetrachloride (Anachemia), and dichloromethane (Fisher) were dried by refluxing over calcium hydride chips (Fisher) for at least 12 h and distilled therefrom prior to use. Deuteriochloroform was prepared by a slight modification [13] of the method of Paulsen and Cooke [15]. Phenyltrichlorogermane was prepared by treating tetraphenylgermane with germanium tetrachloride, over freshly sublimed aluminium trichloride, in a Carus combustion tube using the method of Rijkens and Van der Kerk [16]. Sodium and thallium acetylacetonate salts were prepared by standard procedures.

Melting points and analyses. Melting points were determined with a Gallenkamp melting point apparatus (Model MF-370), and are uncorrected. Capillaries were sealed with modeling clay under a dry nitrogen atmosphere in a glove bag.

Elemental analyses were in general performed by Galbraith Laboratories, Knoxville, Tenn.

Syntheses

Diphenylbis(2,4-pentanedionato)germanium(IV) This complex was synthesized by allowing diphenyldichlorogermane (2.69 g, 9.04 mmol) to react with thallos acetylacetonate (5.00 g, 16.4 mmol) in ca. 75 ml of dichloromethane. The mixture was stirred at ambient temperature for about 2 h, and filtered under a nitrogen atmosphere by a method described earlier [17]. The filtrate was concentrated to ~ 30 ml by passing a stream of nitrogen over the surface of the solution. Dry hexane was subsequently added until the first signs of crystallization, and the solution cooled in a freezer (~ 0°) overnight. Recrystallization of the white product from dichloromethane/hexane yielded 1.70 g (49% of theoretical). M.p. 134-136° (dec.), b.p. 243°/1.0 mm Hg; lit. [11] b.p. 201°/0.6 mm Hg. Anal. Found: C, 59.01, 57.77, H, 5.38, 6.32. C₂₂H₂₄O₄Ge calcd.: C, 62.17; H, 5.69%.

The rather poor analysis is a result of the rapid decomposition (ca. 2-3 days) of this product. A low C analysis has also been reported by others [11]. Purity was confirmed by the absence of O-H and uncomplexed CO stretching bands in the infrared spectrum, and by NMR spectra. Chemical shifts in CDCl₃/CCl₄/TMS solvent (10.3 g/100 ml, ~ 31°) 1.93 ppm (CH₃) and 5.31 ppm (CH=).

Phenylchlorobis(2,4-pentanedionato)germanium(IV). This product was obtained in 67% yield from the reaction of phenyltrichlorogermane (2.66 g, 10.4 mmol) with thallos acetylacetonate (6.29 g, 20.7 mmol) in 75 ml of dichloromethane. The mixture was stirred for 30 min and subsequently filtered. Upon concentrating and adding hexane to the filtrate, inevitably, the solution gave an intractable oil upon cooling. Crystallization was induced by scratching the flask. Recrystallization from dichloromethane/hexane yielded 2.65 g of the desired white compound. M.p. 143-145° (dec.); lit. [10] 140-145°. Anal. Found: C, 43.89; H, 4.46. C₁₆H₁₉O₄ClGe calcd.: C, 50.13; H, 5.00%.

Chemical shifts in CDCl₃/CCl₄/TMS (17.6 g/100 ml; ~ 31°), 2.08 ppm (CH₃) and 5.60 ppm (CH=). Purity of the freshly prepared product was ascertained from NMR and infrared spectra. Rapid decomposition (~ 2-3 days) results in an unsatisfactory analysis. A gravimetric determination of chlorine [10] produced 9.10% (calcd. 9.25).

Phenylchlorobis(2,4-pentanedionato)silicon(IV). To a dichloromethane solution (75 ml) of phenyltrichlorosilane (7.96 g, 37.7 mmol) was added 5.20 g of thallos acetylacetonate (17.1 mmol). The mixture was stirred at ambient temperature for 10 min. Filtration under a nitrogen atmosphere and working up the filtrate, as described earlier, produced a white product which was recrystallized from dichloromethane/hexane solution. M.p. 119-121° (dec.); lit. [10] ca. 135°. Purity of a freshly recrystallized sample was confirmed by infrared and NMR spectra. The product decomposes over a period of hours to form a red product, but recrystallization prior to total decomposition yields a white compound. Chlorine determination [10] gave 10.65% (C₁₆H₁₉O₄ClSi calcd.: 10.49). Chemical shifts in CDCl₃/CCl₄/TMS (10.8 g/100 ml; ~ 28°), 2.00 ppm (CH₃) and 5.58 ppm (CH=).

Methylchlorobis(2,4-pentanedionato)silicon(IV). This complex was prepared from the reaction of 4.34 g of thallos acetylacetonate (14.3 mmol) with methyltrichlorosilane (4.71 g, 31.5 mmol) in 50 ml dichloromethane. The mixture was stirred for 10 min and filtered under nitrogen; addition of dry hexane to the filtrate yielded a white product which was recrystallized from dichloromethane/hexane. This product decomposes over a period of 15-30 min in the presence of trace amounts of moisture; no consistent m.p. was obtained, the compound undergoing constant decomposition upon heating. Purity of a freshly prepared sample was ascertained from infrared and NMR spectra. A chlorine determination [10] yielded 13.5% ($C_{11}H_{17}O_4ClSi$ calcd.: 12.6). Chemical shifts in $CDCl_3/CCl_4/TMS$ (12.6 g/100 ml, -75.6°), 2.2 ppm (acac- CH_3) and 6.54 ppm (acac- $CH=$).

Preparation of solutions. Owing to the rapid decomposition of these organo-germanium and organosilicon complexes, solutions were prepared under rigorous anhydrous conditions in a dry nitrogen atmosphere in a glove bag just prior to NMR investigations. NMR samples were flame-sealed in vacuo after degassing by the freeze-thaw-refreeze method. The solvent used consisted of a mixture of 54.5% by weight of deuteriochloroform and 45.6% of carbon tetrachloride to which was added TMS as an internal standard. Such mixture afforded NMR studies to be carried out to temperatures down to ca. -80° [18].

Measurement of NMR spectra. Proton chemical shifts (± 0.02 ppm) and variable temperature NMR spectra were recorded in the frequency sweep mode on a Varian HA-100 high-resolution NMR spectrometer operating at 100.00 MHz and equipped with a V-6040 variable temperature controller and a V-4343 variable temperature probe.

Probe temperatures are based on the Van Geet equations [19] and were measured as described elsewhere [20]. Various possible experimental errors that can affect NMR lineshapes with consequences in the accuracy of the results have also been described previously [20].

Determination of mean lifetimes. Mean lifetimes of a $CH=$ proton in a particular site were extracted from NMR spectra recorded in $CDCl_3/CCl_4/TMS$ over the indicated temperature range: $(C_6H_5)ClGe(acac)_2$, $13.2-62.2^\circ$; $(C_6H_5)ClSi(acac)_2$, -69.6 to -49.3° . In the case of the former compound, these characteristic lineshape parameters were selected from NMR spectra; R , the ratio of maximum intensity to minimum central intensity at $(\nu_a + \nu_b)/2$; $\delta\nu_2$, the chemical shift separation during exchange; $W_{1/4}$, $W_{1/2}$, and $W_{3/4}$, the full linewidths at one-quarter, one-half, and three-quarters of maximum amplitude. Average values of these parameters for five spectral scans are summarized in Table 1 for $(C_6H_5)ClGe(acac)_2$. Mean lifetimes, τ , (Table 1) for exchange of $CH=$ protons in the phenylchlorogermanium compound were obtained from a comparison of experimental lineshape parameters with those from calculated spectra using the Gutowsky-Holm [21] total lineshape equation for a two-site exchange. Details of the method of calculation have already been discussed elsewhere [20, 22]. $\delta\nu$ is temperature dependent (Fig. 1); the transverse relaxation time, T_2 , is also temperature dependent as evidenced from viscosity broadening in the region of slow exchange [e.g. for $(C_6H_5)ClGe(acac)_2$, $W_{1/2}$ at 13.2° is 2.37 Hz for the low field (LF) line and 2.55 Hz for the high field (HF) line, but at -53.9° the corresponding values are 2.68 and 2.75 Hz].

TABLE I
 VARIABLE TEMPERATURE DATA NMR FOR $(C_6H_5)_2C=CH_2$ IN $CDCl_3/CCl_4$ SOLUTIONS

| Temperature (°C) | R | | Linewidths (Hz) | | | | | | $\tau \times 10^2$ (sec) | |
|---------------------|-------|-------|------------------------|------|-------|------|-------|------|-----------------------------|-------------------------|
| | LF | HF | $\delta_{1/2}$ (Hz) | LF | HF | LF | HF | LF | | HF |
| 13.2 | 24.58 | 24.81 | 20.06 ^a | 4.34 | 4.69 | 2.37 | 2.55 | 1.26 | 1.31 | 11.5 ± 1.3 ^b |
| 20.8 | 14.57 | 14.61 | 19.86 ^a | 5.48 | 5.90 | 3.11 | 3.37 | 1.73 | 1.86 | 7.39 ± 0.73 |
| 30.2 | 5.12 | 5.19 | 18.93 | — | — | 4.77 | 5.17 | 2.58 | 2.87 | 4.35 ± 0.23 |
| 38.9 | 1.87 | 1.89 | 16.43 | — | — | — | — | 6.06 | 6.20 | 2.17 ± 0.09 |
| 41.9 | 1.13 | 1.14 | 11.93 | — | — | — | — | — | — | 1.51 ± 0.03 |
| 44.5(T) | — | — | — | — | — | — | 23.25 | — | 18.00 | 1.55 ± 0.21 |
| 53.2 | — | — | — | — | 21.17 | — | 12.40 | — | 7.40 | 0.82 ± 0.04 |
| 62.2 | — | — | — | — | 10.10 | — | 6.50 | — | 3.80 | 0.45 ± 0.02 |

^a Not used to obtain τ values. ^b One standard deviation.

Values of $\delta\nu_0$ (chemical shift separation in the absence of exchange) at temperatures in the region of exchange were obtained from linear-least-squares extrapolation of the temperature dependence of $\delta\nu$ in the slow exchange region. Values for $\delta\nu_e$ (Hz) at slow exchange are for $(C_6H_5)ClGe(acac)_2$: 21.64 (-53.9°), 20.92 (-31.7°), 20.55 (-8.1°), 20.25 (5.6°), 20.06 (13.2°), and 19.86 (20.8°); other values are summarized in Table 1.

Transverse relaxation time values, $T_{2a} = T_{2b}$, were estimated from linewidths of the acetylacetonate CH= proton signal of $(CH_3)_2Sn(acac)_2$ in $CDCl_3/CCl_4/TMS$ [23].

At and above coalescence, τ values were obtained, in general, by comparing experimental and calculated values of $W_{1/4}$, $W_{1/2}$, and $W_{3/4}$. Below coalescence, mean residence times were extracted from a comparison of R , $\delta\nu_e$, $W_{1/4}$, $W_{1/2}$, and $W_{3/4}$. Lifetimes presented in Table 1 represent average τ values in which $\delta\nu_e$ was given a weighting factor of two. In addition, values of $\delta\nu_e$ which fall on or close to the least-squares lines of Fig. 1 were not used as these yield anomalous τ values.

In the case of $(C_6H_5)ClSi(acac)_2$, the above technique was not employed owing to the unavailability of $\delta\nu$ values in the absence of exchange (cf. Fig. 1)

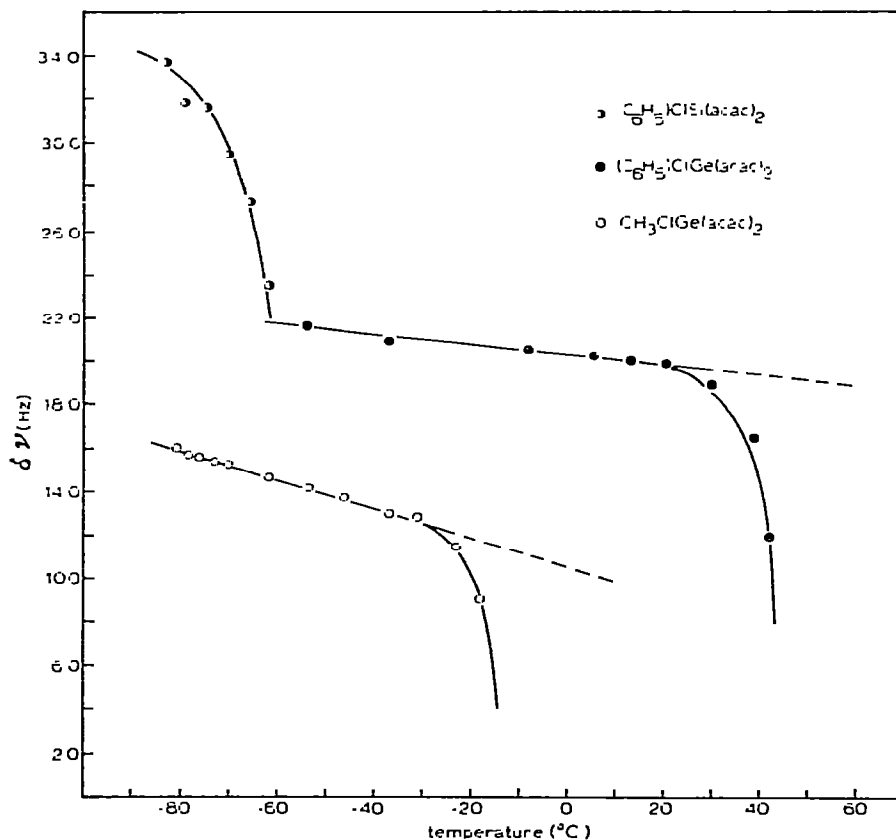


Fig. 1. Temperature dependence of the chemical shift separation, $\delta\nu$, during exchange for the $(C_6H_5)ClM(acac)_2$ ($M = Si, Ge$) and $(CH_3)ClGe(acac)_2$ (see text) complexes in chloroform-*d*/carbon tetrachloride solutions.

TABLE 2

RESULTS FROM COMPUTER FITTING OF NMR SPECTRA OF $(C_6H_5)_2ClSi(acac)_2$ IN $CDCl_3/CCl_4$ SOLUTIONS

| Temperature (°C) | $\tau_a \times 10^3$ (sec) | $\tau_b \times 10^3$ (sec) | $k (= \frac{1}{2\tau})^a$ (sec ⁻¹) |
|-------------------------|-------------------------------|-------------------------------|---|
| -69.6 | 35.7 ± 1.0 ^b | 33.9 ± 0.9 | 29 |
| -64.9 | 28.7 ± 0.9 | 26.9 ± 0.8 | 36 |
| -61.3 | 19.8 ± 0.6 | 18.8 ± 0.6 | 52 |
| -57.7 (T _c) | 12.7 ± 0.1 | 12.1 ± 0.1 | 81 |
| -49.3 | 9.5 ± 0.2 | 7.9 ± 0.2 | 116 |

$$^a \tau = \frac{\tau_a \tau_b}{\tau_a + \tau_b}, \quad ^b \text{ Standard error.}$$

which are required as part of the input data in the computer program. Instead, NMR spectra were digitized point by point as intensity vs. frequency in Hz. Digitization and computer-fitting of the spectra were accomplished as described earlier [24]. Partial data from the computer-fitted spectra are summarized in Table 2.

The order of the kinetics of environmental averaging of CH= protons in the phenylchlorogermanium and phenylchlorosilicon acetylacetonate complexes was ascertained by assessing the mean lifetimes at four or five different concentrations in the range: $(C_6H_5)_2ClGe(acac)_2$, 0.22 to 0.48 M; $(C_6H_5)_2ClSi(acac)_2$, 0.095 to 0.31 M.

Results and discussion

Stereochemistry

The six-coordinate nature of $RCISi(acac)_2$ ($R = CH_3$ and C_6H_5) is confirmed by infrared spectroscopic evidence; there are no carbonyl stretching bands above 1600 cm^{-1} indicating that both carbonyl oxygens are bound [25] to the central metal atom. Phenylchloro- and diphenyl-germanium acetylacetonate are also six-coordinate. Two diastereomeric forms are possible for these complexes; one diastereomer with the monodentate R, Cl ligands *cis* (point group C_1) the other with the R and Cl groups *trans* (C_{2v}) for $RCIM(acac)_2$ complexes. The diphenylgermanium complex may also afford *cis* (C_2) and *trans* (D_{2h}) isomers. Acetylacetonate terminal methyl groups in the C_1 -type compounds are symmetry nonequivalent and thus should give rise to four methyl proton resonances and two ring proton (CH=) signals in the NMR spectrum. The *trans* C_{2v} complexes should afford one acac-methyl and one CH= resonance are expected; the *cis*- $(C_6H_5)_2Ge(acac)_2$, two methyl signals and one CH= resonance are expected; the *trans* form should reveal only one CH₃ and one CH= NMR resonance. Variable temperature NMR spectra of the methyl and ring proton region for the phenylchlorogermanium complex are presented in Fig. 2; those for the silicon analogue are illustrated in Fig. 3. Observation at low temperatures of four methyl proton signals, (the low field doublet unresolved in Fig. 3 at the lowest accessible temperature, -80°) and two acetylacetonate ring proton resonances for both the phenylchlorogermanium and phenylchlorosilicon acetylacetonates is consistent with these complexes adopting the *cis* diastereomeric form. In

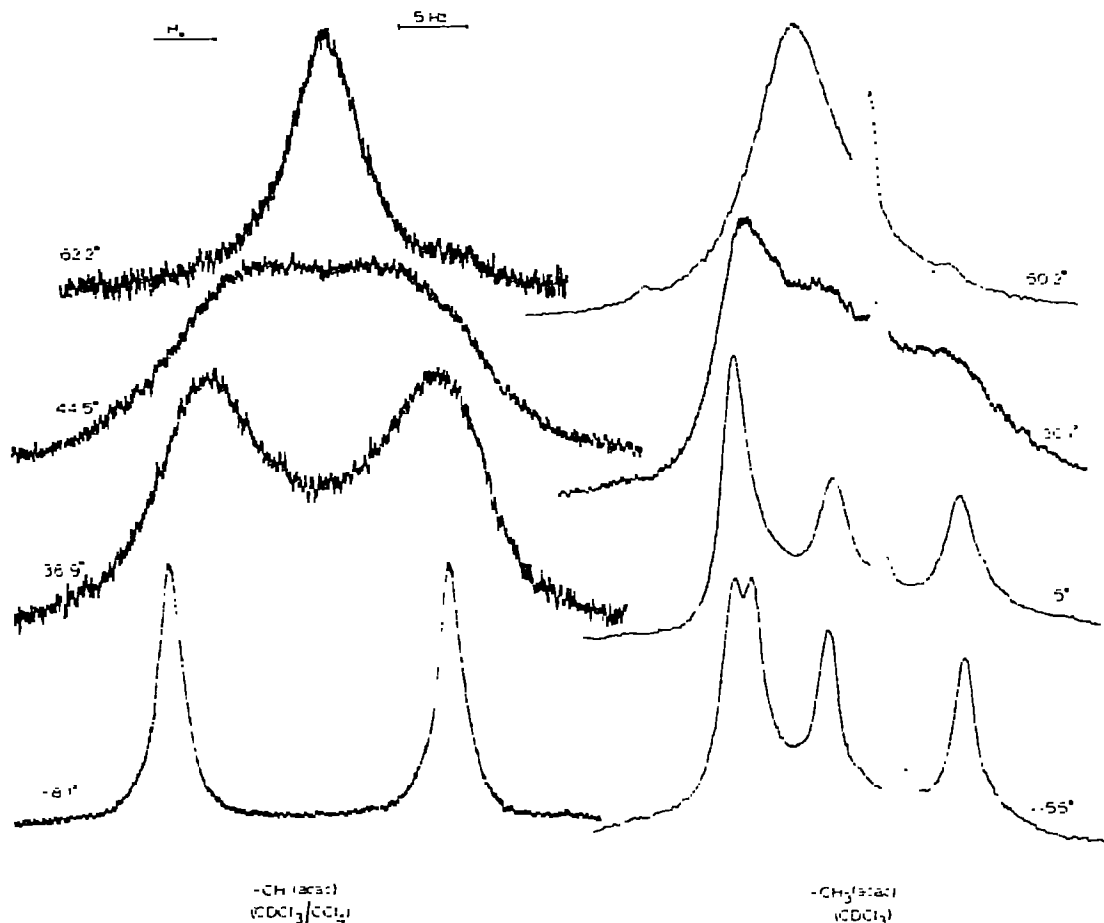


Fig. 2. NMR spectra for the acetylacetonate ring proton region (in $\text{CDCl}_3/\text{CCl}_4$) and methyl region (in CDCl_3) as a function of temperature for $\text{cis}-(\text{C}_6\text{H}_5)\text{ClGe}(\text{acac})_2$. Dashed lines refer to resonances attributed to the *trans* isomer (see text)

addition, a small, but perceptible resonance is likewise observed in the methyl and ring proton spectral regions. This signal (dashed line in Figs. 2 and 3) is attributed to a small amount ($\lesssim 5\%$) of the *trans*- $(\text{C}_6\text{H}_5)\text{ClM}(\text{acac})_2$ complexes [20].

Variable temperature NMR spectra of the methylchlorosilicon acetylacetonate complex in chloroform-*d*/carbon tetrachloride solution (0.457 *M*) reveal two methyl-proton signals (low field resonance more intense), and a single, broad line (linewidth 1.10 Hz at 28° , 3.95 Hz at -68° , and 7.45 Hz at -76°) for the ring proton $\text{CH}=\text{}$. These observations are also suggestive that the compound adopts the *cis* structure, at least at low temperatures. Our efforts with the diphenylgermanium complex proved less successful. Spectra (in $\text{CDCl}_3/\text{CCl}_4$; 0.243 *M*) revealed a single methyl ($W_{1/2} = 4.12$ Hz at -80.6°) and a single $\text{CH}=\text{}$ proton signal ($W_{1/2} = 3.90$ Hz at -80.6°). An unequivocal assignment of stereochemistry in solution is precluded by the above data; linewidths of CH_3 and $\text{CH}=\text{}$ proton resonances are nearly the same (for the *cis* isomer, one

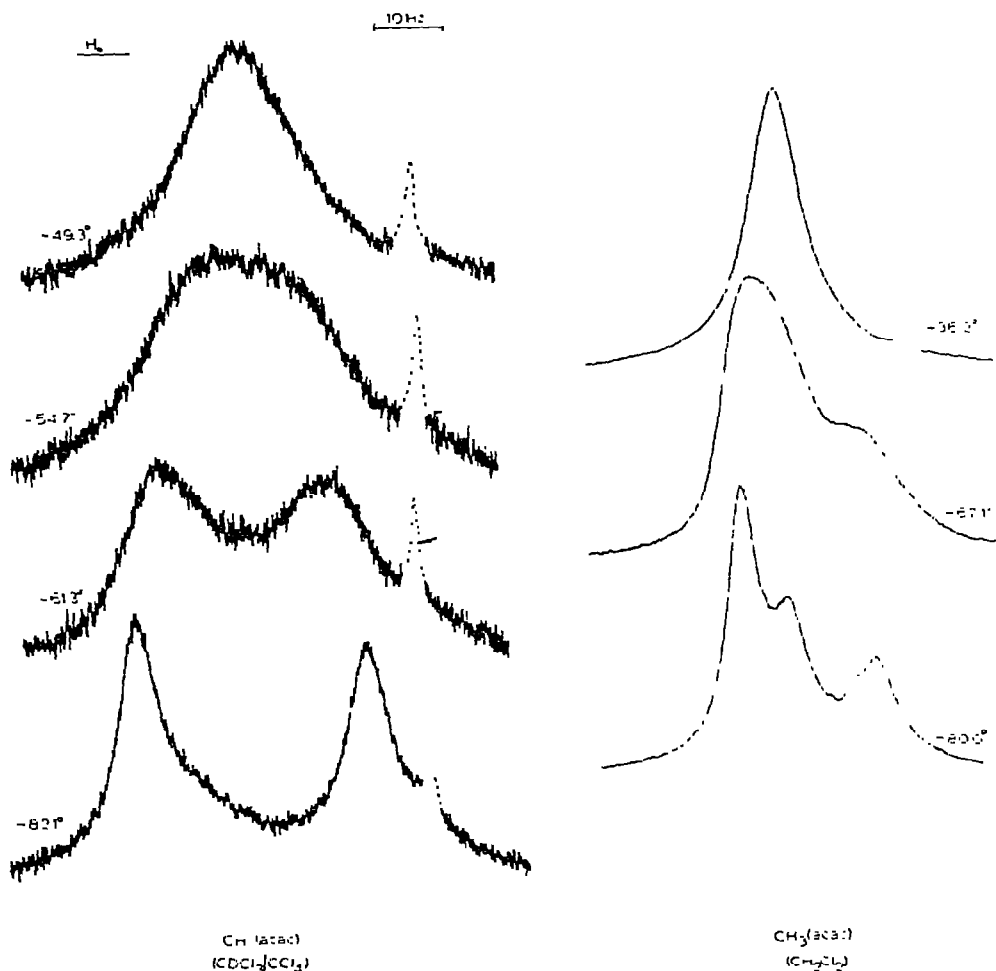


Fig. 3. NMR spectra for the acetylacetonate ring proton (in $\text{CDCl}_3/\text{CCl}_4$) and methyl proton region (in CH_2Cl_2) as a function of temperature for the *cis*-(C_6H_5) $_2\text{ClSi}(\text{acac})_2$ complex. Dashed lines refer to resonances attributed to a small amount of *trans* isomer (see text).

ring proton and two methyl signals are expected, as noted before). However, we believe that the complex probably exists in the *cis* form on the basis of the following evidence. The analogous diphenyltin complex is unequivocally *cis* in solution [26]. Further, phenylchlorogermanium acetylacetonate is more labile [2] (see below) than the corresponding tin complex. Thus, it is not unreasonable to expect that $(\text{C}_6\text{H}_5)_2\text{Ge}(\text{acac})_2$ be more labile than $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{acac})_2$. For the latter complex, T_c for methyl signals $\sim -40^\circ$ and $\delta\nu$ at -60° is about 3.5 Hz [20, 26]. It is not surprising then that coalescence behaviour for the germanium compound has not been observed.

Kinetics of environmental averaging

Broadening and collapse of the two acac ring proton resonances and the four methyl signals (Figs. 2 and 3) into single, sharp lines in the high temperature limit is attributed to an environmental averaging process which time-averages

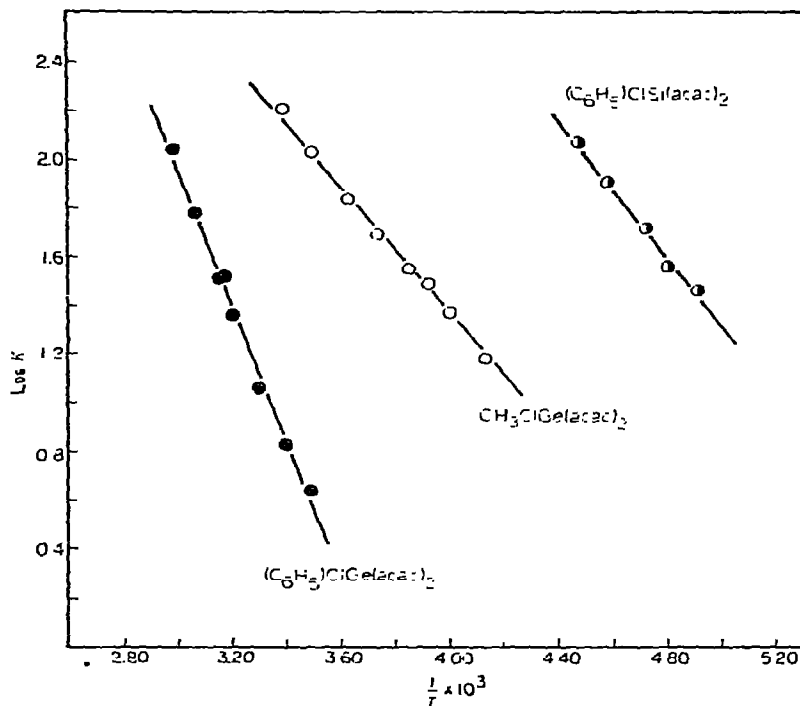


Fig. 4. $\log k$ versus $1/T$ least-squares plots for acetylacetonate ring proton exchange in $(C_6H_5)ClM(acac)_2$ ($M = Si, Ge$) and in $(CH_3)ClGe(acac)_2$ (see text) complexes. $k = (1/2 \tau)$ is the first-order rate constant for the environmental averaging process. For the methylchlorogermanium complex k refers to the second-order rate constant for exchange (cf. ref. 14).

the $CH=$ protons and methyl groups between two and four nonequivalent sites in the *cis* C_t isomer of the $(C_6H_5)ClM(acac)_2$ complexes. Description of the four-site exchange process in these compounds requires six, independent, first-order rate constants. However, owing to the temperature dependence of the transverse relaxation times T_2 , and to the complexity of the analysis of four-site exchange, we have chosen to investigate environmental averaging via line broadening of the acetylacetonate ring proton signals. To describe the latter exchange process requires only one first-order rate constant. Mean residence times, $\tau = \tau_a \tau_b / (\tau_a + \tau_b)$, for the phenylchlorogermanium complex (Table 1) were obtained from a comparison of the experimental spectra with spectra computed by the Gutowsky-Holm [21] equation (see experimental section). Lifetimes for the two-site process in $(C_6H_5)ClSi(acac)_2$ (Table 2) were obtained from a computer fit of the acac ring proton signals. Concentration dependence of the mean residence times demonstrates that the environmental averaging process is independent of concentration and is first order.

Arrhenius activation energy, E_a , and frequency factors, A , were obtained in the usual manner from the slope and intercept, respectively, of the least-squares straight line plots of $\log k$ versus $1/T$ (Fig. 4), where $k = (1/2 \tau)$ is the first-order rate constant for exchange. Entropies of activation, ΔS^\ddagger were obtained from the expression $\Delta S^\ddagger = R[\ln A - \ln RT/Nh] - R$. Arrhenius and Eyring activation parameters, along with values of k at 25° are tabulated in Table 3.

TABLE 3

ARRHENIUS AND EYRING ACTIVATION PARAMETERS AT 25° FOR ENVIRONMENTAL AVERAGING IN SOME (C₅H₅)ClM(acac)₂ COMPLEXES IN CDCl₃/CCl₄ SOLUTIONS

| Parameters | M = Ge | M = Si | M = Sn ^a |
|--------------------------------|-------------------------|-----------------------|---------------------|
| E_a (kcal/mol) | 12.8 ± 1.2 ^b | 6.4 ± 1.0 | 12.7 ± 2.0 |
| $\log \frac{A}{k}$ | 12.3 ± 0.8 | 8.3 ± 1.0 | 9.9 ± 1.4 |
| ΔH^\ddagger (kcal/mol) | 12.2 ± 1.2 | 5.8 ± 1.0 | 12.2 ± 2.0 |
| ΔS^\ddagger (eu) | -13 ± 4 | -22 ± 5 | -15 ± 6 |
| ΔG^\ddagger (kcal/mol) | 16.12 ± 0.07 | 12.5 ± 0.4 | 16.61 ± 0.12 |
| k (sec ⁻¹) | 9.4 | 4.2 × 10 ³ | 4.1 |
| T_c (°C) | 44.5 | -54.7 | 46.0 |

^a In CDCl₃ solutions [20]. ^b Random errors; estimated at the 95% confidence level.

Also included for comparison are values for the two-site exchange process in the phenylchlorotin acetylacetonate complex [20]. Of interest are some recent studies [13] on the dichlorogermanium dipivaloylmethanate complex in equimolar diphenylmethane/*m*-dimethoxybenzene solutions; $E_a = 25.2 \pm 1.4$ kcal/mol., $\Delta S^\ddagger = -1.1 \pm 3.0$ eu, and $k_{25} = 3 \times 10^{-6}$ sec⁻¹.

Owing to the temperature dependence of the transverse relaxation times throughout the temperature range at which kinetic data are reported, values of the activation parameters of Table 3 for the organogermanium and organosilicon chelates may be subject to some appreciable systematic errors. These have been discussed elsewhere [20]. Suffice it to note here that the error limits in the activation parameters (Table 3) represent the random scatter of the data points in Fig. 4, which illustrates $\log k$ versus $1/T$ least-squares plots for the (C₆H₅)ClM(acac)₂ (M = Ge, Si) and for (CH₃)ClGe(acac)₂ chelates. Environmental averaging studies on the latter complex will be reported in a subsequent publication [14]. Also, it may be noted that a reasonable uncertainty in T_2 may lead to systematic errors of the order of ± 1 kcal/mol in the energy of activation and ± 4 eu in the activation entropy [22].

Some features of Table 3 are noteworthy. The rate of environmental averaging of CH= protons in the organo-germanium, -silicon, and -tin complexes increases as the metal varies in the order Sn \approx Ge \ll Si. The energy of activation varies according to Sn \approx Ge \gg Si, E_a for (C₆H₅)ClSi(acac)₂ being about 6 kcal/mol lower than that of the corresponding germanium and tin complexes. This is unexpected if the rearrangement process occurs via a metal-oxygen bond rupture mechanism (vide infra) since metal-oxygen bond strength increases (for gaseous diatomic molecules) in the order Sn-O (125 kcal/mol) < Ge-O (157 kcal/mol) < Si-O (188 kcal/mol) [27]. Of significance is the energy of activation (25.4 \pm 1.4 kcal/mol) in the environmental averaging of terminal *t*-butyl groups in the complex Cl₂Ge(dpm)₂, where the favored mechanism for the rearrangement process was rupture of a germanium-oxygen bond* [13].

* Although the complexes Cl₂Ge(dpm)₂ and (C₆H₅)ClGe(acac)₂ have been investigated in different solvents, diphenylmethane/*m*-dimethoxybenzene versus chloroform-*d*/carbon tetrachloride, respectively, solvent effects are not expected to contribute more than ~ 1 -2 kcal/mol to E_a [cf. ref. 28]. Also, the nature of β -diketonate ligand, dpm vs. acac does not appear to have significance in the value of E_a [cf. ref. 13].

Further, as noted elsewhere for the tin complexes [20], replacement of a chloro group in the dichlorogermanium complex by an aryl or an alkyl [14] group appears to have a dramatic influence on the stereochemical nonrigidity of these germanium chelates ($3 \times 10^{-6} \text{ sec}^{-1}$ for the dichloro complex; 9.4 sec^{-1} for phenylchlorogermanium acetylacetonate). The difference of ca. 12-13 kcal/mol in the two complexes may probably be ascribed to different mechanisms for the exchange process.

Mechanism of environmental averaging

Before discussing the possible pathways which may lead to environmental averaging of the particular groups mentioned earlier, it should be noted, as evidenced in Figs. 2 and 3, that whatever the mechanism(s) both CH= protons and terminal acetylacetonate methyl groups are exchanged amongst their respective sites by the same physical pathway(s). Several paths have been presented and discussed in some detail [29]. Among these are (1) complete dissociation of a bidentate ligand to produce a four-coordinate intermediate, (2) dissociation of a monodentate ligand to yield a five-coordinate intermediate, (3) twisting of opposite triangular faces in the octahedral framework to give idealized trigonal prismatic (TP) transition states, and (4) rupture of a M—O bond resulting in trigonal bipyramidal (TBP) transition state(s) with an axial or equatorial dangling ligand, or in square pyramidal (SP) transition states with a basal or axial dangling ligand.

Without reviewing arguments presented earlier [30] both pathways (1) and (2) are considered unlikely processes in the complexes reported here. In the case of the organotin(IV) acetylacetonates, it was argued [30] that if rearrangements proceeded via a sole reaction pathway, averaging of CH= proton and methyl group environments most likely occurs through twisting motions about the various four threefold axes. Evidence was presented to support this contention. As noted above and in Table 3, the energy of activation for the rearrangement process in the phenylchlorosilicon(IV) complex is much lower by ca. 6 kcal/mol than in the analogous tin and germanium chelates, and is not in keeping with the order of metal—oxygen bond strengths (vide supra). Moreover, the very large activation energy (25.3 kcal/mol) found for rearrangements in $\text{Cl}_2\text{Ge}(\text{dpm})_2$ as opposed to the value obtained (12.8 kcal/mol) for $(\text{C}_6\text{H}_5)\text{-ClGe}(\text{acac})_2$ is suggestive of a different mechanism(s) for environmental averaging in the two instances. In the former complex, evidence has been presented in support of a bond rupture path [13]. Also, observation of resonances attributable to the *trans* form of these $\text{RCIM}(\text{acac})_2$ complexes before, during, and after coalescence precludes involvement of the *trans* form in the rearrangement processes. We therefore conclude that time-averaging of CH= proton and methyl group environments in the complexes reported here (Table 3) also proceeds through twist motions as described earlier [30]. Unfortunately, pathways involving TBP and SP transition states cannot be unequivocally precluded.

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