PART I
A NOVEL STEREOCHEMICAL REARRANGEMENT PROCESS FOR AN ISOMER OF TRIMETHYLSILICON ACETYLACETONATE, A SILYL ENOL ETHER
PART II
DYNAMIC STEREOCHEMICAL PROPERTIES OF SOME CYCLOPENTADIENYLZIRCONIUM β-DIKETONATE COMPLEXES

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This is to certify that the

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PART I. A NOVEL STEREOCHEMICAL REARRANGEMENT PROCESS FOR AN ISOMER OF TRIMETHYLSILICON ACETYLACETONATE, A SILYL ENOL ETHER

PART II. DYNAMIC STEREOCHEMICAL PROPERTIES OF SOME CYCLOPENTADIENYLZIRCONIUM β-DIKETONATE COMPLEXES

presented by

Jerry J. Howe

has been accepted towards fulfillment
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Major professor

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ABSTRACT

PART I

A NOVEL STEREOCHEMICAL REARRANGEMENT PROCESS FOR AN ISOMER OF TRIMETHYLSILICON ACETYLACETONATE, A SILYL ENOL ETHER

By

Jerry J. Howe

Trimethylsilicon acetylacetonate has been prepared from trimethylchlorosilane and acetylacetone as described in the literature.[1] Nuclear magnetic resonance studies of trimethylsilicon acetylacetonate show that the compound possesses an open-chain enol ether structure which gives rise to configurations in which the uncoordinated carbonyl oxygen atom is positioned either cis or trans to the siloxy group. In chlorobenzene at room temperature the equilibrium value of the [cis]/[trans] ratio is equal to 0.33. The cis isomer undergoes a rapid, intramolecular rearrangement process at room temperature which interchanges the nonequivalent allylic and acetyl methyl groups on the acetylacetonate ligand. First-order rate constants for the stereochemical rearrangement of the cis isomer in chlorobenzene solution were determined by proton nmr line-broadening techniques over the temperature range -36.2 to 38.4°. The values of the Arrhenius activation energy and frequency factor are 13.8 $\pm$ 0.5 kcal/mol and exp(13.05 $\pm$ 0.54), respectively. The trans isomer of trimethylsilicon acetylacetonate is stereochemically rigid at temperatures even as high as 120°. The difference in lability is

attributed to the ease of formation of a five-coordinated silicon intermediate or transition state. Comparison of cis-$(CH_3)_3Si(acac)$ with the relative rearrangement rates of the cis-$R(CH_3)_2Si(acac)$ series (R = n-C_4H_9, C_2H_5, CH_2=CH, $CF_3CH_2CH_2$, and C_6H_5) plus cis-$(C_6H_6)_2(CH_3)Si(acac)$ supports a mechanism involving a pentacoordinate silicon intermediate or transition state.

PART II

DYNAMIC STEREOCHEMICAL PROPERTIES OF SOME CYCLOPENTADIENYLZIRCONIUM β-DIKETONATE COMPLEXES

The eight-coordinate complex $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$, where dpm = dipivaloylmethanate, exists in solution on the basis of an octahedron in which the π-C_5H_5 ring occupies one stereochemical position, the chlorine atom is positioned cis to the ring, and the oxygen atoms of the diketonate ligands occupy the remaining coordination sites. At elevated temperatures, the compound undergoes a kinetically first-order stereochemical rearrangement process which interchanges the nonequivalent environments of the diketonate ligands. The rate of ligand interchange is determined by nmr line-broadening techniques. Since the rate is found to be comparable to the rates of stereochemical rearrangement for analogous acetylacetonate complexes, the steric requirements of the terminal groups on the diketonate ligands are not an important factor in the activation process.

An ionic complex, $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$, has been prepared. The cation possesses a configuration based on a trigonal bipyramid in which the π-C_5H_5 ring occupies an axial vertex and the oxygen atoms

of the diketonate ligands are positioned at the remaining coordination sites. At room temperature, the nonequivalent diketonate ligands are rapidly interchanged on the nmr time scale.

Tris(β-diketonato)-π-cyclopentadienylzirconium complexes, which possess a stereochemistry based on a pentagonal bipyramid in which the center of the cyclopentadienyl ring occupies an axial vertex, undergo two distinct types of stereochemical rearrangement processes. The faster process (process I) interchanges the nonequivalent environments of the terminal groups on the equatorial diketonate ligands, and the slower process (process II) exchanges the equatorial ligands with the unique ligand spanning an equatorial-axial edge. An intramolecular mechanism operates in process I and first-order rate constants have been determined by nmr line-broadening techniques. In the $(\pi\text{-}C_5H_5)Zr(dik)_3$ series, the lability increases in the order dpm < hfac < acac. Process II has been studied for the hexafluoroacetylacetonate and acetylacetonate derivatives, $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and $(\pi\text{-}C_5H_5)Zr(acac)_3$, with the latter complex being more labile. Plausible mechanisms are discussed for both processes.

1. R. West, J. Amer. Chem. Soc., 80, 3246 (1958).

PART I

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PART II

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By

Jerry J. Howe

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To Jennifer

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I would like to extend my appreciation to Dr. Thomas J. Pinnavaia for his interest, guidance, probing discussions, and patience during this investigation.

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TABLE OF CONTENTS

PART I

PART II

LIST OF TABLES

LIST OF FIGURES

PART I

I. INTRODUCTION

In spite of the extensive research on organometallic compounds of silicon, only a few investigations of silicon β-diketonates have been reported. Most of the recent investigations have been concerned with the structure and reactivity of these compounds. A brief yet comprehensive review of work in this area of silicon chemistry has been provided by Pike.[2]

The silicon β-diketonates can be divided into three classes of compounds: (1) tris chelated silicon compounds containing the hexacoordinate siliconium ion, $Si(dik)_3^+$ (dik = β-diketonate), and a suitable anion;[1,3,4] (2) hexacoordinate molecular compounds of the general formula $Si(dik)_2XY$ (X = Cl, Y = alkyl;[1] or X = Y = Cl,[5] alkyl,[1] acetoxy[6]); and (3) four-coordinate enol ethers of the general formula $R_3Si(dik)$ (R = alkyl, C_6H_5).[1,8,9]

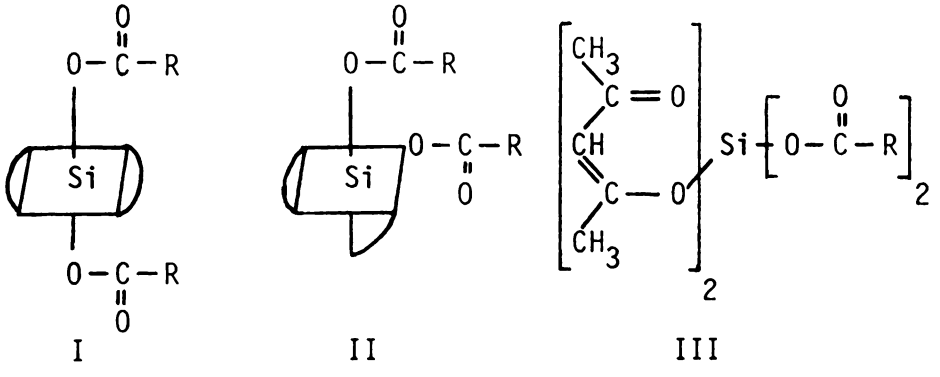
The first silicon acetylacetonates were prepared by Dilthey[3] in 1903. From the reaction of silicon tetrachloride with acetylacetone, Dilthey isolated a solid product which he postulated had the ionic formula $(C_5H_7O_2)_3Si^+ HCl_2^-$. Salts of several other β-diketonates and anions were isolated and characterized by Dilthey and much later by Muetterties and Wright.[4] The assigned octahedral geometry has been established by ir spectroscopy,[1] partial resolution of the optical isomers,[10] and nmr spectroscopy.[11] In general, the reaction between a silicon tetrahalide and a β-diketone gives tris-substituted ionic compounds.

An apparent exception to this reaction has recently been reported by D. W. Thompson.[5] The reaction of equimolar quantities of acetylacetone and silicon tetrachloride in methylene chloride solution gave a solid product with the formula $Si(C_5H_7O_2)_2Cl_2$. The chelated nature of the β-diketonate ligands was indicated by the ir spectrum. The compound was insoluble in nonpolar organic solvents and only very sparingly soluble in nitrobenzene, nitromethane, methylene chloride, acetonitrile, and chloroform. In solution the compound apparently disproportionated according to the reaction

$$3Si(C_5H_7O_2)_2Cl_2 \rightarrow 2Si(C_5H_7O_2)_3Cl + SiCl_4.$$

Both the nmr and ir solution spectra of $Si(C_5H_7O_2)_2Cl_2$ indicated the presence of a $Si(C_5H_7O_2)_2Cl_2$ - $Si(C_5H_7O_2)_3Cl$ mixture. However, the nmr spectrum of $Si(C_5H_7O_2)_2Cl_2$ did not provide conclusive evidence for a cis or trans octahedral geometry. The number of nmr peaks, one $-CH_3$ and one -CH= peak, indicated a trans configuration, but the chemical shift of the -CH= proton suggested a cis-octahedral or ionic structure for $Si(C_5H_7O_2)_2Cl_2$. The very limited solubility and apparent disproportionation in solution precluded any conclusive studies, and the exact nature of $Si(C_5H_7O_2)_2Cl_2$ is yet to be determined.

Pike and Luongo[6] found that when organocarboxysilanes are allowed to react with a β-diketone, neutral hexacoordinate silicon derivatives were formed (I and II).

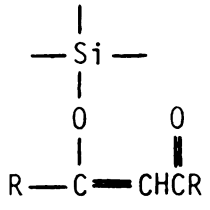


I II III

The proposed structures were based on ir, ultraviolet, and nmr data along with mono- and bidentate ligand exchange reactions. In a fresh solution only the trans structure was initially observed but it slowly isomerized to the cis isomer until an equilibrium [cis]/[trans] value of 1.6 was attained. It is of interest to point out that an intermediate of the reaction was isolable if the reaction was carried out at 5°. On the basis of ir data, structure III was assigned to the compound. The ir spectrum showed no absorptions indicative of bidentate chelation of acetylacetone. When the intermediate was heated, compounds I and II were obtained.

Two features common to most of the above compounds are (1) the bidentate nature of the β-diketonate ligand and (2) ground-state structures in which silicon achieves a coordination number of six. However, silyl enolates of the type $R_3Si(acac)$[1,8,9] or $R_2Si(acac)_2$[1] result when organosilicon halides are used in place of $SiCl_4$. In these compounds the silicon atom is bonded to only one donor oxygen atom of the acetylacetonate ligand. The uncoordinated or "dangling" oxygen atom is ketonic.

West[1] and Knoth[9] independently prepared a series of trialkyl silicon enol ethers (IV) by the reaction of a β-diketone with a

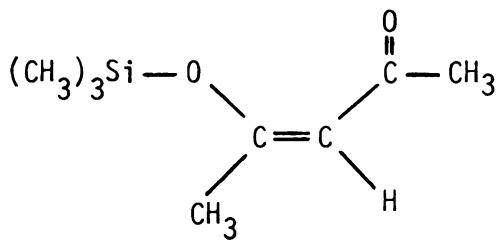


IV

trialkylchlorosilane. The identification of the enol ether structure was based on ir data. West showed that chelated silicon diketonates exhibit a carbonyl stretching vibration near 1555 cm^{-1}. In silyl enol

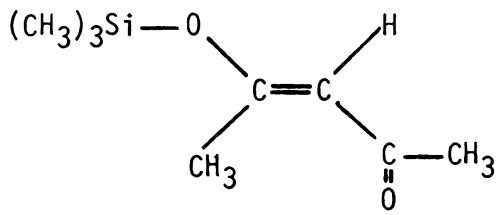
ethers the ketonic carbonyl stretching frequency is found near 1670 cm^{-1}, and a C=C stretching frequency occurs near 1590 cm^{-1}. The identification of these latter frequencies was based on a comparison with the spectrum of 2-ethoxy-2-pentene-4-one, and organo enol ether of acetylacetone. Both monodentate and bidentate kiketonates of silicon also exhibit a strong ir band in the 1010 - 1040 cm^{-1} region which was attributed to the Si-O stretching vibration.

Knoth[9] postulated cis-trans isomerism for $(CH_3)_3Si(acac)$. It was suggested that the isomers (V and VI) exist in equilibrium based on



cis

V



trans

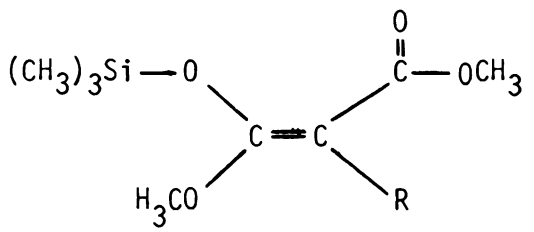
VI

the coincidence of the ir spectrum of $(CH_3)_3Si(acac)$ with the analogous isomers of 2-methoxy-2-pentene-4-one. Three facts concerning 2-methoxy-2-pentene-4-one[12] are worth noting: (1) the pure cis and trans isomers could be isolated, (2) the equilibrated methyl enol ether was almost pure trans isomer, and (3) starting with the pure cis isomer, equilibrium was reached in eight days at ambient conditions and in three hours at 100°. However, Knoth was unable to verify his postulate by isolating the isomers of $(CH_3)_3Si(acac)$.

This research was undertaken to characterize $(CH_3)_3Si(acac)$ by nmr spectroscopy. The existence of the enol ether structure and an equilibrium mixture of cis and trans-$(CH_3)_3Si(acac)$ have been confirmed. Of primary interest, however, was the discovery of a stereochemical rearrangement for the cis isomer which interchanges the nonequivalent

environments of the methyl groups on the acetylacetonate moiety. Mechanisms which are consistent with the kinetic data have been proposed.

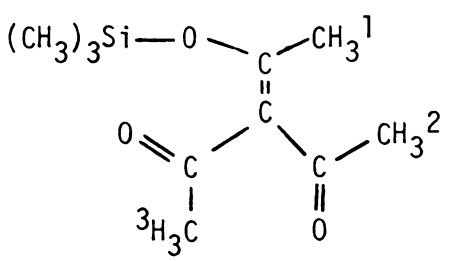
Subsequent to our report of the dynamic properties of cis-$(CH_3)_3Si(acac)$, two very recent articles by Ainsworth[13] and Shvo[35] have appeared which suggest that rearrangements occur for related compounds. Ainsworth reports that the cis isomers of several ketene methyl trimethylsilyl acetals, $R(CH_3O_2)C{=}C(OCH_3)OSi(CH_3)_3$ (R = H, CH_3, C_6H_5) (VII) interchange CH_3O environments. He based his conclusions



VII

on the presence of only one CH_3O signal in the nmr spectrum. Also, when R = CO_2CH_3, all three signals were equivalent. Apparently, the presence of a CO_2CH_3 group at the α position causes rapid rotation about the C=C bond at room temperature. It should be stated, however, that cooling the solution of the R = CO_2CH_3 derivative to -40° failed to show the expected three methyl lines of equal intensity.

Shvo[35] has found that the trimethylsilyl enol ether of triacetylmethane (VIII) also exhibits fluctional behavior. At room temperature



VIII

methyl groups 1 and 3 are being interchanged. At 178° the coalesced

peak of methyl groups 1 and 3 coalesces with the peak of methyl group 2. The latter process must involve rotation about the C=C bond. Activation free energies of 15.4 $\pm$ 0.5 kcal/mol and 24.3 $\pm$ 0.5 kcal/mol were determined at the coalescence temperatures for the two processes.

The work of Ainsworth[13] and Shvo[35] complement the results presented in Part I of this thesis.

II. EXPERIMENTAL

A. Reagents and Solvents

Trimethylchlorosilane was obtained from the Chemical Research Department of the Dow Corning Corporation. It was fractionally distilled in a dry N_2 atmosphere before use (bp 56°), and its purity was checked by nmr spectroscopy.

Matheson, Coleman, and Bell white label acetylacetone was freshly distilled in a N_2 atmosphere before use (bp 136-140°).

The hexane, carbon tetrachloride, benzene, chlorobenzene and methylene chloride solvents were Fisher Certified, A.C.S. chemicals and were dried by refluxing them over calcium hydride for at least 48 hrs.

Fisher Reagent grade chloroform was purified by treatment with activated alumina.

Baker Analyzed Reagent grade pyridine was freshly distilled from Drierite prior to use.

Fisher Certified, A.C.S. nitrobenzene was purified by distilling it under vacuum from over P_2O_5. The distilled nitrobenzene was allowed to stand over Linde Type 5A molecular sieves for two days and then redistilled under vacuum from the molecular sieves. Only one fraction of nitrobenzene was collected, bp 50-53° (ca. 0.5 torr).

B. Synthesis of 2-Trimethylsiloxy-2-pentene-4-one

2-Trimethylsiloxy-2-pentene-4-one was prepared and purified according to the general method described by West.[1] In an atmosphere

of dry N_2, 54 g (0.50 mol) trimethylchlorosilane was slowly added to a stirred mixture of 40 g (0.50 mol) pyridine and 51 g (0.50 mol) acetylacetone in 200 ml hexane. The mixture was heated at reflux temperature for 5 hr and then permitted to cool to room temperature. Pyridinium chloride was removed from the reaction mixture by filtration, dried in vacuo at room temperature for several hours, and identified from its ir spectrum. Hexane was removed from the mother liquor under reduced pressure at room temperature. The resultant $(CH_3)_3Si(acac)$ was purified by vacuum distillation through a 30-cm Vigreux column to give 25 g (29% yield) of the colorless liquid. Bp = 66-68° (4 torr), $n_D^{23.6}$ = 1.4507; lit.[1] bp = 66-68° (4 torr), n_D^{25} = 1.4546.

Anal. Calcd for $SiC_8H_{16}O_2$: Si, 16.30; C, 55.77; H, 9.39; mol wt, 172. Found: Si, 16.51; C, 55.70; H, 9.21; mol wt ($C_6N_5NO_2$), 184.

C. Analytical Data

Microanalysis of $(CH_3)_3Si(acac)$ was performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

D. Index of Refraction

The index of refraction of $(CH_3)_3Si(acac)$ was measured on a Bausch and Lomb ABBE-3L refractometer equipped with a constant temperature bath.

E. Molecular Weight Determination

The molecular weight of $(CH_3)_3Si(acac)$ was determined cryoscopically in purified nitrobenzene. Recrystallized benzil was used as the calibrating solute in the determination of the molal freezing point depression constant of nitrobenzene (5.88°/m). Freezing point depressions were measured in the concentration range 0.034 to 0.448 m

with a Beckman differential thermometer graduated at intervals of 0.01°. Temperature readings, however, were estimated to ±0.001° with the aid of a magnifying thermometer reader.

F. Vapor Phase Chromatography

Attempts were made to separate the cis and trans isomers of $(CH_3)_3Si(acac)$ on a dual-column F & M Model 810 gas chromatograph equipped with a thermal conductivity detector cell. The column dimensions and packings were as follows: 4 ft X 1/4 in., 10% silmethylene on Chromosorb W; 6 ft X 1/4 in., FS 1265 fluorosilicone gum on an unknown Chromosorb; 6 ft X 1/4 in., SE-30 silicon rubber on Chromosorb W. Numerous chromatograms were obtained under isothermal and temperature-programmed column conditions in the temperature range 100-300°. In all cases no separation of the two isomers was observed. Attempts to separate the isomers on a 20-ft Carbowax column at 150-180° with an Aerograph A 90-P3 chromatograph were also unsuccessful.

G. Infrared Spectra

Infrared spectra were determined either as nujol mulls or as neat liquids between KBr salt plates on a Unicam SP.200 ir spectrophotometer. The 2851 and 1603 cm^{-1} peaks of polystyrene were used as reference frequencies.

H. Nuclear Magnetic Resonance Spectra

Proton magnetic resonance spectra were obtained with a Varian A56/60D analytical spectrometer operated at 60.000 MHz. The probe temperature was controlled to ±0.5° with a Varian Model V-6040 temperature controller. Temperatures were determined by measuring the chemical shift differences between the proton resonances of methanol or

ethylene glycol and applying the equations of Van Geet.[14] Magnetic field sweep widths were calibrated by the audio-frequency side-band technique. At least three spectral copies were averaged in the determination of line-shape parameters and chemical shift values in order to reduce any error caused by variations in the field sweep. All spectra were recorded at a radiofrequency field strength well below the value necessary to observe saturation. Chemical shifts were measured by using tetramethylsilane as an internal standard.

The double resonance experiment was performed on a Varian HA100 analytical spectrometer operated at 100.000 MHz.

I. Preparation of Solutions

All solutions used in the nmr studies were prepared in a nitrogen-filled glove bag and sealed in nmr tubes which had been previously dried at 150° and cooled in a calcium sulfate desiccator. All solvents were carefully dried as previously described. Despite these precautions to avoid hydrolysis, small amounts (2-3%) of free acetylacetone and $[(CH_3)_3Si]_2O$ could be detected in the nmr spectrum of the solutions after they had aged several days at room temperature. Presumably, $(CH_3)_3Si(acac)$ undergoes slow reaction with hydroxyl groups or strongly bound water on the surface of the glass nmr tubes. The rates of stereochemical rearrangement of the cis isomer, however, showed no dependence on the concentration of hydrolysis products.

J. Computer Computations

A CDC 3600 computer of the Michigan State University Computer Laboratory was used for linear least squares and theoretical nmr spectral calculations. The nmr spectra were calculated from the

Rogers-Woodbrey modification[15] of the Gutowsky-Holm equation[16] as 100 or more coordinate points spaced in intervals of 0.1 Hz. Both computer programs are listed in the Appendix.

III. RESULTS AND DISCUSSION

A. Preparation Chemistry

Trimethylsilicon acetylacetonate is readily obtained from the reaction

$$(CH_3)_3SiCl + H(acac) + py \xrightarrow[\text{hexane}]{\Delta} (CH_3)_3Si(acac) + [pyH]Cl$$

as described by West.[1] The [pyH]Cl byproduct can be separated from the reaction mixture by filtration. $(CH_3)_3Si(acac)$ is a colorless liquid and is isolated by fractional distillation at 4 torr pressure. $(CH_3)_3Si(acac)$ undergoes hydrolysis on contact with atmospheric moisture and slow thermal decomposition at elevated temperatures.

B. Characterization of Trimethylsilicon Acetylacetonate

The experimental molecular weight of $(CH_3)_3Si(acac)$ was found to be 184 *vs.* a theoretical value of 172. Therefore, the compound is monomeric in nitrobenzene solution.

Infrared vibrational frequencies of the acetylacetonate ligand $\nu_{C=O}$ (1684, 1659 cm^{-1}), $\nu_{C=C}$ (1588, 1625 cm^{-1}) and ν_{Si-O} (1032 cm^{-1}) are in agreement with the reported values.[1] The absence of the bidentate vibrational frequency $\nu_{C=O}$ at 1555 cm^{-1} verifies the previously assigned enol ether structure. If the acetylacetonate ligand were C-silylated, ν_{Si-O} would be absent.[17]

Nuclear magnetic resonance spectroscopy confirms the existence of an equilibrium mixture of *cis* (V) and *trans* (VI) enol ether isomers for $(CH_3)_3Si(acac)$. The lines observed in the nmr spectrum of the

compound at room temperature are shown in Figure 1. The acetylacetonate moiety gives rise to a -CH= proton multiplet at τ 4.40, a -CH= singlet at τ 4.75, two methyl doublets at τ 7.70 and 8.01 and a methyl singlet at τ 8.08. Two partially resolved Si-CH_3 lines are present near τ 9.82. As the temperature is decreased the methyl line at τ 8.08 broadens markedly and then splits into two rather sharp lines (see Figure 2). At -53.7°, the two Si-CH_3 lines are completely resolved, and the two -CH= lines remain essentially as observed at room temperature. The presence of two -CH= and two Si-CH_3 lines indicates that the $(CH_3)_3Si(acac)$ molecule occurs in two geometric forms. Furthermore, the line broadening phenomenon shows that one of the isomers undergoes a rapid configurational rearrangement process which averages two nonequivalent acetylacetonate methyl group environments.

The lines at τ 4.40, 7.70, and 8.01 in the room-temperature spectrum have relative integral intensities of 1:3:3 and, along with the more intense Si-CH_3 line, are assigned to the trans isomer VI. A double-resonance experiment, illustrated in Figure 3, has shown that the two types of methyl protons are both coupled to the vinylic proton but not to each other. The temperature dependence of the coupling constants, 0.6 and 0.4 Hz at 38.6° vs. 0.45 and less than 0.3 Hz at -53.7°, respectively, is probably due to shifts in the equilibrium distribution of methyl group rotamers.

The line at τ 4.75 and the time-averaged methyl line at τ 8.08 of the labile isomer have relative integral intensities of 1:6. These lines and the less intense Si-CH_3 line are assigned to the cis isomer V. In the absence of rapid acetylacetonate methyl group exchange at -53.7°, some coupling (ca. 0.5) is observed between the vinylic proton and the acetylacetonate methyl group which appears at higher

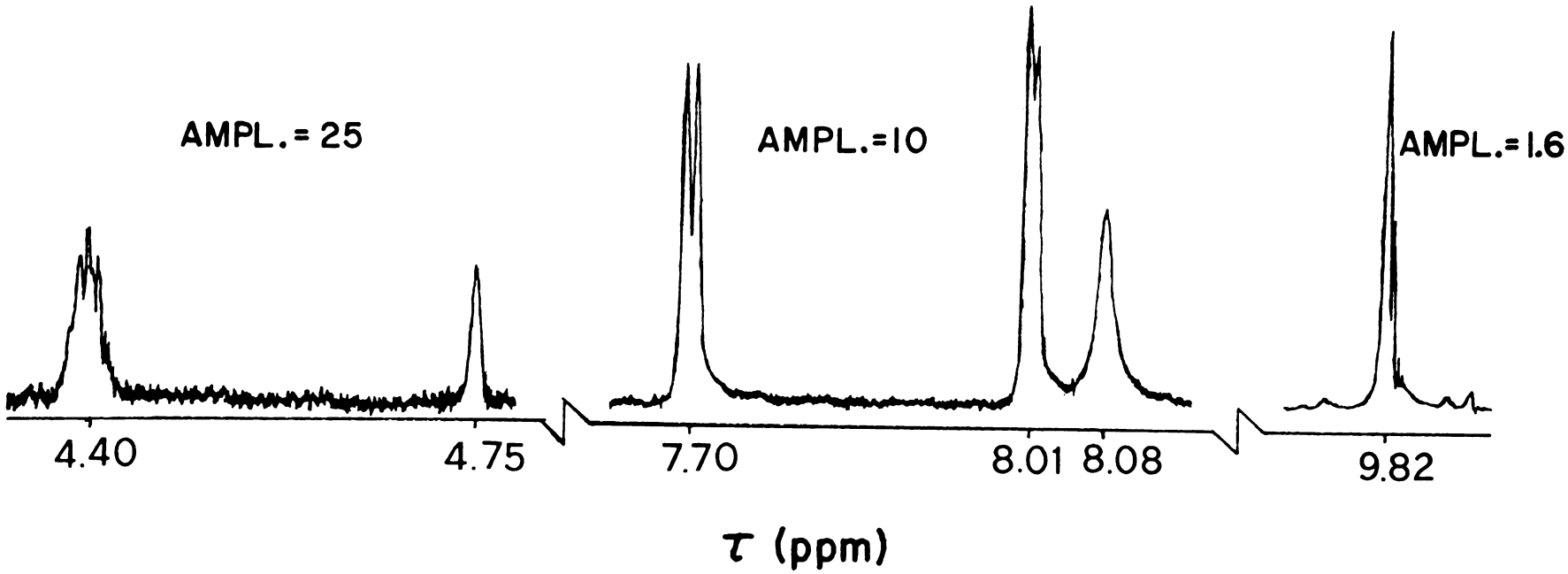


Figure 1. Proton nmr spectrum of $(CH_3)_3Si(acac)$ in chlorobenzene solution at 38.5° (60 MHz); concentration 11.4 g/100 ml of solvent.

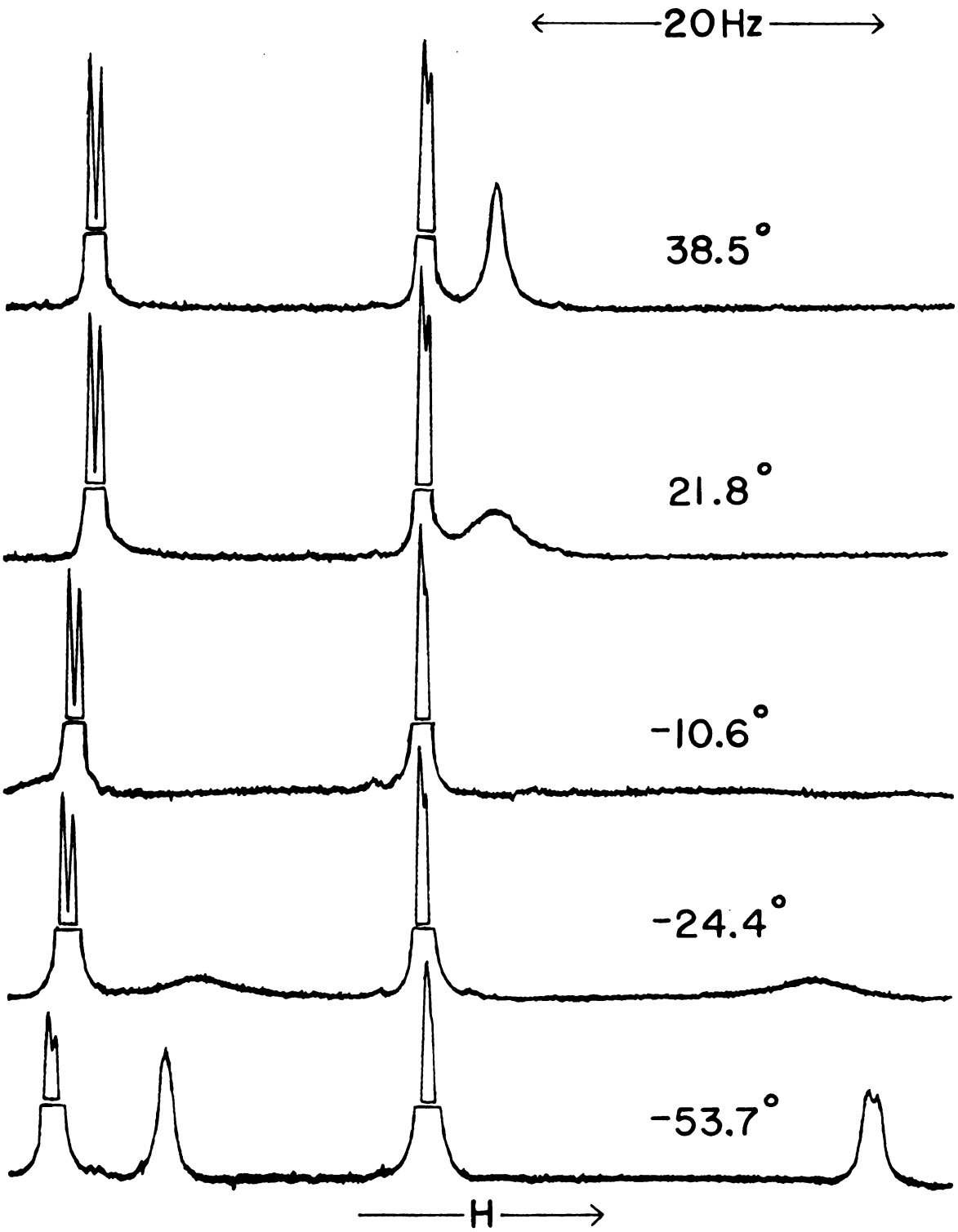


Figure 2. Temperature dependence of the acetylacetonate methyl proton resonance lines of $(CH_3)_3Si(acac)$; concentration 11.4 g/100 ml of chlorobenzene.

Figure 3. Spin-spin decoupling of trans-$(CH_3)_3Si(acac)$. A. The spectrum at 100.0 MHz. B. Irradiation of the sample at the -CH= frequency. C. Irradiation of the sample at the $=CCH_3$ frequency. D. Irradiation of the sample at the $COCH_3$ frequency. The concentration of the solution is 11.4 g/100 ml of chlorobenzene.

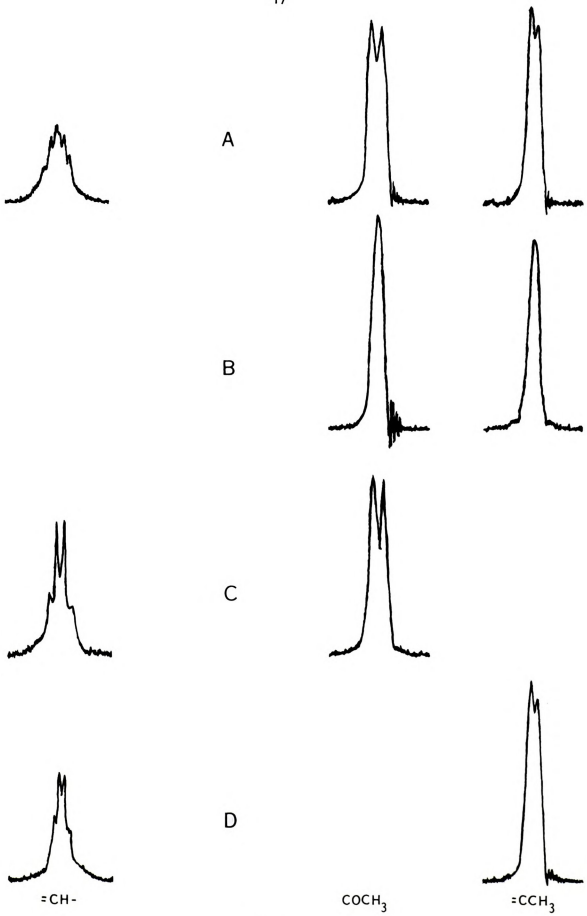


Figure 3.

field (cf. Figure 2). The magnitude of the coupling constants for both the cis and trans isomers is in very good agreement with those previously reported for certain β-dicarbonyls.[18]

Chemical shifts in carbon tetrachloride, benzene, chloroform, and methylene chloride, and as the neat liquid for the acetylacetonate and Si-CH_3 protons of $(CH_3)_3Si(acac)$ are collected in Table I; shifts for $(C_6H_5)(CH_3)_2Si(acac)$ and $(C_6H_5)_2(CH_3)Si(acac)$ in carbon tetrachloride are included for comparison. No significant concentration dependence was observed for $(CH_3)_3Si(acac)$ in carbon tetrachloride over the range 3.0-20.0 g/100 ml of solvent. Since some concentration dependence was found in benzene, the shifts in this solvent were extrapolated to infinite dilution. The concentration dependence of the chemical shifts in chloroform and methylene chloride was not investigated. In each trans isomer the magnitude of the coupling between the -CH= and $COCH_3$ protons is $\sim$ 0.6 Hz, and the allylic coupling constant is 0.4 Hz or less. It is to be noted that the relative chemical shifts for the $COCH_3$ and $=CCH_3$ protons of the trans isomer are not in agreement with the empirical "ene-one" rule of Anteunis and Schamp[19] for assigning chemical shifts of similar types of protons in β-diketone enol ethers. The "ene-one" rule states that for organic compounds of the type

the "ene" protons (R-C=) resonate at lower field than the same protons in the "one" position (COR). However, at least three pieces of evidence can be cited in support of the assignments made here. (1) Replacement of alkyl groups on silicon by phenyl groups leads to 0.09-0.14 ppm upfield shifts for the $=CCH_3$ protons, whereas the $COCH_3$ and -CH= protons

Table I. Proton Chemical Shift Data for cis- and trans-Triorganosilicon Acetylacetonates.[a]

Compound	Solvent	trans isomer				cis isomer		
		-CH=	$COCH_3$	$=CCH_3$	$SiCH_3$	-CH=	CH_3[b]	$SiCH_3$
$(CH_3)_3Si(acac)$	CCl_4	4.53	7.82	8.00	9.74	4.81	8.03	9.74
	$CHCl_3$	4.41	7.73	7.88	9.68	4.73	7.88	9.71
	CH_2Cl_2	4.41	7.77	7.93	9.69	4.79	7.93	9.73
	C_6H_6[c]	4.45	7.63	8.10	9.95	4.74	8.22	9.95
	d	4.41	7.81	8.00	9.74	4.81	8.03	9.67
$(C_6H_5)(CH_3)_2Si(acac)$	CCl_4[e]	4.57	7.82	8.09	9.51	4.83	8.09	9.47
$(C_6H_5)_2(CH_3)Si(acac)$	CCl_4[e]	4.53	7.77	8.14	9.26	4.81	8.11	9.22

[a]All shifts reported as τ (ppm) values; temperature is 40°; concentration is 10 g/100 ml of solvent unless otherwise noted. [b]Time-averaged acetylacetonate resonance. [c]All shifts in benzene are extrapolated to infinite dilution. [d]Neat liquid. [e]Reference 8.

show little or no change in chemical shift. An examination of molecular models of the trans phenylsilyl derivatives reveals that reasonable configurations are possible in which the $=CCH_3$ protons are within the diamagnetic cone of a phenyl group, but that configurations which can lead to upfield shifts for the $COCH_3$ protons without also appreciably influencing the chemical shifts of the -CH= protons are unlikely. (2) The upfield shifts for the $Si-CH_3$ protons of both cis- and trans-$(CH_3)_3Si(acac)$ in benzene solution show that these protons experience the diamagnetic anisotropy of the benzene ring to a greater extent than the internal TMS reference. Apparently, a stereospecific solvent-solute association results from the interaction of the π-electrons on benzene and the siloxy group. Indeed, similar stereospecific interactions between benzene and a variety of other types of solute molecules are well known.[20] Such an interaction should be expected to lead to upfield shifts for the $=CCH_3$ protons, which is indeed the result observed for the trans isomer. (3) For $(CH_3)_3Si(acac)$ in dichloromethane solution at -40°, where the $COCH_3$ and $=CCH_3$ resonances of the cis isomer are well resolved, the $=CCH_3$ and $COCH_3$ protons of the trans isomer are deshielded by 0.12 ppm and shielded by 0.04 ppm, respectively, relative to the analogous protons of the cis isomer. Deshielding of the $=CCH_3$ protons in the trans isomer is expected because of the paramagnetic anisotropic effect of the adjacent $COCH_3$ group.[21] Finally, it might be mentioned that for $(CH_3)_3Si(acac)$ at -40°, the magnitude of the allylic coupling is slightly greater in the cis isomer ($\sim$ 0.5 Hz) than in the trans isomer ($<$ 0.3 Hz). Under the same conditions, the long-range coupling between the -CH= and $COCH_3$ protons is smaller in the cis isomer ($\sim$ 0.0 Hz) than is the trans isomer ($\sim$ 0.5 Hz). The relative magnitudes of the allylic systems, viz., that cisoid coupling is slightly larger than

transoid coupling.[22] The coupling constants alone, however, would not constitute a reliable basis for the chemical shift assignments, because no relationship exists between allylic coupling constants and the stereochemistry of related α,β-unsaturated esters.[23]

Several unsuccessful attempts to separate the cis and trans isomers of $(CH_3)_3Si(acac)$ by gas chromatography (cf. Experimental Section) or by vacuum distillation at 68° through a spinning band column suggest that equilibrium is established readily between the two isomers. Facile isomerization is further supported by the fact that a freshly distilled sample contained the same ratio of isomers as a sample that had aged 6 months at room temperature. Also, after 12 hr. at 120° the cis-to-trans ratio (0.38 ± 0.04) was equal, within the 95% confidence level estimated error, to the ratio observed at room temperature (0.34 ± 0.04). Both the sample aged at room temperature and the sample heated at 120° should be at equilibrium because the cis methyl enol ether of acetylacetone is known to undergo conversion to "pure" trans isomer within 8 days at ambient temperature and within 3 hr. at 100°.[12] Thus, solutions of the compound in chlorobenzene were assumed to be at equilibrium after one week at room temperature, and the cis-to-trans ratio, shown in Table II, was determined by planimetric integration of -CH= nmr lines. Other triorganosilicon acetylacetonates are included for comparison. With the exception of the phenylsilyl derivatives, the equilibrium amount of cis isomer increases with increasing electron-withdrawing ability of the substituents on silicon. This relationship between the cis-to-trans ratios and the polarity of the silicon substituents suggests that a long-range electrostatic interaction may exist between silicon and the dangling carbonyl oxygen atom in the cis isomers. Such an interaction would also account, in part, for the

Table II. Equilibrium Ratio of *cis*-to-*trans* Enol Ether Isomers for Triorganosilicon Acetylacetonates.[a]

Compound	[*cis*]/[*trans*]
$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$	0.28[b] ± 0.02[c]
$(C_2H_5)(CH_3)_2Si(acac)$	0.29 ± 0.02
$(CH_3)_3Si(acac)$	0.34 ± 0.04
$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$	0.39 ± 0.03
$(CH_2{=}CH)(CH_3)_2Si(acac)$	0.38 ± 0.02
$(C_6H_5)(CH_3)_2Si(acac)$	0.31 ± 0.02
$(C_6H_5)_2(CH_3)Si(acac)$	0.25 ± 0.02

[a]In chlorobenzene solution at room temperature; concentration is 0.60 *m*. Compounds other than $(CH_3)_3Si(acac)$ from Reference 8. [b]All values are averages of five spectral copies. [c]Errors are estimated at the 95% confidence level.

enhanced stability of these cis-triorganosilicon acetylacetonates relative to the cis form of the methyl enol ether of acetylacetone. The cis-to-trans ratios for $(C_6H_5)(CH_3)_2Si(acac)$ and $(C_6H_5)_2(CH_3)Si(acac)$ are lower than expected on the basis of inductive effects, but steric factors and ligand → metal $p\pi$-$d\pi$ bonding could weaken the long-range silicon-oxygen interaction in the cis isomers of these derivatives.[8]

It is noteworthy that a ground-state stereochemistry based on a trigonal bipyramid in which acetylacetonate acts as a bidentate ligand and spans an axial-equatorial edge cannot be assigned in place of the cis isomer. A trigonal-bipyramidal structure of this type should give rise to two Si-CH_3 lines in the absence of exchange. However, only one sharp Si-CH_3 resonance line is observed for the labile isomer at -53.7°, which is the result predicted for the cis enol ether structure.

The ability of the cis isomer to undergo rapid rearrangement which leads to environmental averaging of nonequivalent acetylacetonate methyl groups is attributed to the facile formation of a five-coordinated silicon intermediate. Five-coordinated silicon intermediates have also been postulated by Pike[6b] and Ainsworth.[13] Two possible mechanisms for the rearrangement process are illustrated in Schemes I and II, Figure 4.

In Scheme I, the five-coordinate silicon intermediate possesses either a trigonal bipyramidal or a square pyramidal geometry in which both Si-O bonds are equivalent. This equivalence dictates equal probability for the rupture of either Si-O bond therefore permitting the environmental interchange of the two methyl acetylacetonate groups.

Scheme II also utilizes a trigonal bipyramidal intermediate; however, the acetylacetonate ligand now spans an axial-equatorial edge. This is in accordance with two "preference" rules for trigonal bipyramidal

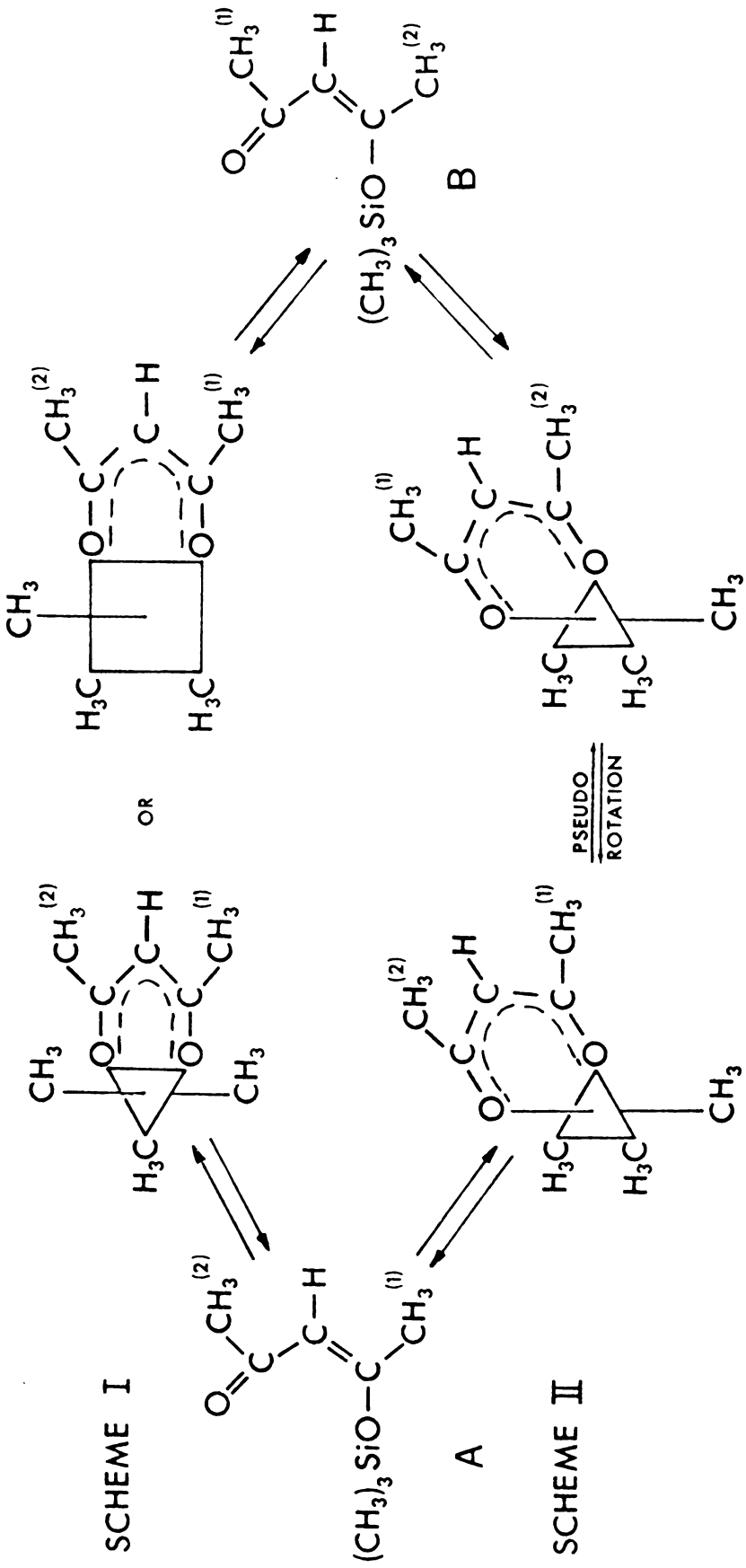


Figure 4. Mechanisms which would account for the exchange of the nonequivalent acetylacetonate methyl groups in cis-$(CH_3)_3Si(acac)$

phosphorus molecules. Muetterties et al.[28] have observed that the more electronegative ligand will preferentially occupy the axial positions, and they have rationalized this on the basis of more ionic character in an axial bond than in an equatorial bond. Secondly, five-membered chelates preferentially tend to span an axial-equatorial edge rather than an equatorial-equatorial edge of the trigonal bipyramid.[29,30] In Scheme II the Si-O bonds of the intermediate are no longer equivalent and hence the bond rupture step is no longer equally probable for both Si-O bonds. Instead, bond rupture of the same Si-O bond as was initially formed in the formation of the trigonal bipyramidal intermediate from the four-coordinate ground state should predominate. In order to interchange the nonequivalent methyl acetylacetonate groups utilizing the intermediate of C_s symmetry in Scheme II, the intermediate itself must undergo psuedo rotation analogous to that of certain five-coordinate phosphorus compounds.[28-34] In addition to its being necessary to explain the observed rearrangement, it is totally permissible according to the second preference rule.

It should also be mentioned that the rule of microscopic reversibility does not require pseudo rotation in Scheme II. Although not as aesthetically pleasing as pseudo rotation, initial formation of an axial Si-O bond and subsequent rupture of an equatorial Si-O bond would successfully interchange the methyl groups of the acetylacetonate ligand.

Since the more common ground state for five-coordinate compounds is a trigonal bipyramid, and also since bridging of an axial-equatorial edge would seem preferable by analogy to phosphorus chemistry, it is easy to emphasize Scheme II more than Scheme I. However, no experimental data for the $(CH_3)_3Si(acac)$ system permit the elimination of either Scheme I or Scheme II.

A similar process for the trans isomer should be more hindered by the additional energy needed for rotation about the C=C bond. Even though Ainsworth[13] and Shvo[35] have reported examples of apparent rapid rotation about the C=C bond in some silyl derivatives, such rotation was not observed in $(CH_3)_3Si(acac)$. Indeed broadening of the acetylacetonate methyl lines for the trans isomer was not observed even at 120°, a temperature at which the rate of rearrangement of the cis isomer is very fast. This subject will be further discussed in relation to the kinetic parameters for cis-$(CH_3)_3Si(acac)$ which follow.

Both Schemes I and II have formally been depicted as forming intermediates during the rearrangement reaction. It should be clearly stated, however, that only Scheme II, with its pseudo-rotation mechanism, must formally involve an intermediate. The mechanism shown in Scheme I could also be formulated as involving a transition state instead of an intermediate. The transition states would possess the same geometries as the intermediates of Scheme I, but would formally involve the simultaneous formation and rupture of the respective Si-O bonds.

Eaborn[37] has addressed the question of an intermediate versus a transition state in reactions of tetravalent silicon, and has reached the following conclusions pertinent to this discussion:

(1) The d-orbitals of silicon are used in a reaction with a nucleophilic reagent.

(2) A pentacoordinated-silicon intermediate probably results from the use of the d-orbitals of silicon.

(3) Even if an intermediate is not formed, the use of d-orbitals facilitates nucleophilic attack by lowering the energy of the transition state.

(4) However, there is no direct evidence that a pentacoordinated intermediate is involved in substitution at the silicon atom.

Likewise, the data for $(CH_3)_3Si(acac)$ are insufficient to conclude either the presence or absence of an intermediate. However, the inability to detect the intermediate does not preclude its existence, and therefore the terms transition state and intermediate are used interchangeably in the following discussions.

C. Kinetic Study of Trimethylsilicon Acetylacetonate

In chlorobenzene solution below -40°, the interchange of the nonequivalent acetylacetonate methyl groups in cis-$(CH_3)_3Si(acac)$ is sufficiently slow to observe two well-resolved methyl proton resonance lines. Above -40° the two lines broaden and merge into a very broad line, which then sharpens above the coalescence temperature (see Figure 2). The temperature dependence of the half-widths at half maximum amplitude for the $COCH_3$ resonance below the coalescence temperature and for the time-averaged acetylacetonate methyl resonance above coalescence is shown in Figure 5, curves A and B, respectively. Accurate line widths could not be determined in the region near the coalescence temperature, because the lines were very broad and partially obscured by the acetylacetonate methyl resonances of the trans isomer.

Gutowsky and Holm[16] have shown that the mean lifetime, τ_A and τ_B, of protons exchanging between two nonequivalent sites can be determined from the nmr line shapes if $\delta\nu$, the frequency separation between the resonance components in the absence of exchange, and T_2, the transverse relaxation time, are known. The mean lifetimes are related to the quantity τ by $\tau = \tau_A\tau_B/(\tau_A + \tau_B)$. Since the two nonequivalent sites in the system considered here are equally populated, $\tau_A = \tau_B = 2\tau$.

Figure 5. Temperature dependence of nmr line-shape parameters for the acetylacetonate methyl protons of cis-$(CH_3)_3Si(acac)$ in chlorobenzene: curve A, line width of the $COCH_3$ resonance; curve B, line width of the time-averaged methyl resonance; curve C, frequency separation between the resonance components, $\delta\nu$. Curve D shows the temperature dependence of $\delta\nu$ for trans-$(CH_3)_3Si(acac)$.

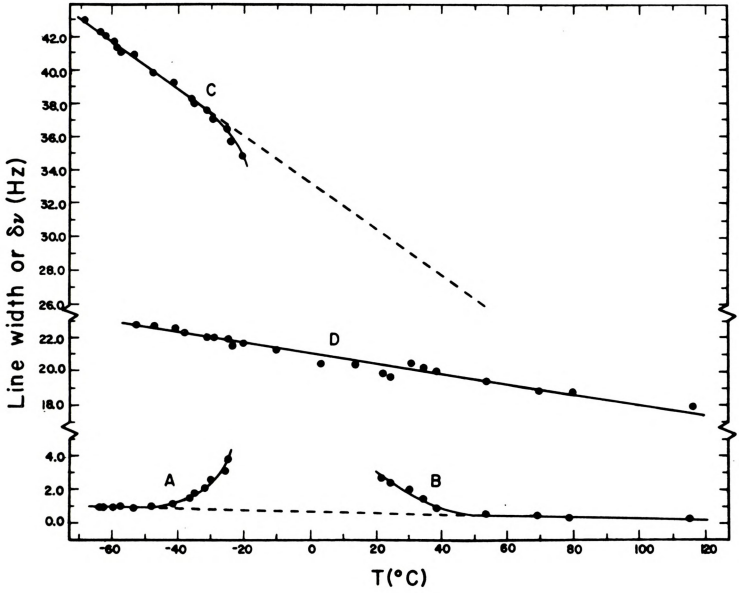


Figure 5.

In the region of slow exchange (below -40°), $\delta\nu$ for cis-$(CH_3)_3Si(acac)$ is temperature-dependent, presumably, because of temperature-dependent solvation effects. Since the line widths of both the uncoupled $COCH_3$ resonance in the region of slow exchange and the time-averaged resonance in the region of fast exchange (above 50°) vary with temperature, T_2 is also temperature dependent. The temperature dependence for $\delta\nu$ and T_2 is analogous to the behavior found previously for the non-equivalent methyl protons in chelated metal acetylacetonates.[24,25] Values of $\delta\nu$ in the region of exchange (-36.2 to 38.4°) were obtained by linear extrapolation of data in the region of slow exchange, as shown in Figure 5C. The validity of such an extrapolation is supported by the linear temperature dependence of $\delta\nu$ for the stereochemically rigid trans isomer over the same temperature region (Figure 5D). Similarly, values of T_2 in the region of exchange were determined from the extrapolated values of the line widths (cf. Figure 5, the dashed line connecting curves A and B). The relaxation times of the $-CCH_3$ protons below coalescence, where they are slightly coupled to the -CH= proton, were assumed to be equal to the relaxation times found for the $COCH_3$ protons.

Values of τ for cis-$(CH_3)_3Si(acac)$ in the region of exchange below the coalescence temperature were determined by comparing the observed width at half maximum amplitude of the uncoupled $COCH_3$ resonance with the width calculated from the Gutowsky-Holm equation for various trial values of τ. Although the small coupling between the -CH= and $-CCH_3$ protons below coalescence was not included in the calculated spectra, the error generated in the computer values of τ is estimated to be only $\sim$ 2%. This error was estimated from τ values for which T_2 was calculated from the total width of the coupled peaks. Above the

coalescence temperature τ was determined by comparing the observed and computed widths of the time-averaged resonance line. The reliability of this line-shape method of analysis was checked by plotting several randomly selected coordinate points of the computer calculated spectra on the experimental spectra at one temperature above (21.8°C) and one temperature below (-31.7°C) the coalescence temperature (see Figure 6). The line widths, extrapolated values of $\delta\nu$, and the computed values of τ in the region of exchange are collected in Table III. A plot of log k vs. 1/T, where $k = (2\tau)^{-1}$, is shown in Figure 7. Within experimental error, the slopes of the best straight lines through the sets of data points above and below the coalescence temperature are equal. Linear least-squares treatment of all 11 data points gave an Arrhenius activation energy and frequency factor of 13.8 $\pm$ 0.5 kcal/mol and exp (13.05 $\pm$ 0.54), respectively, and an extrapolated value of 851 sec^{-1} for the first-order rate constant at 25°. The errors in the activation parameters are estimated at the 95% confidence level. An activation entropy of -0.8 $\pm$ 2.5 eu at 25° was calculated from the frequency factor by assuming that the Eyring equation holds.

No change in mean lifetimes was observed on doubling the solute concentration in chlorobenzene. Also, a solution containing $(CH_3)_3Si(acac)$ and free acetylacetone in relative amounts 3:1 showed no broadening of the free ligand methyl line under conditions where rearrangement of the cis isomer is fast. These results, which indicate that the rearrangement is first order and that an intramolecular mechanism operates, are in agreement with the processes shown in Schemes I and II, Figure 4.

At selected temperatures, Collins[8] has determined first-order rate constants in chlorobenzene solution for the stereochemical

Figure 6. Comparison of theoretical and experimental spectra. A. -31.7° and τ = .127. B. 21.8° and τ = .000691. The solid lines represent the experimental spectra, and the solid dots are random coordinate points of the computer calculated spectra.

Table III. Nmr Line-Shape Parameters and Kinetic Data for cis-$(CH_3)_3Si(acac)$.[a]

Temp, °C	Line width,[b] Hz	δν, Hz	10^3 τ, sec
-36.2	1.57	38.27	276
-35.5	1.82	38.17	194
-31.7	2.17	37.62	137
-29.8	2.68	37.35	96.4
-25.4	3.10	36.72	77.6
-24.4	3.91	36.57	56.7
21.8	2.72	29.84	0.691
24.2	2.45	29.60	0.618
30.3	2.09	28.72	0.525
34.2	1.54	28.16	0.351
38.4	0.98	27.56	0.146

[a]In chlorobenzene solution; concentration is 0.60 m. [b]Widths below coalescence (-36.2 to -24.4°) refer to the uncoupled $COCH_3$ resonance component; above coalescence (21.8 to 38.4°) the widths are for the time-averaged acetylacetonate methyl resonance line.

Figure 7. Log k *vs.* 1/T plot for *cis*-$(CH_3)_3Si(acac)$ in chlorobenzene solution.

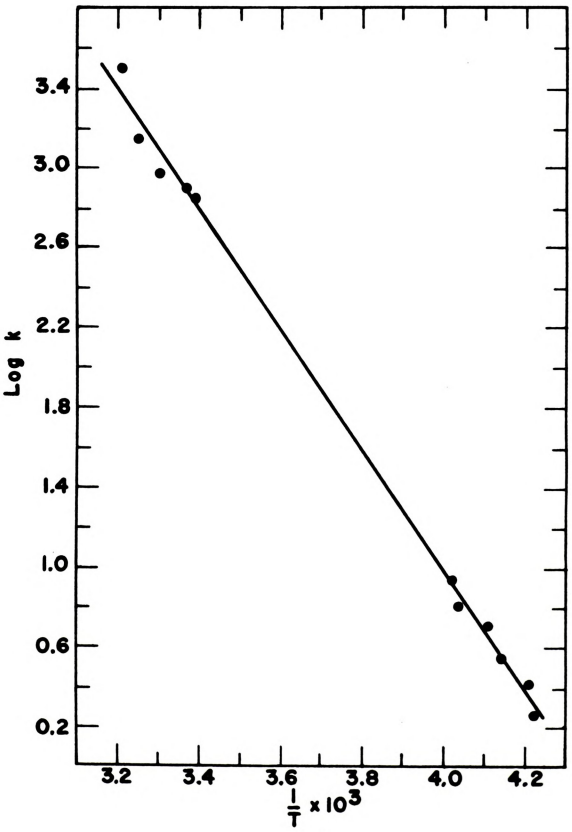


Figure 7.

rearrangement of other cis-triorganosilicon acetylacetonates by using procedures analogous to those described above for cis-$(CH_3)_3Si(acac)$. In the determination of the mean lifetimes, the transverse relaxation times were assumed to be equal to those obtained for cis-$(CH_3)_3Si(acac)$. This latter assumption is supported by the fact that each cis isomer exhibited a time-averaged line width in the limit of fast exchange which was equal to the line width found for cis-$(CH_3)_3Si(acac)$ under similar conditions. Values of the first-order rate constants are shown in Table IV, along with values of the Arrhenius activation energies which were calculated from the first-order rate constants by assuming that the frequency factor is equal to the value obtained for cis-$(CH_3)_3Si(acac)$.

From the combined data on cis-$(CH_3)_3Si(acac)$ and the work by Collins, it may be concluded that there is a general increase in the rate of acetylacetonate methyl group exchange with increasing polarity of the substituents on silicon. For the cis-$R(CH_3)_2Si(acac)$ compounds, the rate increases in the order R = n-C_4H_9 < C_2H_5 < CH_3 < CH_2=CH, C_6H_5 < $CF_3CH_2CH_2$, and the lability of cis-$(C_6H_5)_2(CH_3)Si(acac)$ is comparable to that of $(CF_3CH_2CH_2)(CH_3)_2Si(acac)$. The dependence of the rates on the polarity of the silicon substituents is also consistent with a mechanism involving formation of a five-coordinated silicon intermediate or transition state such as illustrated in Schemes I and II, Figure 4. Although several factors contribute to the energy required for such a bond-making activation process, as the electron-withdrawing ability of the substituents is increased, the resulting increase in positive charge on silicon should facilitate the use of a metal d orbital in achieving the transition state.[26] Relative to the alkyl-substituted silicon derivatives, the phenylsilyl derivatives are less labile than might be expected on the basis of σ inductive effects.

Table IV. Kinetic Data for Acetylacetonate Methyl Group Exchange in *cis*-Triorganosilicon Acetylacetonates.[a]

Compound	Temp.,[b] °C	k, sec^{-1}	E_a kcal/mol
(*n*-C_4H_9)$(CH_3)_2$Si(acac)	-23.3	5.35 ± 0.16[c]	14.1
(C_2H_5)$(CH_3)_2$Si(acac)	-23.3	5.96 ± 0.10	14.0
$(CH_3)_3$Si(acac)	-23.3	9.51[d]	13.8
	-12.7	29.5[d]	13.8
	0.7	108[d]	
(CH_2=CH)$(CH_3)_2$Si(acac)	0.7	500 ± 30	13.0
(C_6H_5)$(CH_3)_2$Si(acac)	-12.7	>91.9, <300	<13.2, >12.6
($CF_3CH_2CH_2$)$(CH_3)_2$Si(acac)	-12.7	621 ± 118	12.2

[a]In chlorobenzene solution; total concentration of R_3Si(acac) is 0.60 *m*. [b]Temperature at which k was determined. [c]Basis for estimates of error are described in Reference 8. [d]Extrapolated value from Arrhenius plot. [e]Results other than those for $(CH_3)_3$Si(acac) are from Reference 8.

Similar rearrangement phenomena with other diketonate or pseudo-diketonate ligands have been observed.[8,13,35] Unfortunately, those studies are not detailed enough to permit a quantitative comparison to the cis-$(CH_3)_3Si$(acac) results.

Collins[8] reports that the 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfac) and 2,2,6,6-tetramethyl-3,5-heptanedione (dpm) derivatives of $(CH_3)_3Si$(dik) exist solely as the trans and cis isomers, respectively. He rationalizes the cis-trans distribution by the relative long-range interaction of the nonbonded carbonyl oxygen atoms in the two ligands. The relative negative charges on the free carbonyl oxygen atoms, based on inductive effects, would be hfac < acac < dpm. Hence, if only the cis isomers are capable of interaction between the silicon and nonbonded carbonyl oxygen atoms, the cis-trans distributions are rational. Finally, Collins states that even at temperatures as low as -95°C, cis-$(CH_3)_3Si$(dpm) undergoes a very fast stereochemical rearrangement process analogous to that of cis-$(CH_3)_3Si$(acac).

Ainsworth's data[13] for several ketene methyl trimethylsilyl acetals suggest stereochemical rearrangements, but they are insufficient to permit even a qualitative comparison with the present work.

Shvo[35] found a free energy of activation (15.4 $\pm$ 0.5 kcal/mol) for the analogous process in the triacetylmethane derivative. This value is to be compared with an Arrhenius activation energy of 13.8 $\pm$ 0.5 kcal/mol for the similar process in cis-$(CH_3)_3Si$(acac). The parameters E_a and $\Delta G^{\ddagger}$ are related through $\Delta H^{\ddagger}$ by the equations

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S$$

and

$$E_a = \Delta H^{\ddagger} + RT.^{38}$$

Therefore, for the rearrangement process of cis-$(CH_3)_3Si(acac)$, $E_a \approx \Delta G^{\ddagger}$ since $\Delta S_{25°}$ is essentially zero (-0.8 ± 2.5 eu) and RT at 25° is very small (0.6 kcal/mol). The Taft constant for the acetyl group ($\sigma^* = 0.874$[39]) indicates that the acetyl moiety functions as an electron-withdrawing substituent relative to the hydrogen atom. Therefore, the cis ketonic oxygen atom of the triacetylmethanate derivative would be less nucleophilic than the analogous oxygen atom of the acetylacetonate compound, and would account for the higher activation energy of the triacetylmethanate enol ether if bond-making is an important step in the activation process. However, the experimental technique and the basis for the ±0.5 kcal/mol uncertainty are inadequately described for the triacetylmethanate complex, and the error inherrent in such a determination of $\Delta G^{\ddagger}$ from a single experimental temperature prohibit placing any significance on the absolute difference between the activation energies.

In conclusion, all data support the mechanisms proposed in this work and suggest that a bond-making process is an important step in the stereochemical rearrangement of these compounds.

PART II

I. INTRODUCTION

The history of β-diketonate coordination can be traced back to 1894 with the preparation of $Be(C_5H_7O_2)_2$.[40] Since then the growth of this area of organometallic chemistry has been phenomenal. Compounds containing acetylacetone and other β-diketones as ligands are known for almost every metallic or semi-metallic element. Activity in this area continues to be very brisk, as verified by the appearance of six review articles[2,40-44] in the last six years.

The organometallic chemistry of cyclopentadiene began shortly after the arrival of the twentieth century with the preparation of potassium cyclopentadienide from cyclopentadiene and potassium metal.[45] Although other group IA and IIA cyclopentadienides were prepared subsequently, the current interest in metal derivatives of cyclopentadiene stems from the independent discovery of ferrocene by Kealy and Pauson,[46] and Miller, Tebboth and Tremaine[47] in 1951. Since the synthesis and characterization of ferrocene, cyclopentadiene derivatives have been prepared for almost every transition and post-transition metal. Interest has been so keen that individual investigators have found it nearly impossible to review the entire field, but the reviews of several authors[48-51] do provide a good overview of the area.

It was inevitable that the areas of β-diketonate and cyclopentadienyl organometallic chemistry would soon meet. In 1956 Thomas[52] prepared a chromium compound of the formula $C_5H_5Cr(C_5H_7O_2)Br$. The compound was

obtained in 3% yield by the reaction of chromium(III) acetylacetonate and cyclopentadienylmagnesium bromide. Thomas suggested that an entire class of compounds of this type should exist. However, not until 1961 was another example of a cyclopentadienylmetal β-diketonate reported.

Brainina and her coworkers[53] prepared chlorobis(2,4-pentanedionato)cyclopentadienylzirconium, $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$, by the reaction of zirconocene dichloride and the neat diketone and, also, by the metathesis reaction of $Zr(acac)_2Cl_2$ and $Na(C_5H_5)$ in tetrahydrofuran. Additional means of preparation which were discovered later by Brainina[54,55] involve a redistribution reaction between $(\pi\text{-}C_5H_5)_2ZrCl_2$ and $Zr(acac)_4$, and the reaction of $[(\pi\text{-}C_5H_5)ZrCl_2]_2O$ or $(\pi\text{-}C_5H_5)Zr(OC_2H_5)_2Cl$ and the neat diketone. The reaction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ and H(acac) is preferred as the experimental technique is simple and the product is obtained in high yield. All of Brainina's synthetic methods, however, have been used[56,58,61,65] to prepare a variety of cyclopentadienylzirconium β-diketonate complexes of the general type $(\pi\text{-}C_5H_4R)Zr(dik)_2X$, where R may be H, CH_3, or tert-C_4H_9, and X = Cl, Br, or $OCOCH_3$. Similar hafnium derivatives have also been prepared by analogous procedures.[58,61] More recently, Newton[62] has modified Brainina's original method for the preparation of $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ by carrying out the reaction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ and H(acac) in the presence of triethylamine. The addition of a base apparently represents a significant improvement as the method is applicable to a wider variety of diketonate derivatives including tropolonate. Newton has also succeeded in preparing the first cyclopentadienyltitanium derivative, $(\pi\text{-}C_5H_5)Ti(acac)_2Cl$. A hexafluoroacetylacetonate complex, $(\pi\text{-}C_5H_5)Ti(hfac)_2Cl$, has been reported,[63] but no preparative details were given.

Brainina has also discovered two additional types of cyclopentadienylzirconium β-diketonates which have the general empirical formulas $[(\pi\text{-}C_5H_5)Zr(dik)_2]_2O$ and $(\pi\text{-}C_5H_5)Zr(dik)_3$. The zirconoxanes, which contain a Zr-O-Zr linkage, were prepared by hydrolysis of $(\pi\text{-}C_5H_5)Zr(dik)_2X$ complexes in the presence of triethylamine and ethanol.[64] The $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes were obtained by the reaction of the highly reactive compound $(C_5H_5)_4Zr$ and the free diketone.[66] Some fluorinated β-diketonate analogues of the latter type of complex have been recently reported by Graham et al.,[63] presumably by a method different from that used by Brainina, but the experimental procedure has not yet been described.

Three transition metals have been found to form cationic complexes of the type $[(\pi\text{-}C_5H_5)_2M(dik)]^+$, where M = Ti, V, or Mo.[66,67] These complex cations are formed by the reaction of the metallocene dichloride and free diketone in aqueous solution and are isolated as salts of large uninegative anions, such as ClO_4^-, BF_4^-, or PF_6^-. A neutral complex with squarate, $(\pi\text{-}C_5H_5)_2Ti(C_4O_4)$, has also been isolated.[68]

Since the initiation of this study, the structures of two cyclopentadienyl metal β-diketonates, viz., $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(hfac)_3$, have been determined by X-ray diffraction methods.[59,69,64] The stereochemistry of $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ is best described in terms of a D_{2d} dodecahedron in which the $(\pi\text{-}C_5H_5)$ occupies a triangular face, the chlorine is positioned at a vertex cis to the cyclopentadienyl group, and the donor oxygen atoms of the bidentate acac ligands occupy the remaining coordination position. A simpler description of the molecule can be formulated in terms of an octahedral coordination polyhedron in which the center of the C_5H_5 ring is at a vertex cis to the chlorine atom. In $(\pi\text{-}C_5H_5)Zr(hfac)_3$ the center of the C_5H_5

group is at an axial vertex of a pentagonal bipyramid. Although it appears acceptable from a stereochemical viewpoint to consider the C_5H_5 group as occupying a single coordination position of higher coordination number polyhedrons, it is likely that three metal orbitals are used in bonding to the C_5H_5 group. Thus it is preferable to regard $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(dik)_3$ as being eight- and nine-coordinate complexes, respectively. No definitive structural data are available for other cyclopentadienyl metal π-diketonates, but $(\pi\text{-}C_5H_5)Cr(acac)Br$ and the $[(\pi\text{-}C_5H_5)_2M(dik)]^+$ complexes are believed to possess stereochemistries in which the center of the C_5H_5 groups are at tetrahedral vertices.[52,66,67]

Recent nmr studies in this laboratory[70,71] have shown that in solution $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ adopts the same type of stereochemistry that is found in the solid state. Moreover, the complex undergoes a rapid stereochemical rearrangement which interchanges the nonequivalent acac ligands. Similar properties were observed for the hafnium and bromine analogues, $(\pi\text{-}C_5H_5)Hf(acac)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(acac)_2Br$. Graham, et al.,[63] subsequently showed that $(\pi\text{-}C_5H_5)Zr(hfac)_3$ is also nonrigid but that the molecule undergoes two discrete rearrangement processes. The faster process (process I) results in the interconversion of nonequivalent environments of the CF_3 terminal groups on the two diketonate ligands which span the equatorial edges of the pentagonal bipyramid. In the second process (process II), the unique diketonate ligand which spans an axial-equatorial edge undergoes exchange with the two equatorial ligands. The cyclopentadienyl ring plays an important role in influencing the stereochemical lability of these higher coordination number compounds. They represent the first examples of

higher coordination number metal chelates for which dynamic stereochemical information can be obtained.

The objectives of this work were (1) to investigate the stereochemical lability of a new $(\pi\text{-}C_5H_5)Zr(dik)_2X$ complex with dipivaloylmethanate and (2) to study quantitatively the kinetics and possible mechanisms for the rearrangement processes of type I and II for a series of $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes. There is reason to suspect that the steric requirement of the tert-C_4H_9 groups in $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$, may cause the stereochemistry of the molecule in solution to be much more complex than that observed for the acac analogues. Butler[70] has pointed out that a D_{2d} dodecahedral coordination polyhedron can lead to as many as 12 geometric isomers with C_1 symmetry for a complex of the general type $(\pi\text{-}C_5H_5)M(dik)_2X$. Although $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ exhibits only one C_1 isomer in solution, $(\pi\text{-}C_5H_5)Ti(hfac)_2Cl$ is reported to exhibit two such isomers. Clearly, the cis-octahedral formalism is adequate for describing the stereochemistry of the former complex but not of the latter. It was hoped that $(\pi\text{-}5\text{-}H_5)Zr(dpm)_2Cl$ would exhibit two or more C_1 isomers in solution and that an investigation of their stereochemical labilities would provide mechanistic information. The second objective of the work involved preparing several new $(\pi\text{-}C_5H_5)Zr(dik)_3$ derivatives and, also, a new complex cation of the type $[(\pi\text{-}C_5H_5)Zr(dik)_2]^+$. Diketonate abbreviations used throughout this section of the thesis are summarized for ready reference in Table V.

Table V. Abbreviations and Formulas for Some β-Diketonate Ligands.

Abbreviation	Ligand	Formula
acac	acetylacetonate	$[H_3CCOCHCOCH_3]^-$
bzac	benzoylacetonate	$[H_3CCOCHCOC_6H_5]^-$
bzbz	dibenzoylmethanate	$[H_5C_6COCHCOC_6H_5]^-$
dpm	dipivaloylmethanate	$[H_9C_4COCHCOC_4H_9]^-$
pvac	pivaloylacetonate	$[H_3CCOCHCOC_4H_9]^-$
tfac	trifluoroacetylacetonate	$[F_3CCOCHCOCH_3]^-$
hfac	hexafluoroacetylacetonate	$[F_3CCOCHCOCF_3]^-$
pvtf	pivaloyltrifluoroacetonate	$[H_9C_4COCHCOCF_3]^-$
dik	any diketonate	$[R'COCHCOR]^-$

II. EXPERIMENTAL

A. Reagents and Solvents

Zirconocene dichloride was purchased from Aldrich Chemical Co., Inc., and used without further purification.

Acetylacetone was purchased from Matheson, Coleman & Bell and was fractionally distilled before use (bp 136-140°). Trifluoroacetylacetone was purchased from Columbia Organic Chemical Co. and was fractionally distilled before use (bp 107°). Benzoylacetone and dibenzoylmethane (Eastman Organic) were used without further purification. Hexafluoroacetylacetone, dipivaloylmethane pivaloylacetone, and pivaloyltrifluoroacetone were prepared by slight modification of previously described procedures.[72-75]

Tetrakiscyclopentadienylzirconium was prepared according to the method described by Brainina and coworkers.[76,77] Since the compound does not melt sharply, its purity was checked by chemical analysis, a molecular weight determination, and nmr spectroscopy.

Anal. Calcd for $(C_5H_4)_4Zr$: C, 68.32; H, 5.73; mol wt, 352. Found: C, 67.70; H, 5.50; mol wt (C_6H_6), 350. Nmr (saturated solution in $CDCl_3$ at 40°) δ 5.83 (lit.[77] δ 5.75).

Antimony pentachloride (Matheson, Coleman & Bell) was distilled under reduced pressure through a 30 cm column packed with glass helices. The pressure was adjusted to 30 torr by controlling a flow of dry argon through the system. The fraction boiling at 90-91° was collected.

The antimony pentachloride was subsequently manipulated in an argon or dry nitrogen atmosphere and stored in the dark.

Chlorobis(2,4-pentanedionato)cyclopentadienylzirconium and bromobis-(2,4-pentanedionato)cyclopentadienylzirconium were obtained from E. D. Butler and A. L. Lott respectively. Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium was obtained from J. T. Woodard. All were used without further purification.

All organic solvents used in the synthesis and/or studies of the compounds were dried over suitable dessicants. Benzene (Mallinckrodt), hexane (Matheson, Coleman & Bell), diethyl ether (Fisher), diisopropylether (Fisher), di-n-butylether (Fisher), o-xylene (Fisher), toluene (Fisher), and tetrahydrofuran (Matheson, Coleman & Bell) were distilled from lithium aluminum hydride. Dichloromethane (Matheson, Coleman & Bell), acetonitrile (Matheson, Coleman & Bell), and tetrachloroethylene (Matheson, Coleman & Bell) were distilled from calcium hydride. Carbon disulfide (Fisher) and triethylamine (Eastman Organic) were dried over phosphorus pentoxide and anhydrous magnesium sulfate respectively. Acetone (Fisher Certified, A.C.S.) was distilled from over Drierite.

Fisher Certified A.C.S. nitrobenzene was purified by distilling it *in vacuo* from over phosphorus pentoxide. The distilled nitrobenzene was allowed to stand over Linde Type 5A molecular sieves for two days and then redistilled *in vacuo* from the molecular sieves. Only one fraction of nitrobenzene was collected, bp 50-53° (*ca.* 0.5 torr).

Only benzene-d_6 (Diaprep) and chloroform-d_1 (Diaprep) were used without further purification.

B. General Synthetic Techniques

The compounds used in this study are sensitive to atmospheric moisture. Therefore, all preparative reactions and manipulations of the products were conducted under a dry argon atmosphere [$(\pi\text{-}C_5H_5)Zr(dik)_3$ compounds] or under nitrogen [$(\pi\text{-}C_5H_5)Zr(dik)_2X$ compounds]. As an extra precaution against hydrolysis in the preparation and manipulation of the $(\pi\text{-}C_5H_5)Zr(dik)_3$ compounds, solvents were deaerated by dispersing argon through the liquid for several minutes. All glassware was dried at 175°, cooled in a calcium sulfate desiccator whenever possible, and flushed with argon before use. Filtrations were carried out in sintered glass Buchner funnels equipped with ground glass joints. Ground glass joints were usually greased with silicone grease.

The compounds were generally more stable towards hydrolysis by atmospheric moisture as solids than in solution. Among the $(\pi\text{-}C_5H_5)Zr(dik)_3$ compounds, only the hexafluoroacetylacetonate derivative could be safely stored in a screw-cap vial fitted with a Teflon cap liner. All other $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes were stored under vacuum. In general, the $(\pi\text{-}C_5H_5)Zr(dik)_2X$ complexes were less sensitive to atmospheric moisture than were the $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes, and they were stored in screw-cap vials in a calcium sulfate desiccator.

C. Preparation of Compounds

1. Chlorobis(2,2,6,6-tetramethyl-3,5-heptanedionato)cyclopentadienylzirconium. A mixture of dipivaloylmethane (4.97 g, 27.0 mmol) and triethylamine (1.88 ml, 13.4 mmol) in 90 ml acetonitrile was added dropwise to a suspension of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (3.92 g, 13.4 mmol) in 100 ml acetonitrile. The mixture was stirred at ambient temperature

for 39 hr. The white insoluble solid (identified as $(\pi\text{-}C_5H_5)Zr(dpm)_3$ by its nmr spectrum) was separated by filtration washed with four 30-ml portions of acetonitrile, the acetonitrile washings were combined with the original mother liquor, and the solvent was removed under vacuum. The resultant white solid was suspended in 100 ml benzene, and the insoluble portion (identified as $(C_2H_5)_3N\cdot HCl$ by its ir spectrum) was removed by filtration. The product was isolated from the filtrate by vacuum distillation of the benzene at room temperature. The white compound was recrystallized from 200 ml acetonitrile at -78° and was dried in vacuo at room temperature; mp 175-177°. The yield was 5.76 g (76.8%).

Anal. Calcd for $(C_5H_5)Zr(C_{11}H_{19}O_2)_2Cl$: C, 58.09; H, 7.76; Cl, 6.35; mol wt, 558. Found: C, 57.93; H, 7.64; Cl, 6.37; mol wt (C_6H_6), 579; Λ (1.84×10^{-3} M solution in $C_6H_5NO_2$ at 25°), 0.151 ohm^{-1} cm^2 mol^{-1}.

2. Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)cyclopentadienylzirconium. A mixture of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (10.0 g, 34.2 mmol) and hexafluoroacetylacetone (25 ml, 170 mmol) was heated at reflux temperature until all of the $(\pi\text{-}C_5H_5)_2ZrCl_2$ dissolved (ca. 11 hr). The excess hexafluoroacetylacetone was removed by vacuum distillation at room temperature to obtain a yellow mass. The mass was dissolved in a minimum amount of dichloromethane at room temperature and the solution was cooled in a Dry Ice-acetone bath. The resulting yellow crystals were separated from the cold solution by filtration and dried in vacuo at room temperature; mp 92-95°. The yield was 26.3 g (98.8%). The compound was recrystallized from dibutyl ether; mp 98-100°.

Anal. Calcd for $(C_5H_5)Zr(C_5HO_2F_6)_3$: C, 30.88; H, 1.11; F, 43.95; mol wt, 777. Found: C, 31.01; H, 1.04; F, 44.16; mol wt (C_6H_6),

790; Λ (1.45 X 10^{-3} M solution in $C_6H_5NO_2$ at 25°), 0.014 ohm^{-1} cm^2 mol^{-1}.

3. Tris(1,1,1-trifluoro-2,4-pentanedionato)cyclopentadienylzirconium. A mixture of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (2.50 g, 8.56 mmol) and trifluoroacetylacetone (20 ml, 160 mmol) was heated just below reflux temperature for 1 hr. The reaction mixture was cooled to room temperature and 50 ml of diethyl ether was added. The green-brown solution was evaporated to dryness at room temperature under reduced pressure. The residue gave a white crystalline product upon recrystallization from benzene-hexane and subsequent vacuum sublimation at 70°; mp 87-90°. The yield was 2.25 g (42.7%).

Anal. Calcd for $(C_5H_5)Zr(C_5H_4O_2F_3)_3$: C, 39.03; H, 2.78; F, 27.78; Zr, 14.82; mol wt, 615. Found: C, 38.89; H, 2.76; F, 27.60; Zr, 14.83; mol wt (C_6H_6), 630; Λ (1.79 X 10^{-3} M solution in $C_6H_5NO_2$ at 25°), 0.028 ohm^{-1} cm^2 mol^{-1}.

4. Tris(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)zirconium.

a. From zirconocene dichloride in triethylamine. Pivaloyltrifluoroacetone (4.52 g, 23.1 mmol) was added to a suspension of $(\pi\text{-}C_5H_5)_2ZrCl_2$ in 45 ml triethylamine, and the mixture was stirred at room temperature for 10 hr. After the white precipitate $[(C_2H_5)_3N{\cdot}HCl]$ had been separated from the mixture by filtration, the volume of the solution was reduced to ca. 10 ml, and the solution was cooled in a Dry Ice-acetone bath. The resultant white crystalline solid was collected by filtration and dried in vacuo at room temperature; mp 115-118°. The yield was 2.97 g (52.0%).

Anal. Calcd for $(C_5H_5)Zr(C_8H_{10}F_3O_2)_3$: C, 46.96; H, 4.76; Zr, 12.30; mol wt, 742. Found: C, 47.04; H, 4.84; Zr, 12.39;

mol wt (C_6H_6), 752; Λ (7.81 X 10^{-3} M solution in $C_6H_5NO_2$ at 25°), <0.010 ohm^{-1} cm^2 mol^{-1}.

b. From zirconocene in neat pivaloyltrifluoroacetone. A mixture of (π-$C_5H_5)_2ZrCl_2$ (0.64 g, 2.19 mmol) and pivaloyltrifluoroacetone (5.00 ml, 28.8 mmol) was heated at 100° for 6 hr. The excess pivaloyltrifluoroacetone was removed by vacuum distillation at room temperature, yielding a brown mass. Two vacuum sublimations at 75° produced a white crystalline solid, mp 102-106°. The yield was 1.52 g (99.3%). The product was identified as (π-$C_5H_5)Zr(C_8H_{10}F_3O_2)_3$ by its nmr spectrum in benzene. Since a few minor, unidentifiable impurities were also observed in the nmr spectrum, this product was not used for any physical measurements.

5. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)cyclopentadienylzirconium.

a. From tetrakiscyclopentadienylzirconium. Dipivaloylmethane (7.40 g, 40.2 mmol) was added to a solution of $(C_5H_5)_4Zr$ (4.71 g, 13.4 mmol) in 150 ml of dichloromethane, and the mixture was heated at reflux temperature for 20 hr. After the solvent was removed by vacuum distillation at room temperature, the residue was slurried in 150 ml of boiling hexane and the solution was filtered. The nmr spectrum of the hexane-insoluble fraction of the residue (1.48 g) was identical with that of $(C_5H_5)_4Zr$. The volume of the hexane filtrate was reduced under reduced pressure, giving 4.46 g of off-white crystals. The yield based on the amount of $(C_5H_5)_4Zr$ that had reacted is 62.4%. A second recrystallization of the product from acetone gave colorless crystals. The crystals were dried in vacuo at 80° for 4 hr; mp $\sim$ 230° dec.

Anal. Calcd for $(C_5H_5)Zr(C_{11}H_{19}O_2)_3$: C, 64.64; H, 8.85; Zr, 13.17; mol wt, 706. Found: C. 64.86; H, 9.01; Zr, 12.92; mol wt

(C_6H_6), 720; Λ (1.25 X 10^{-3} M solution in $C_6H_5NO_2$ at 25°), 0.059 ohm^{-1} cm^2 mol^{-1}.

b. From zirconocene dichloride in triethylamine. Dipivaloylmethane (5.67 g 30.8 mmol) was added to a suspension of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (3.01 g, 10.3 mmol) in 35 ml triethylamine, and the mixture was stirred for 5 hr at ambient temperature. The insoluble white precipitate $[(C_2H_5)_3N\cdot HCl]$ was removed by filtration, and the filtrate was cooled in a Dry Ice-acetone bath. The resultant white crystals (2.42 g) were separated from the cold solution by filtration and dried in vacuo at room temperature for several hours; mp 238-240° dec. The remainder of the solvent was removed under reduced pressure, yielding an additional 0.59 g of the product. A third fraction of the compound (0.98 g) was extracted from the $(C_2H_5)_3N\cdot HCl$ precipitate with anhydrous diethyl ether. The total yield was 3.99 g (55.2%). All three fractions of the product were identified by nmr as $(\pi\text{-}C_5H_5)Zr(C_{11}H_{19}O_2)_3$ free of proton-containing impurities.

6. Tris(2,4-pentanedionato)cyclopentadienylzirconium.

a. From zirconocene dichloride in triethylamine. A suspension of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (5.00 g, 17.2 mmol) and acetylacetone (5.25 ml, 51.3 mmol) in 50 ml triethylamine was stirred at room temperature for 6 hr. The white precipitate of $(C_2H_5)_3N\cdot HCl$ was separated from the solution by filtration, and the filtrate was cooled to -25° overnight. The resultant white, crystalline solid was collected by filtration and dried in vacuo at room temperature for several hours; mp 135-137°. The yield was 4.65 g (59.7%). Cooling the mother liquor in a Dry Ice-acetone bath resulted in no further crystallization.

Anal. Calcd for $(C_5H_5)Zr(C_5H_7O_2)_3$: C, 52.96; H, 5.78; Zr, 20.11; mol wt, 454. Found: C, 53.11; H, 5.80; Zr, 20.44; mol wt (C_6H_6), 448; Λ (2.65×10^{-3} M solution in $C_6H_5NO_2$ at 25°), <0.029 ohm^{-1} cm^2 mol^{-1}.

b. From tetrakiscyclopentadienylzirconium. A mixture of $(C_5H_5)_4Zr$ (6.09 g, 17.4 mmol) and acetylacetone (5.39 ml, 55.3 mmol) in 100 ml benzene was stirred at ambient temperature for 2 hr. The solvent was removed by vacuum distillation at 50°. The resultant brown oil was dissolved in ca. 75 ml of hot hexane, and the solution was cooled to -25°. A heterogeneous precipitate formed over the period of several days. The majority of the precipitate was an amorphous brown solid, but it was covered with spherulites of off-white crystals. The cold mother liquor was decanted from the heterogeneous mass, and the heterogeneous product was dried in vacuo at room temperature overnight. The crystalline spherulites were manually separated from the parent mass; mp 133-136° dec. The yield was ca. 1.0 g (ca. 13%). The product was identified as $(\pi\text{-}C_5H_5)Zr(C_5H_7O_2)_3$ free of proton-containing impurities by its nmr spectrum in benzene. Attempts to recrystallize the compound from hexane were unsuccessful.

7. Tris(1,3-diphenyl-1,3-propanedionato)cyclopentadienylzirconium. A mixture of $(C_5H_5)_4Zr$ (0.94 g, 2.68 mmol) and dibenzoylmethane (1.79 g, 8.00 mmol) in 125 ml benzene was heated at reflux temperature for 1 hr. The reaction mixture was cooled to room temperature, and the solvent was removed by vacuum distillation. The resultant yellow solid was recrystallized from a 1:1 benzene:hexane solution and dried in vacuo at room temperature; mp 189-191° (lit.[66] 186-187°). The yield was 1.21 g (54.8%).

Anal. Calcd for $(C_5H_5)Zr(C_{15}H_{13}O_2)_3$: C, 72.70; H, 4.63; mol wt,

826. Found: C, 72.82; H, 4.70; mol wt (C_6H_6), 840; Λ (0.95 X 10^{-3} M solution in $C_6H_5NO_2$ at 25°), 0.063 ohm^{-1} cm^2 mol^{-1}.

8. Tris(5,5-dimethyl-2,4-hexanedionato)cyclopentadienylzirconium.

a. From zirconocene dichloride in triethylamine. A mixture of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (2.00 g, 6.84 mmol) and pivaloylacetone (2.92 g, 20.5 mmol) in 25 ml triethylamine was stirred at room temperature for 5 hr. The $(C_2H_5)_3N{\cdot}HCl$ was separated by filtration, and the solvent was removed by vacuum distillation at ambient temperature. The resultant white solid was recrystallized from acetone at -78° (Dry Ice-acetone bath), separated from the cold solution by filtration, and dried in vacuo at room temperature overnight; mp 149-152°. The yield was 2.96 g (74.4%).

Anal. Calcd for $(C_5H_5)Zr(C_8H_{13}O_2)_3$: C, 60.07; H, 7.65; Zr, 15.73; mol wt, 580. Found: C, 59.88; H, 7.77; Zr, 15.95; mol wt (C_6H_6), 557; Λ (1.93 X 10^{-3} M solution in $C_6H_5NO_2$ at 25°), <0.040 ohm^{-1} cm^2 mol^{-1}.

b. From tetrakiscyclopentadienylzirconium. Tetrakiscyclopentadienylzirconium (1.35 g, 3.84 mmol) was added to a solution of pivaloylacetone (1.62 g, 11.5 mmol) in 50 ml benzene, and the mixture was stirred at ambient temperature for 16 hr. The solvent was removed by vacuum distillation at room temperature. The resultant white solid was recrystallized from 20 ml hot hexane, separated by filtration, and dried in vacuo at room temperature for several hours; mp 150-153°. The yield was 0.80 g (35.9%). The compound was identified as $(\pi\text{-}C_5H_5)Zr(C_8H_{13}O_2)_3$ free of proton-containing impurities from its nmr spectrum in benzene.

9. Tris(1-phenyl-1,3-butanedionato)cyclopentadienylzirconium. A suspension of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (2.24 g, 7.67 mmol) and benzoylacetone (3.73 g, 23.0 mmol) in 40 ml triethylamine was stirred at room temperature for 3.5 hr. The white precipitate was separated from the solution by filtration and washed with three 25-ml portions of benzene. The volume of the combined benzene washings was reduced to ca. 25 ml by vacuum distillation at ambient temperature. Hexane (ca. 50 ml) was added to commence precipitation, and the solution was cooled in a Dry Ice-acetone bath. The resulting white powder was separated from the cold mixture by filtration and dried in vacuo at room temperature; mp 144-147° (lit.[66] 141-142°). The amine mother liquor was removed by vacuum distillation at room temperature, but no additional product was obtained.

Anal. Calcd for $(C_5H_5)Zr(C_{10}H_{10}O_2)_3$: C, 65.70; H, 5.04; Zr, 14.26; mol wt, 640. Found: C, 65.61; H, 5.24; Zr, 14.15; mol wt (C_6H_6), 624; Λ (2.31×10^{-3} M solution in $C_6H_5NO_2$ at 25°), 0.052 ohm^{-1} cm^2 mol^{-1}.

10. Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)cyclopentadienylzirconium hexachloroantimonate. A solution of $SbCl_5$ (1.34 g, 4.48 mmol) in 30 ml acetonitrile was added dropwise to a suspension of $(\pi\text{-}C_5H_5)Zr(C_{11}H_{19}O_2)_2Cl$ (2.50 g, 4.48 mmol) in 20 ml acetonitrile at 0°, and the mixture was stirred at 0° for 0.5 hr. The volume of the solution was reduced to ca. 30 ml by vacuum distillation at 0°, and the solution was cooled to -25° for 12 hr. The resultant yellow crystalline solid was separated from the cold solution by filtration and dried in vacuo for 3 hr at Dry Ice temperature. The yellow crystals slowly decompose at room temperature to give a black oil. The product was insoluble

in benzene but was readily soluble in polar solvents such as acetonitrile, acetone, dichloromethane, and nitrobenzene.

Anal. Calcd for $(C_5H_5)Zr(C_{11}H_{19}O_2)_2SbCl_6$: C, 37.83; H, 5.06; Cl, 24.81. Found: C, 39.06; H, 5.20; Cl, 25.07; Λ (2.81 X 10^{-3} M in $C_6H_5NO_2$ at 25°), 18.6 ohm^{-1} cm^2 mol^{-1}. Ir and nmr data (cf. Results and Discussion, Section D) indicate the presence of CH_3CN; hence, calcd for $(C_5H_5)Zr(C_{11}H_{19}O_2)_2SbCl_6(CH_3CN)$: C, 38.77; H, 5.16; Cl, 23.68.

D. Analytical Data

The microanalyses of all compounds were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

E. Molecular Weight Determinations

The molecular weights of the compounds were determined cryoscopically in dry benzene. Recrystallized benzil was used as the calibrating solute in the determination of the molal freezing point depression constant of benzene (5.38° m^{-1}). Freezing point depressions were measured in the concentration range 0.030 to 0.057 m with a Beckman differential thermometer graduated at 0.01° intervals. Temperature readings, however, were estimated to $\pm$0.001° with the aid of a magnifying thermometer reader.

F. Conductance Measurements

Molar conductivities were measured with a Wayne Kerr Model B221 universal bridge and a Freas-type solution cell with bright platimum electrodes. The cell constant was determined to be 0.194 cm^{-1} at 25° by using a standard KCl solution. Purified nitrobenzene was used for molar conductance measurements. The conductivity cell was also used for conductometric titrations.

G. Melting Point Determinations

Melting points were determined in sealed glass capillaries with a Thomas-Hoover 6406-H capillary melting point apparatus.

H. Electron Paramagnetic Resonance Spectra

The absence of paramagnetic impurities in the compounds were verified with a Varian E/4 spectrometer. Spectra were taken at room temperature and 77°K in sealed quartz-glass tubing. High gain settings and a 1500 to 5500 gauss scan range produced no evidence of any paramagnetic species in the samples.

I. Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance spectra were recorded on a Varian A56/60D analytical spectrometer operated at 60.0 (^{1}H spectra) or 56.4 MHz (^{19}F spectra). The probe temperature was controlled to within $\pm$0.5° by a Varian V-6040 variable-temperature controller. The methanol and ethylene glycol nmr thermometers described by Van Geet[14] were used to determine the probe temperature. Magnetic field-sweep widths were calibrated by the audiofrequency side-band technique. All spectra were recorded at low radio frequency field strengths in order to avoid saturation effects. Occassionally, a Varian A/60 or a Varian T/60 analytical spectrometer were used to obtain routine spectra.

J. Infrared Spectra

Infrared spectra over the range 4000 to 250 cm^{-1} were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer. Spectra were obtained as nujol or fluorolube mulls between CsI plates. The 2851, 1603 and 907 cm^{-1} peaks of polystyrene were used as reference frequencies.

K. Preparation of Solutions for Nmr Studies

All solutions used in the nmr studies were prepared in an argon atmosphere. Diisopropyl ether and o-xylene were used as solvents for $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and $(\pi\text{-}C_5H_5)Zr(dpm)_3$, respectively. In the selection of a solvent for studying the exchange of terminal CF_3 groups on the equatorial ligands of $(\pi\text{-}C_5H_5)Zr(hfac)_3$, the following solvents were rejected, because of the low solubility of the complex or extensive overlapping of the CF_3 resonances at 56.4 MHz: dichloromethane, chloroform, toluene, hexane, acetone, m-dimethoxybenzene, and 1:1 mixtures of m-dimethoxybenzene with diphenylmethane, diethyl malonate, benzaldehyde, anisole, and chlorobenzene. Unfavorable $t\text{-}C_4H_9$ proton chemical shift differences were observed for $(\pi\text{-}C_5H_5)Zr(dpm)_3$ in carbon tetrachloride, chlorobenzene, dichloromethane, and 1,2-dichloroethane. The choice of solvents for the study of $(\pi\text{-}C_5H_5)Zr(acac)_3$ was dictated by the liquid range and nmr chemical shift values of the solvent. Carbon disulfide was selected for variable temperature studies below -100°. For studies of the complex above ambient temperature, none of the above solvents was suitable, but tetrachloroethylene proved to be useful. Benzene was chosen as the solvent for $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ because it was used in an earlier study of similar compounds.[71]

L. Determination of Mean Lifetimes

Each of the stereochemical rearrangement processes studied in the present work results in the interchange of nuclei between two nonequivalent sites. Rates of exchange were determined by comparing the experimentally observed nmr spectra with spectra calculated for various mean lifetimes, τ. The Gutowsky-Holm equation,[16] as expanded by Rogers and Woodbrey,[15] was used to calculate the theoretical spectra. Each calculated spectrum

consisted of 100-250 coordinate points spaced at maximum intervals of 0.15 Hz. The calculations were carried out on a CDC 3600, CDC 6500, or IBM 1130 computer. In some cases the populations of the two sites and/or the values of the transverse relaxation times of the nuclei in the two environments are unequal. In the region of exchange below the coalescence temperature, the observed and calculated spectra were compared with respect to the widths at half-maximum amplitude of the two resonance components and/or the parameter, r, which is defined as the ratio of the maximum to central minimum intensities. Whenever possible, the best value of τ was taken to be the average value obtained by fitting each line width and r. Above the coalescence temperature, values of τ were determined by fitting the width of the time-averaged resonance line. All line widths and values of r were obtained by averaging the results of at least three spectral copies.

III. RESULTS AND DISCUSSION

A. Reactions for the Preparation of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(dik)_3$ Complexes

The tris-hexafluoroacetylacetonate, -trifluoroacetylacetonate, and -pivaloyltrifluoroacetonate cyclopentadienylzirconium complexes were prepared by the reaction of zirconocene dichloride and the neat β-diketone under anhydrous conditions (eq. 1). Earlier work[53,70] has

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + 3H(hfac) \rightarrow (\pi\text{-}C_5H_5)Zr(hfac)_3 + 2HCl + C_5H_6 \qquad (1)$$

shown that reactions of zirconocene dihalides and nonfluorinated diketones under similar conditions yield products of the type $(\pi\text{-}C_5H_5)Zr(dik)_2X$. Apparently, the substitution of the second chlorine atom by a nonfluorinated diketone is slow, especially in the absence of a base. An appreciable difference in the relative ease of chlorine substitution by fluorinated and nonfluorinated diketones is also found in the substitution reactions of $ZrCl_4$. The reaction of $ZrCl_4$ with hexafluoroacetylacetone[78] or trifluoroacetylacetone,[79] for example, readily affords the tetrakis (β-diketonato)zirconium complex, whereas the reaction with acetylacetone[69,80] and certain other nonfluorinated diketones[80,81] gives mainly the chlorotris(diketonato)metal complex. Although replacement of chlorine in $Zr(acac)_3Cl$ by acetylacetonate can be achieved in the presence of water,[82] the hydrolyses of $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ and analogous β-diketonates afford stable dizirconoxanes of the type $[(\pi\text{-}C_5H_5)Zr(dik)_2]_2O$.[56,83,84]

The only preparative pathway previously reported for $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes containing nonfluorinated diketonate ligands involves the reaction of $(C_5H_5)_4Zr$ and the free diketone[84] (eq. 2). In the present

$$(C_5H_5)_4Zr + 3H(dpm) \rightarrow (\pi\text{-}C_5H_5)Zr(dpm)_3 + 3C_5H_6 \qquad (2)$$

study, analogous reactions with the appropriate diketones gave $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes where dik = dpm, pvac, bzbz, and acac. An easier method which produces a higher yield of products was discovered during the course of this study. The replacement of both chlorine atoms and one cyclopentadienyl group of $(\pi\text{-}C_5H_5)_2ZrCl_2$ by nonfluorinated diketones readily occurs under ambient conditions in a triethylamine medium (eq. 3). The acetylacetonate, dipivaloylmethanate, benzoylacetonate,

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + 3H(acac) + 2(C_2H_5)_3N \xrightarrow{(C_2H_5)_3N} (\pi\text{-}C_5H_5)Zr(acac)_3 + 2(C_2H_5)_3N\cdot HCl + C_5H_6 \qquad (3)$$

and pivaloylacetonate derivatives have been prepared successfully in this manner. The method is also applicable for at least one fluorinated derivative, $(\pi\text{-}C_5H_5)Zr(pvtf)_3$, and it may be applicable for the preparation of all $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes.

The preparation of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ by utilizing a stoichiometric amount of base is an adaptation of the work by Newton[62] (eq. 4). This

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + 2H(dpm) + (C_2H_5)_3N \rightarrow (\pi\text{-}C_5H_5)Zr(dpm)_2Cl + (C_2H_5)_3N\cdot HCl + C_5H_6 \qquad (4)$$

method does not use excess ligand and is most advantageous with the more expensive diketones. It has the disadvantage of also producing $(\pi\text{-}C_5H_5)Zr(dpm)_3$ as a by-product. At 1:1 molar amounts of $(\pi\text{-}C_5H_5)_2ZrCl_2$ and $(C_2H_5)_3N$, the major product is $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ (76.8% yield).

However, comparable amounts of $(\pi\text{-}C_5H_5)Zr(dpm)_3$ and $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ are obtained when the $(\pi\text{-}C_5H_5)_2ZrCl_2$ to $(C_2H_5)_3N$ molar ratio is increased to 1:2. In a triethylamine medium, the reaction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with H(dpm) gives only $(\pi\text{-}C_5H_5)Zr(dpm)_3$ as a product regardless of the molar ratio of $(\pi\text{-}C_5H_5)_2ZrCl_2$ to H(dpm).

B. Constitution of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(dik)_3$ Complexes in Solution.

The molecular weight and conductivity data for each compound are presented in the Experimental Section. $(\pi\text{-}C_5H_5)Zr(dmp)_2Cl$ and all of the $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes are monomeric in benzene solution and very weak electrolytes in nitrobenzene solution. Their molar conductances range from <0.010 to 0.060 ohm^{-1} cm^2 mol^{-1} at a concentration of ca. 10^{-3} M. At this concentration a typical 1:1 electrolyte, such as $[Ti(acac)_3][SbCl_6]$, exhibits a molar conductance slightly greater than 20 ohm^{-1} cm^2 mol^{-1}.[87]

The ir spectra of the compounds show that the carbonyl stretching vibrations of the diketonate ligands occur in the region 1650 to 1500 cm^{-1}. The vibrations are shifted to lower energy by ca. 75 cm^{-1} from their respective absorptions as "free" ketone carbonyl groups in open chain silyl enol ethers.[8] Thus bidentate coordination of the diketonate ligands is verified. For each compound a weak, sharp band is observed near 3,100 cm^{-1} which is characteristic of the C-H stretching vibration a π-bonded C_5H_5 group.[70] The appearance of a single, sharp C_5H_5 resonance at ca. τ 3.50 in the nmr spectra of the compounds is also indicative of a π-bonded cyclopentadienyl group.[90] These data indicate that the constitution of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ and the $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes in solution is analogous to that found in the solid state for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$[59] and $(\pi\text{-}C_5H_5)Zr(hfac)_3$.[64]

C. Dynamic Stereochemical Properties of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$.

$(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ is sufficiently stereochemically rigid at room temperature to deduce its stereochemistry by nmr spectroscopy. The proton nmr spectrum of the compound in benzene solution is presented in Figure 8. The resonance line at τ 3.53 is attributed to the protons on the cyclopentadienyl ring. The remaining six lines are due to the -CH= and tert-C_4H_9 protons on the dipivaloylmethanate ligands. The two -CH= lines at τ 4.16 and 4.24 have equal relative intensities. Four tert-C_4H_9 lines of equal relative intensity occur in the region τ 8.85 to 9.06. The -CH= and tert-C_4H_9 proton resonances result from nonequivalent environments for these groups in the $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ molecule. The existence of a single, sharp cyclopentadienyl resonance is attributed to rapid rotation of the ring about the metal-ring axis.

The simplest configuration which places each of the -CH= and tert-C_4H_9 groups in nonequivalent environments is based on an octahedron with the center of the C_5H_5 ring at one stereochemical position and the chlorine atom at a position cis to the ring (see Figure 9I). A trans configuration (cf. Figure 9II), which would have apparent C_{2v} symmetry in the presence of rapid rotation of the C_5H_5 ring, cannot be present in an appreciable amount, as judged from the relative intensity data. Thus the dipivaloylmethanate complex has the same stereochemical configuration as the other known $(\pi\text{-}C_5H_5)Zr(acac)_2X$ complexes.[57,58,81] The cis-octahedral formalism used to describe the gross stereochemical features of the complex is an approximation of the D_{2d} dodecahedral description given for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ in the solid state.[59,60] In this higher polyhedron (Figure 10) it is assumed that the ring occupies a triangular face, an AAB (1,2,3) face for example, in forming three π bonds to zirconium. The two dipivaloylmethanate ligands would

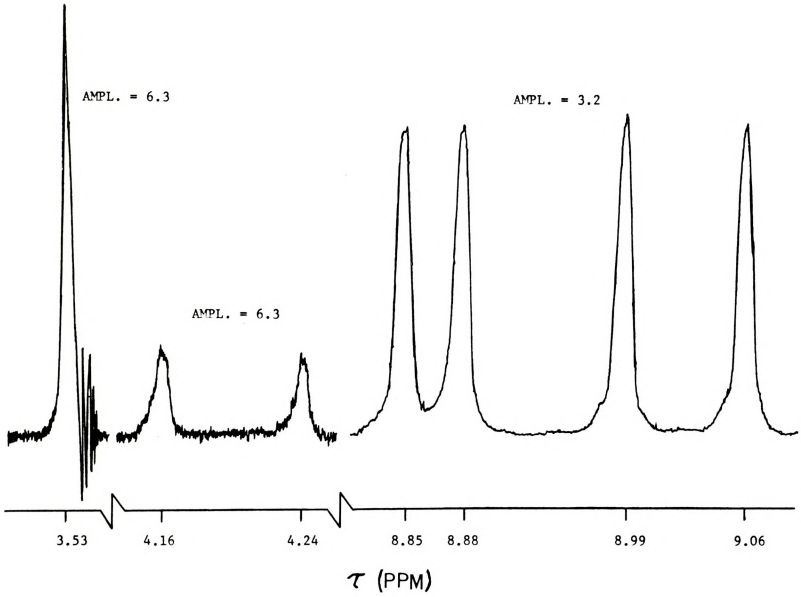


Figure 8. Proton nmr spectrum of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ in benzene solution at 39° (60 MHz); concentration, 10.0 g/100 ml of solvent.

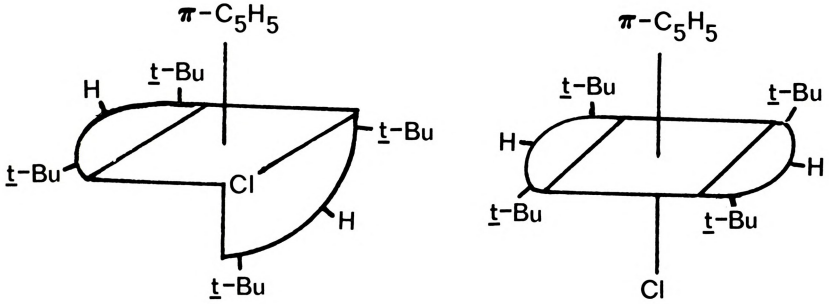


Figure 9. Possible cis and trans configurations for $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ based on a simple octahedral model.

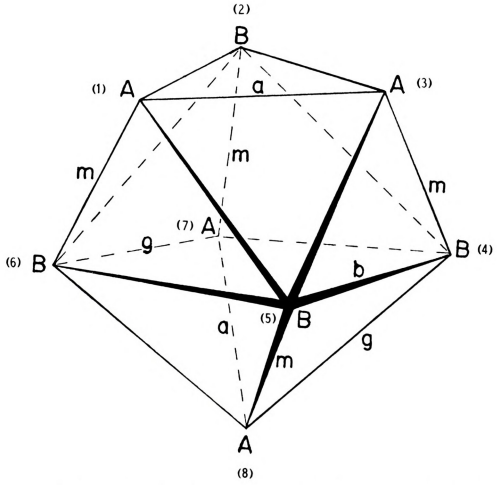


Figure 10. The D_{2d} dodecahedron. Alphabetic edge and vertex notation is from J. L. Hoard and J. V. Silverton, Inorg. Chem., 2, 235 (1963).

span a g-g (6,7 and 4,8) pair of edges, and the chlorine atom would occupy vertex B (5). Seven additional isomers are possible if the C_5H_5 ring is capable of bonding through the ABB triangular faces. However, since only one C_1 isomer is detectable, the octahedral formalism is adequate to describe the stereochemical features of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$. The zirconium complexes, $(\pi\text{-}C_5H_5)Zr(acac)_2X$ and $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$, are in direct contrast to a related titanium compound $(\pi\text{-}C_5H_5)Ti(hfac)_2Cl$, which exists as two C_1 isomers in solution. Thus, one must conclude that steric factors due to the terminal groups of the diketonate ligands are not a critical stereochemical factor.

The temperature dependence of the nmr spectrum of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ (Figure 11) is very similar to that observed for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$[70,71] and $(\pi\text{-}C_5H_5)Zr(acac)_2Br$.[71] As the temperature of a benzene solution of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ is increased above ca. 60°, the two -CH= resonances broaden and coalesce into a single line which becomes very narrow by ca. 130°. The four tert-C_4H_9 lines broaden and coalesce into a single sharp line, but the C_5H_5 resonance remains sharp over the entire temperature range. The temperature dependence of the -CH= and tert-C_4H_9 resonances indicates that the molecule undergoes a stereochemical rearrangement process which interchanges the two nonequivalent dipivaloylmethanate ligands. Analogous rearrangements have been observed for the $(\pi\text{-}C_5H_5)Zr(acac)_2X$ molecules.

The mean lifetimes τ_A and τ_B for the nonequivalent dipivaloylmethanate ligands were determined by comparing the experimental -CH= nmr line shapes with line shapes calculated for various trial values of τ, where $\tau = \tau_A/2 = \tau_B/2$. Curve A in Figure 12 indicates that the frequency separation between the -CH= resonances in the region of slow exchange, $\delta\nu$, is temperature-dependent, presumably, because of

Figure 11. Temperature dependence of the -CH= and tert-C_4H_9 proton nmr lines for $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ in benzene. Concentration is 11.0 g/100 ml of solvent.

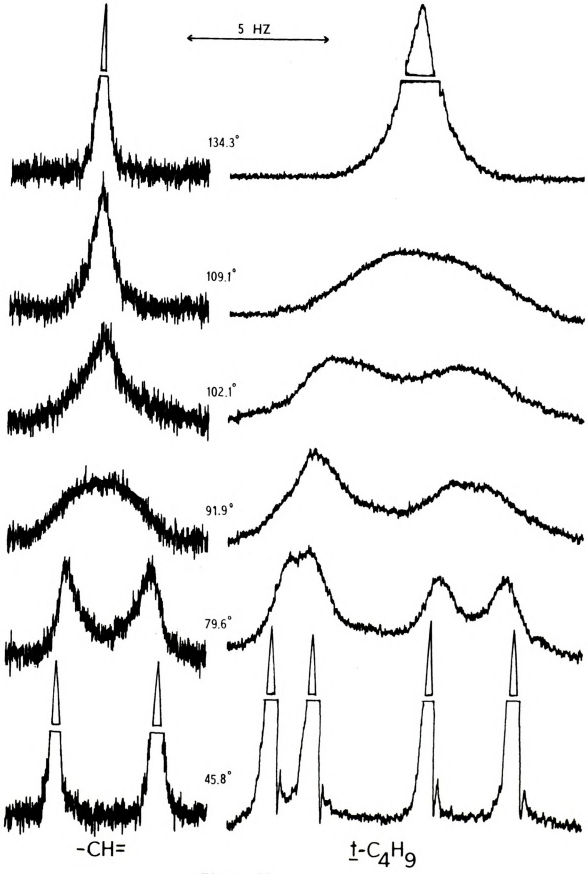


Figure 11.

temperature-dependent solvation effects. Therefore, values of $\delta\nu$ in the region of exchange were determined by linear least-squares extrapolation of the temperature dependence of $\delta\nu$ in the slow-exchange region. The widths of the two -CH= lines are equal within experimental error in the region of slow exchange, thus the apparent transverse relaxation times, T_{2A} and T_{2B} were determined by estimating a small temperature dependence, $(9.1 \pm 5.5) \times 10^{-4}$ Hz/°C, for the line width in the region of slow exchange as shown by the dashed line connecting curves B and C in Figure 12. A similar temperature dependence, $(33.4 \pm 5.5) \times 10^{-4}$ Hz/°C, for the -CH= lines of $Zr(dpm)_4$ is observed over the temperature range 42.0 to 104.5°.

Values of the nmr line-shape parameters and the calculated values of τ for the nonequivalent dipivaloylmethanate ligands of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ in benzene are given in Table VI. Shown in Table VII are the Arrhenius activation energy, E_a, the frequency factor, A, the activation entropy, $\Delta S^{\ddagger}$, the activation enthalpy, $\Delta H^{\ddagger}$, and the extrapolated value of the first-order rate constant at 25°, $k_{25°}$. The Arrhenius activation energy and the frequency factor were determined from linear least-squares plot of log k vs. 1/T (Figure 13) where $k = (2\tau)^{-1}$. The activation entropy and activation enthalpy were determined from the Eyring plot of log (k/T) vs. 1/T. The activation parameters are rather insensitive to choices of $\delta\nu$, T_{2A}, and T_{2B}. The uncertainty in the linear least-squares temperature dependence of $\delta\nu$ propagates a 0.4 kcal/mol error in E_a and a 0.30 error in the value of log A. A reasonable uncertainty of 0.07 Hz (17% error) in estimating T_2 values generates 1.1 kcal/mol and 0.68 errors in E_a and log A, respectively.

The mean lifetimes of the -CH= protons are independent of the concentration of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ over the range 0.195 to 0.393 M.

Figure 12. Temperature dependence of the proton nmr line-shape parameters for the -CH= protons on the dipivaloylmethanate ligands of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ in benzene. Curve A is the frequency separation between the resonance components below coalescence. Curve B is the mean width at half-maximum amplitude of the resonances below coalescence; Curve D, the width of the time-averaged resonance above coalescence. The significance of the extrapolated (dashed) lines is described in the text.

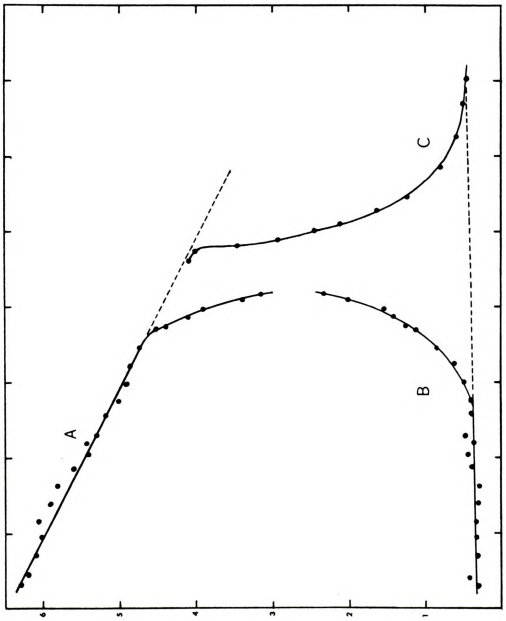

LINE WIDTH OR δν (Hz)
0
1
2
3
4
5
A
B
C
20
40
60
80
100
120
140
$\frac{1}{T} \times 10^3$

Figure 12.

Table VI. ^{1}H Nmr Line-Shape Parameters and Kinetic Data for the Interchange of the Nonequivalent Dipivaloylmethanate Ligands on $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$.[a]

Temp, °C	T_2[b] sec	$\delta\nu$[c] Hz	r[d]	Line Width,[e] Hz	$10^2\tau$, sec
69.4	0.777	4.74		.86	37.2
74.1	0.769	4.62	5.71	1.10	23.3
75.3	0.767	4.59	4.92	1.26	20.6
77.7	0.763	4.53	4.01	1.40	18.0
79.6	0.760	4.48	3.67	1.53	16.8
82.1	0.756	4.42	2.33	2.04	12.7
83.6	0.753	4.38	2.11	2.33	11.8
85.3	0.750	4.34	1.86	5.41	9.42
87.2	0.747	4.29	1.40	5.25	7.98
89.7	0.744	4.23	1.15	4.90	6.79
91.7	0.740	4.18	1.00	4.22	5.45
94.5	0.736	4.11		4.04	5.15
96.0	0.734	4.07		3.47	4.52
97.5	0.731	4.03		2.95	3.97
100.0	0.728	3.97		2.46	3.47
102.1	0.724	3.92		2.13	3.07
105.5	0.719	3.83		1.64	2.39
109.1	0.714	3.74		1.26	1.77

[a]In benzene; concentration is 0.20 M. [b]Transverse relaxation time for the -CH= resonances. [c]Frequency separation between the -CH= resonances in absence of exchange. [d]Ratio of the maximum to central

Table VI. (Continued)

minimum intensities. [e]Widths in the range 69.4-83.6° refer to the mean line widths of the two -CH= lines below coalescence; in the range 85.3-91.7°. The values are for the total widths of the overlapping resonance lines; above 91.7°,the widths are for the time-averaged line above coalescence.

Table VII. Kinetic Parameters for Exchange of Nonequivalent -CH= Groups in $(\pi\text{-}C_5H_5)Zr(dik)_2X$ Complexes in Benzene.

Complex	$k_{25°}$, sec^{-1}	E_a, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$	19.8×10^{-3} [a]	19.5 ± 0.6[b]	12.60 ± 0.37	18.8 ± 0.6	-3.3 ± 1.7
$(\pi\text{-}C_5H_5)Zr(acac)_2Cl$[c]	6.8×10^{-3}	23.1 ± 2.0	14.77 ± 1.18	22.5 ± 1.8	6.9 ± 5.0
$(\pi\text{-}C_5H_5)Hf(acac)_2Cl$[c]	11.3×10^{-3}	24.2 ± 2.2	14.86 ± 1.26	23.3 ± 2.4	6.5 ± 6.2
$(\pi\text{-}C_5H_5)Zr(acac)_2Br$[c]	6.1×10^{-3}	22.8 ± 1.8	14.47 ± 1.05	21.7 ± 1.6	4.3 ± 4.2

[a]All first order rate constants at 25° are extrapolated values. [b]All errors are estimated at the 95% confidence level. [c]From Reference 71.

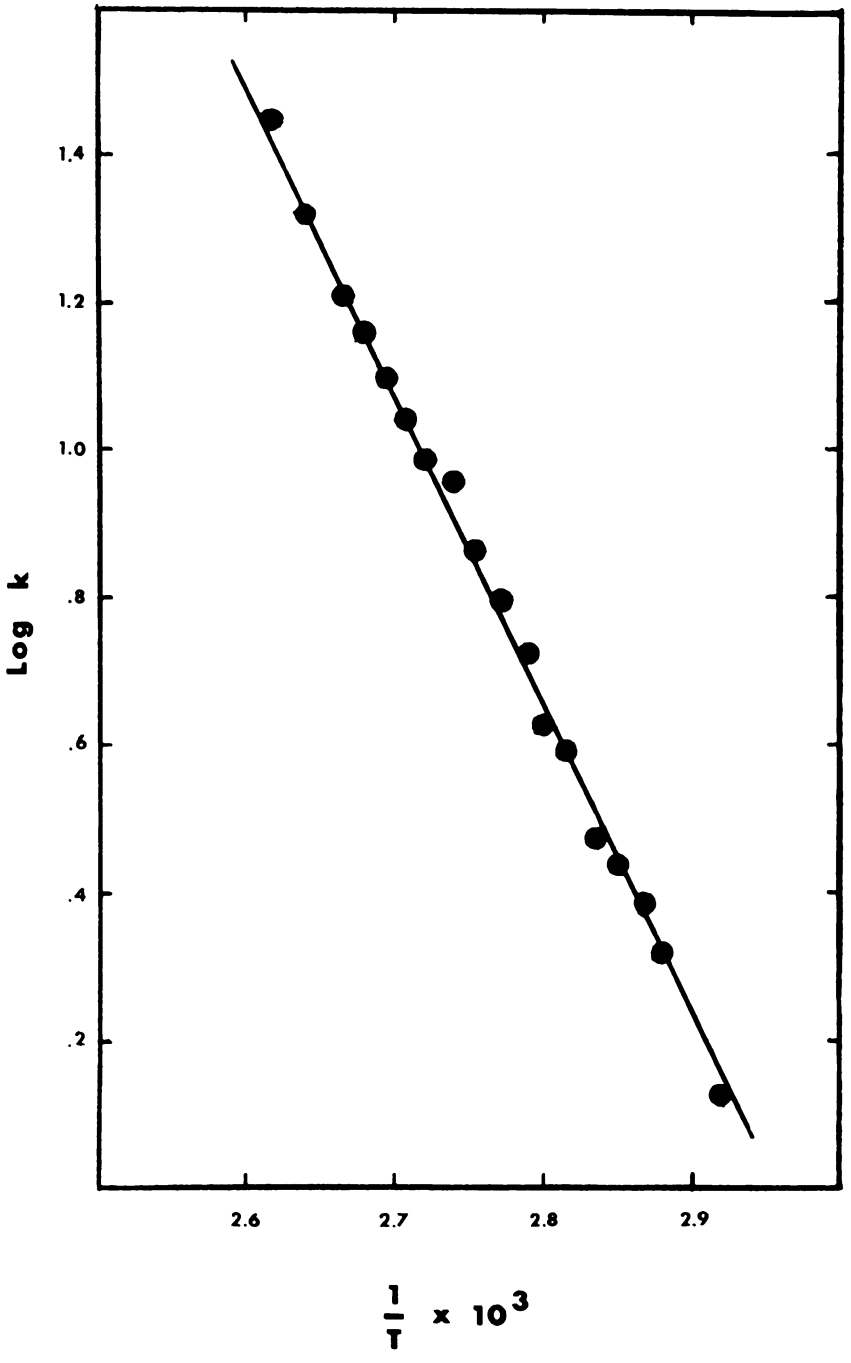


Figure 13. Log k vs. 1/T plot for $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ in benzene solution.

Also, in the presence of an equimolar amount of H(dpm), no exchange is observed between the coordinated and free ligand at 116°. Therefore, the rearrangement process is first order, and the mechanism does not involve total dissociation of the diketonate ligands.

Other workers in this laboratory[71] have determined the activation parameters for similar first-order, intramolecular, stereochemical rearrangement processes of some acetylacetonate complexes (see Table VI). The difference in E_a for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ is greater than the experimental uncertainty expressed at the 95% confidence level. Only a systematic propagation of errors in $\delta\nu$ and T_2 values would eliminate the differences in the activation parameters. Furthermore, the systematic errors would have to be in opposite directions for the two compounds. For example, only if the values of T_2 for $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ were all too large by 20% and those for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ were all too small by an equivalent amount, would the Arrhenius activation energies become equal. This seems very unlikely since the technique used in both studies is identical. Therefore, the difference in the Arrhenius activation energies is undoubtedly real.

It is possible that $(\pi\text{-}C_5H_5)Zr(dpm)_2^+$, formed by the dissociation of the chlorine atom, is an intermediate in the rearrangement process for the $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ molecule since a salt which contains that cation has been isolated in the solid state (cf. Section D). A conductometric titration of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ with $SbCl_5$ in nitrobenzene solution (See Figure 14) indicates that such a cationic species can exist in solution. A similar titration curve was also obtained for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$.[86] The nmr spectrum of a mixture of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ and $SbCl_5$ in dichloromethane exhibits a dependency on the concentration of $SbCl_5$. In the absence of $SbCl_5$, the nmr spectrum consists of one

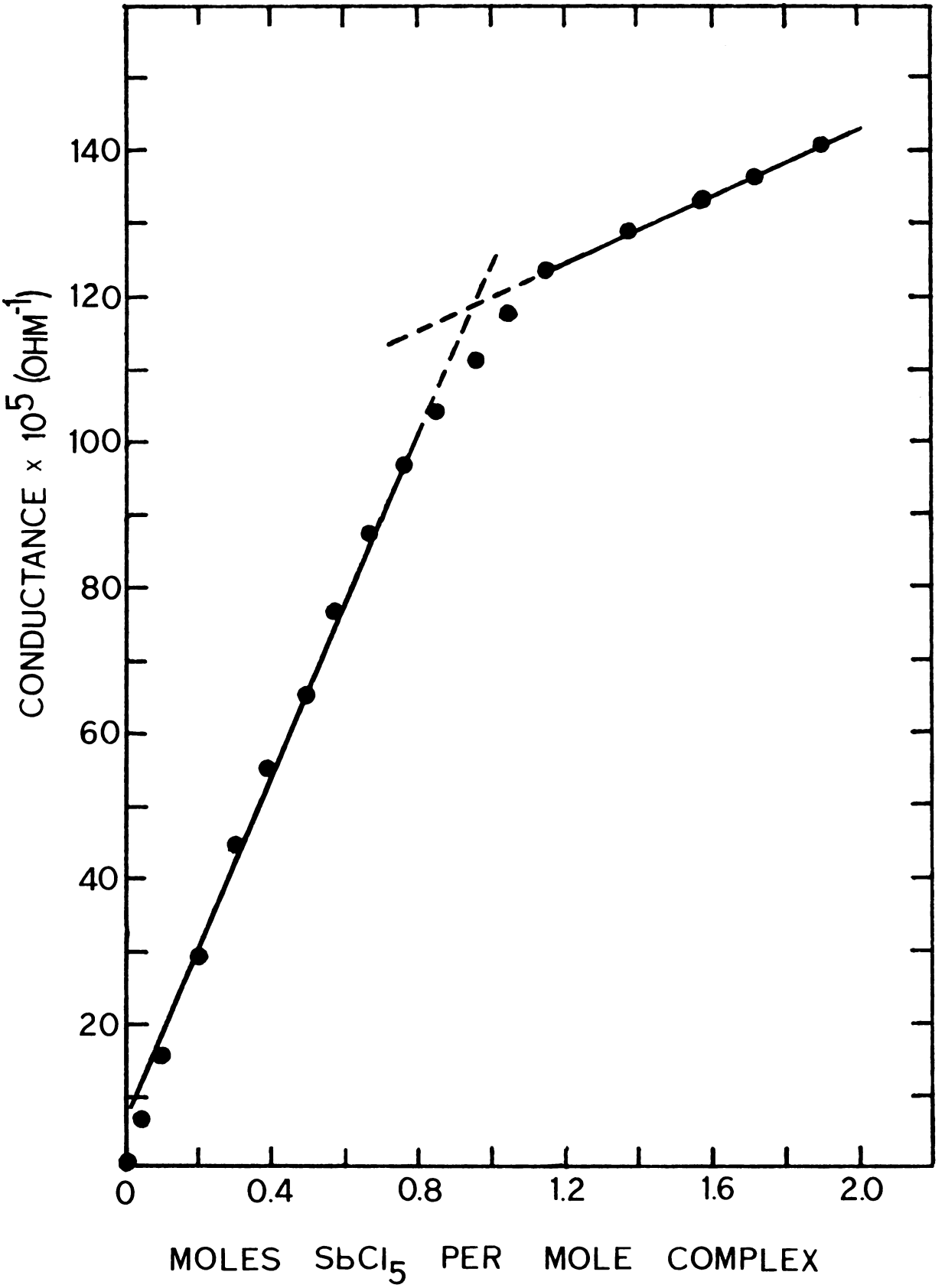


Figure 14. Conductometric titration of 1.69×10^{-2} M $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ with 0.161 M $SbCl_5$ in dichloromethane at room temperature.

sharp π-C_5H_5 line, two sharp -CH= lines, and four sharp tert-C_4H_9 lines at 0.4°. The tert-C_4H_9 peaks have become slightly broader in a 1:75 molar amount of $SbCl_5$ to complex. Increasing the relative concentration of $SbCl_5$ produces progressively broader tert-C_4H_9 and -CH= peaks until the peaks coalesce into a very broad peak at ca. 1 to 1 molar ratio of $SbCl_5$ to complex.

Pinnavaia and Lott[71] have disfavored the formation of a bis(β-diketonato)cyclopentadienylzirconium cation as an intermediate in the stereochemical rearrangement process of the acetylacetonate analogues since (π-C_5H_5)Zr(acac)$_2$Cl and (π-C_5H_5)Zr(acac)$_2$Br exhibit a very small difference in their activation energies (0.3 ± 2.7 kcal/mol). This conclusion can be tested by determining the rate of halide exchange between the bromide and chloride complexes. The cyclopentadienyl chemical shifts in (π-C_5H_5)Zr(acac)$_2$Cl and (π-C_5H_5)Zr(acac)$_2$Br differ by 1.8 Hz in a benzene solution in which the concentration of each compound is 0.17 M. Exchange of the halides between the two compounds also interchanges the cyclopentadienyl environments, and the rate of halide exchange can be determined by applying nmr line-broadening techniques to the cyclopentadienyl resonances. A fundamental assumption is that the π-C_5H_5 ligands are incapable of dissociation and subsequent interchange of their environments.

An equimolar mixture of (π-C_5H_5)Zr(acac)$_2$Cl (0.17 M) and (π-C_5H_5)Zr(acac)$_2$Br (0.17 M) in benzene exhibits two sharp π-C_5H_5 lines, four -CH= lines, and five resolvable acetylacetonate CH_3 lines at room temperature. The relative intensities of the acetylacetonate CH_3 lines indicates that some of their chemical shifts are nearly coincidental. When a fresh mixture of the bromide and chloride complexes is heated to 80°, a temperature at which the intramolecular rearrangement of

(π-C_5H_5)Zr(acac)$_2$Cl and (π-C_5H_5)Zr(acac)$_2$Br can be observed by the line-broadening of the -CH= resonances, the two cyclopentadienyl lines remain sharp, indicating that the halogen exchange is slow. However, it should be mentioned that as the mixture ages at 80°, the cyclopentadienyl lines gradually broaden and eventually coalesce into a single sharp peak. After ca. 75 hours at 80°, only one cyclopentadienyl line with a peak width of ca. 2.0 Hz at half-maximum amplitude is observed. After a moderate length of time at 80° (ca. 8 hr), partial collapse of the two C_5H_5 lines is observed. If the same solution is allowed to age at room temperature for several days and then reheated at 80°, the mean lifetimes of the cyclopentadienyl protons are initially equivalent to those for a freshly-prepared mixture. However, after prolonged heating at 80° (ca. 200 hr), the broadening of the two C_5H_5 lines is no longer reversible in the above manner. A new, unassigned nmr peak in the acetylacetonate methyl region and a distinct yellow coloration of the sample were observed after the prolonged heating period. Apparently, the line-broadening phenomenon is catalyzed by a disproportionation product and a decomposition product of the complexes at elevated temperatures. The disproportionation reaction must be reversible, but the decomposition reaction apparently is not. Even though an appropriate nmr signal is not observed, it is possible that (π-C_5H_5)$_2$ZrCl$_2$ is a disproportionation product which catalyzes the coalescence of the C_5H_5 lines. The cyclopentadienyl lines immediately coalesce at 80° in a freshly-prepared mixture of (π-C_5H_5)Zr(acac)$_2$Cl (0.16 mmol), (π-C_5H_5)Zr(acac)$_2$Br (0.20 mmol), and (π-C_5H_5)$_2$ZrCl$_2$ (0.01 mmol). Thus, regardless of the origin of the line-broadening phenomenon in a mixture of the chloride and bromide analogues, the initial rate of exchange is at least ten times lower than the rate of the stereochemical rearrangement process. More

importantly, the rate of stereochemical rearrangement is independent of the rate of catalyzed "halide" exchange since the mean lifetimes of the acetylacetonate methyl protons in a equimolar mixture of the bromide and chloride complexes do not change after 200 hr of heating at 80°. Therefore it can be concluded that the dissociation of a halide ion to form a $(\pi\text{-}C_5H_5)Zr(acac)_2^+$ intermediate is not an important step in the rearrangement process of the $(\pi\text{-}C_5H_5)Zr(acac)_2X$ complexes.

A plausible intramolecular mechanism involving formation of an eight-coordinate symmetric intermediate, in which the halogen is position trans to the $\pi\text{-}C_5H_5$ ring, has been proposed for the acetylacetonate complexes.[71] It has been suggested that the formation of the symmetric intermediate may occur via the rupture of a Zr-O bond. Random Zr-O bond rupture to form the intermediate would account for the fact that random terminal R group interchange accompanies the interchange of the diketonate ligands. It is also possible for the molecules to form the symmetric intermediate via a twisting motion which does not involve bond rupture. It should be noted, however, that whether the mechanism involves bond rupture or a twisting motion, the steric requirements of the terminal groups on the diketonated ligands do not drastically affect the activation energy for the rearrangement process.

D. Preparation and Properties of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl\cdot SbCl_5$

The reaction of equimolar quantities of $SbCl_5$ and $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ at 0° gives a yellow crystalline compound which slowly decomposes into a black oily substance at room temperature. The chemical analysis of the compound suggests its formulation as a 1:1 adduct of the reactants. Admittedly the analytical data are not as good as hoped for, but the disagreement between the calculated and theoretical elemental analyses

is probably due to the unstable nature of the compound and the presence of an impurity (see below).

The compound has a molar conductivity at 25° of 18.6 ohm^{-1} cm^2 mol^{-1} (2.81×10^{-3} M in $C_6H_5NO_2$), and hence must be appreciably dissociated in solution. The relatively high conductivity cannot be attributed directly to either of the reactants. Antimony pentachloride and $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ exhibit molar conductivities of 0.799 (17.0×10^{-3} M) and 0.151 ohm^{-1} cm^2 mol^{-1} (1.84×10^{-3} M) in nitrobenzene, respectively. A typical 1:1 electrolyte, $[Ti(acac)_3][SbCl_6]$, has a molar conductivity at 25° of 19.5 ohm^{-1} cm^2 mol^{-1} in a 1.0×10^{-2} M solution in nitrobenzene.[87] Thus, the formulation of the compound as a 1:1 electrolyte, $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$, seems reasonable.

The solubility of the compound is also consistent with an ionic substance. It is insoluble in the nonpolar solvent benzene, but it is readily soluble in such polar solvents as dichloromethane, acetone, and acetonitrile.

The carbonyl stretching bands in the ir spectrum appear between 1660 and 1500 cm^{-1}, a shift to lower energy of ca. 50 cm^{-1} from the uncoordinated β-diketone, and indicate bidentate coordination of the dipivaloylmethanate ligands. The weak band at ca. 3100 cm^{-1} due to the C-H vibrations of the cyclopentadienyl group is absent, but its absence is inconsequential in view of the nmr spectrum of the compound (see below). A band at ca. 342 cm^{-1} typically occurs for $SbCl_6^-$ anions,[89] and indeed a strong absorption is observed at 345 cm^{-1} in this case. However, a strong band of similar shape occurs at 325 cm^{-1} in the parent complex, $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$, and hence the 342 cm^{-1} absorption cannot be unambiguously attributed to the $SbCl_6^-$ anion.

The nmr chemical shifts offer further support for the $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$ formulation. The nmr spectra for $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ and $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$ are compared in Figure 15. The shift of the $\pi\text{-}C_5H_5$, -CH=, and tert-C_4H_9 resonances to lower field strength is consistent with the formation of a cationic cyclopentadienylmetal-β-diketonate complex. Fay and Serpone[88] report 0.25 to 0.54 ppm and 0.54 to 1.37 ppm shifts to lower fields for the -CH= and CH_3 chemical shifts for several acetylacetonate cationic complexes relative to analogous neutral species. Due to the inductive effect of the tert-C_4H_9 groups, the electric field effects would be less for a dipivaloylmethanate complex cation and would account for the observed smaller changes in chemical shifts. Shifts to higher field strength would be expected for anionic complexes.[88] The chemical shift of τ 3.53 for the C_5H_5 groups suggests that the ligand is π-bonded to zirconium. The chemical shift of a time-averaged $\sigma\text{-}C_5H_5$ peak is usually ca. 1.0 ppm downfield relative to a $\pi\text{-}C_5H_5$ peak.[90] The $\pi\text{-}C_5H_5$ chemical shifts for two compounds whose structure is known, $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(hfac)_3$, are τ 3.69 and 3.54 in dichloromethane respectively. In addition, the C_5H_5 chemical shifts in $(\pi\text{-}C_5H_5)Zr(dpm)_3$ and $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$, occur at τ 3.99 and 3.69, respectively. The temperature-independence of the cyclopentadienyl resonance (Figure 17) also suggests, in part, a $\pi\text{-}C_5H_5$ ligand.

Although, the chemical analysis, molar conductivity, solubility, and ir and nmr spectral data are consistent with the suggested ionic formulation, it should be noted that the data could be interpreted in terms of the formulation $[Zr(dpm)_2Cl][(\sigma\text{-}C_5H_5)SbCl_5]$. The expected 1.0 ppm downfield shift for a $\sigma\text{-}C_5H_5$ chemical shift could be countered by an almost equivalent upfield shift due to the negative charge on the

Figure 15. Comparison of the proton nmr spectra of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ and $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$ in dichloromethane. A. $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$, 10.0 g/100 ml solvent at 40°. B. $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$, 10.0 g/100 ml solvent at 40°. The differences in the mean chemical shifts between $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$ and $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ are as follows: $\pi\text{-}C_5H_5$, -0.16 ppm; -CH=, -0.20 ppm; tert-C_4H_9, -0.04 ppm. The peaks marked with an "x" are ^{13}C or spinning side-band satellites of the solvent peak.

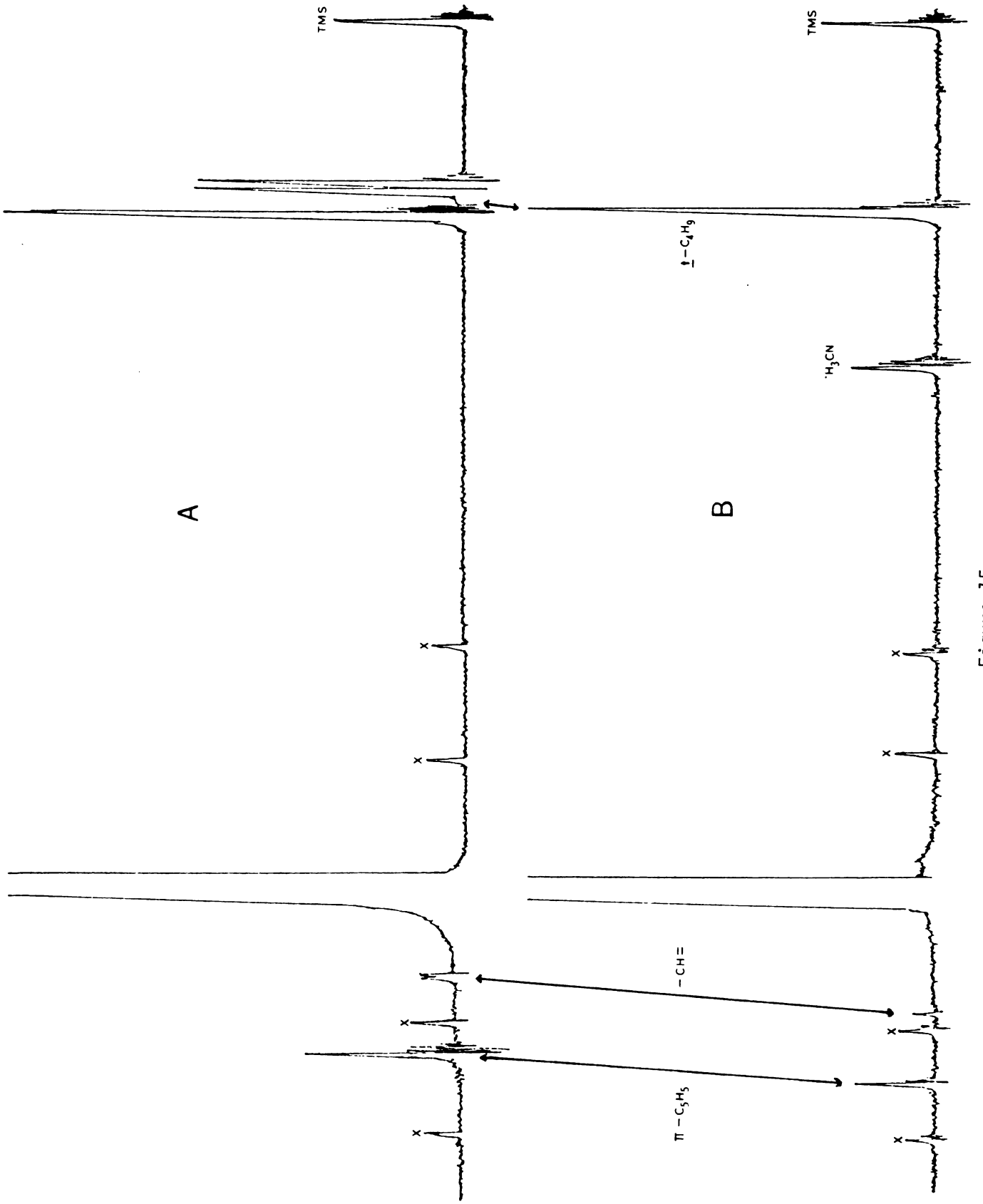


Figure 15.

Figure 16. A. Proton nmr spectrum (60 MHz) of $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$ in dichloromethane at 40°; concentration is 10.0 g/100 ml solvent. B. Spectrum after the addition of 0.05 ml CH_3CN (0.95 mmol) to 0.47 ml of the solution. The peaks designated "X" are either ^{13}C or spinning side-band satellites of the solvent peak. The other resonances have been previously identified in Figure 15.

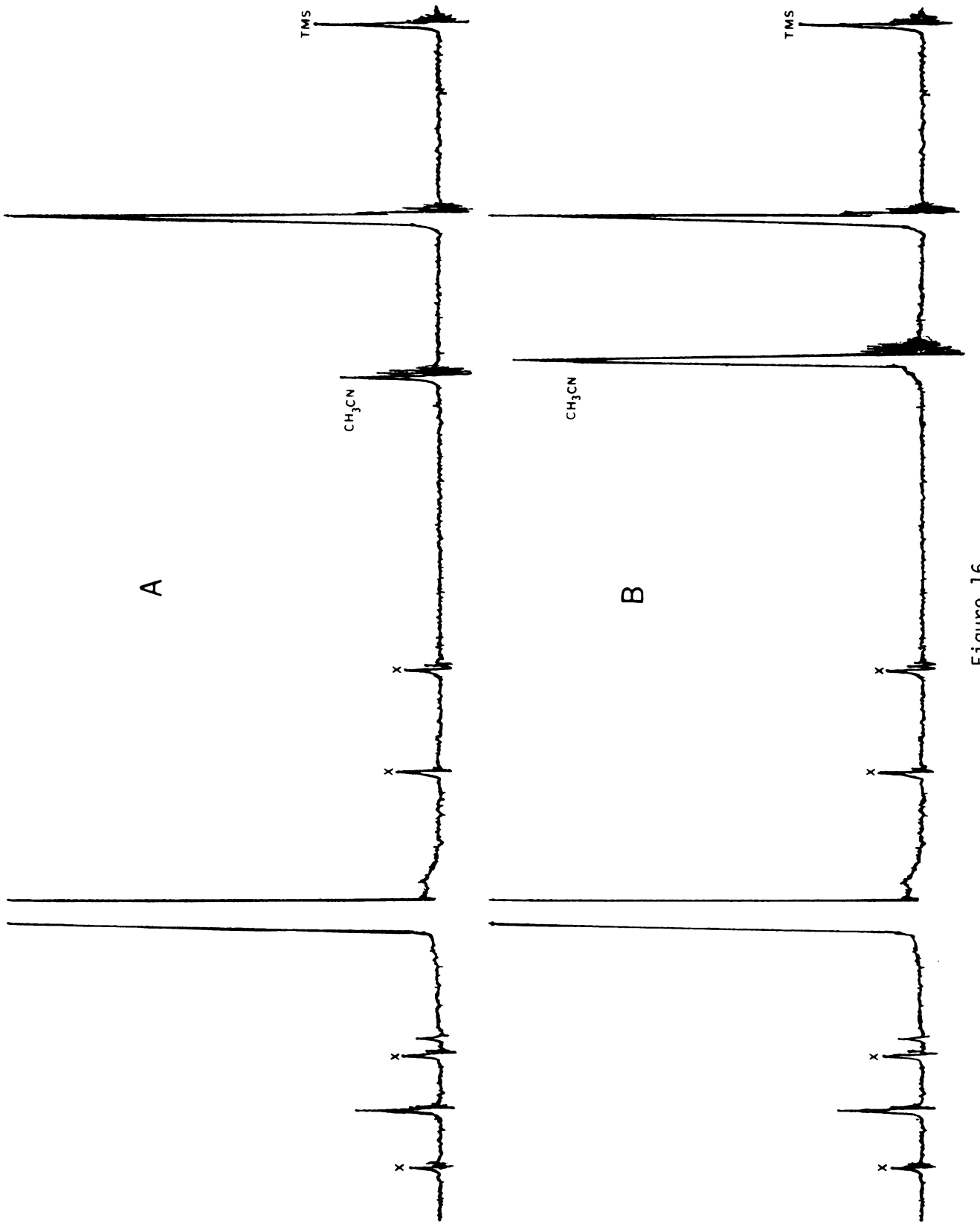


Figure 16.

ion, and the C_5H_5 singlet at -55° could be due to the fluctional character of the ligand. However, $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$ is favored since $SbCl_6^-$ is a stable anion. Furthermore, $(\sigma\text{-}C_5H_5)SbCl_5^-$ is not known, and attempts to prepare $Zr(dik)_2Cl^+$ from $Zr(dik)_2Cl_2$ have been unsuccessful.[93]

The presence of a CH_3CN impurity is clearly indicated by ir and nmr spectroscopy. Two ir bands occur at 2285 and 2315 cm^{-1} where the C≡N stretching frequencies for acetonitrile are expected. Furthermore, the nmr peat at τ 7.91 is due to acetonitrile. Addition of CH_3CN to a solution of $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$ increases the relative intensity of that peak (Figure 16). The shift to a higher field of the chemical shift upon addition of CH_3CN is presumably due to a mean decrease in the interaction of acetonitrile with the complex. At temperatures as low as -75°, one sharp CH_3CN peak is observed in the mixture. This indicates that if CH_3CN is coordinated to the cation, it exchanges rapidly with free CH_3CN.

The temperature dependence of the nmr spectrum of $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$ in dichloromethane is shown in Figure 17. The spectrum at -55° can most simply be interpreted on the basis of a trigonal bipyramidal coordination polyhedron in which the $\pi\text{-}C_5H_5$ ring occupies an axial vertex and the oxygen atoms of the diketonate ligands occupy the remaining coordination sites. As the temperature is increased above -55°, the two -CH= lines of relative intensity 1:1 and the three <u>tert</u>-C_4H_9 lines of relative intensities 1:2:1 broaden and coalesce into sharp singlets. Cooling below -55° results in some broadening again, presumably due to solvent viscosity effects. At all temperatures, only one sharp cyclopentadienyl peak is observed.

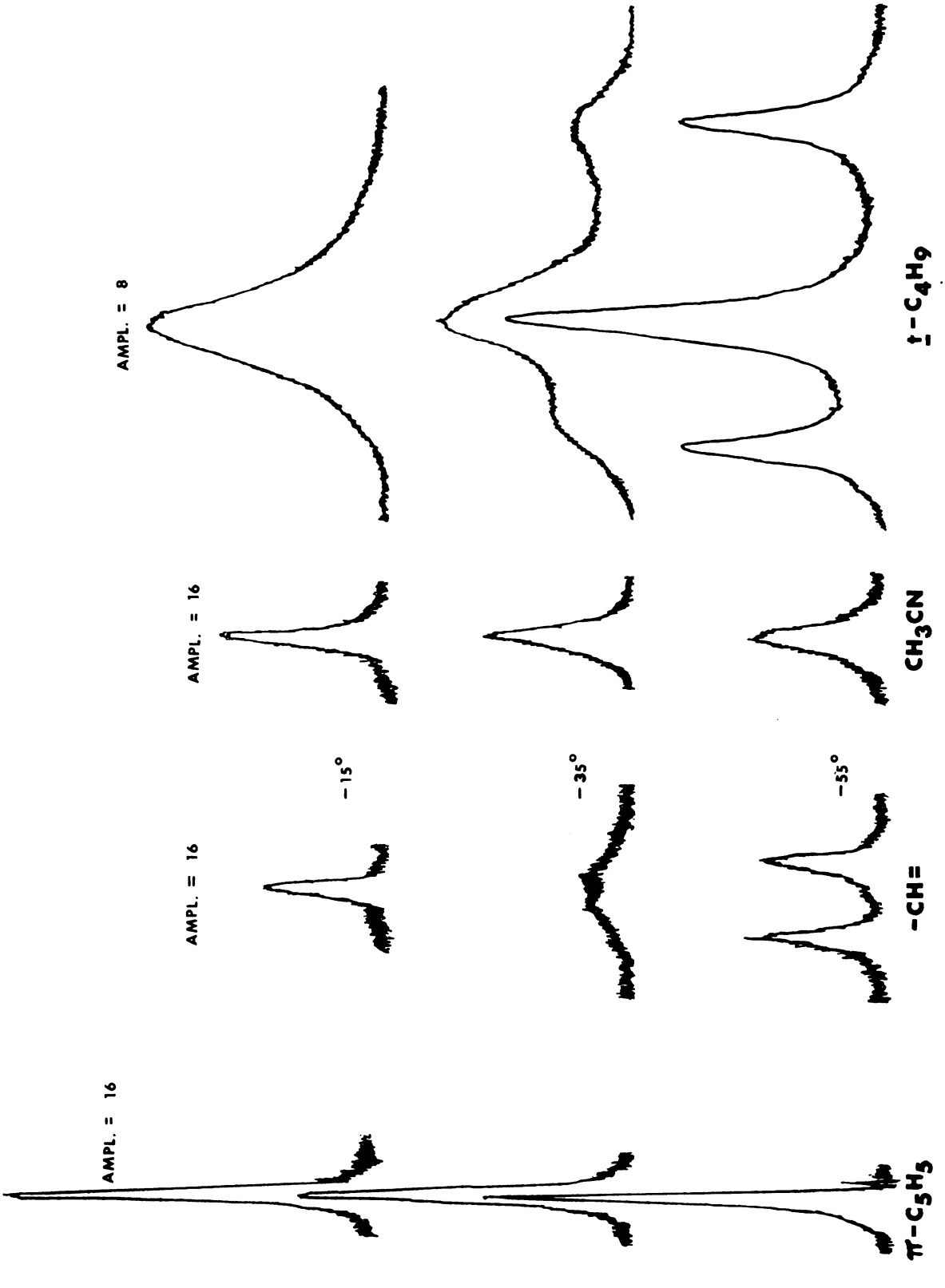


Figure 17. Temperature dependence of the proton nmr spectrum of $[(\pi\text{-}C_5H_5)Zr(dpm)_2][SbCl_6]$ in dichloromethane.

The line-broadening phenomenon identifies a stereochemical rearrangement process which interchanges the nonequivalent dipivaloylmethanate environments. The stereochemical rearrangement process can be interpreted in terms of a symmetric intermediate based on a square pyramidal coordination polyhedron in which the two dipivaloylmethanate ligands span edges of the basal plane. Rapid formation of the intermediate would account for the uniform collapse of the four tert-C_4H_9 lines of $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ as $SbCl_5$ is added to the solution at 0°. It should be noted that $(\pi\text{-}C_5H_5)Zr(dpm)_2^+$ is more labile than the neutral $(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$ complex. This fact precludes a mechanism common to both complexes in which bond-rupture is an important part of the activation process. However, although the lability of the cation, which is coordinately unsaturated, is best explained by a twist mechanism, rupture of a Zr-O bond may be a primary step in the rearrangement mechanism of the neutral molecule.

E. Characterization of the $(\pi\text{-}C_5H_5)Zr(dik)_3$ Complexes

1. Nmr Spectra. The temperature dependence of the ^{19}F nmr spectrum of $(\pi\text{-}C_5H_5)Zr(hfac)_3$ in diisopropyl ether is shown in Figure 18 along with the temperature dependence of the -CH= proton resonance lines. At -42.5° the ^{19}F spectrum consists of four CF_3 lines with relative integral intensities of 2:1:2:1, and the -CH= proton spectrum exhibits two lines with relative intensities of 2:1. At all temperatures only one cyclopentadienyl peak is observed. As the temperature is increased to 50.8°, the more intense pair of CF_3 lines broadens and then merges into a single sharp line. Although the chemical shift difference between the less intense pair of CF_3 lines increases over this temperature range, the widths of these lines show only a small temperature dependence. As the temperature is increased further, the time-averaged CF_3 line and the

Figure 18. Temperature dependence of the ^{19}F and -CH= proton nmr lines for $(\pi\text{-}C_5H_5)Zr(hfac)_3$ in diisopropyl ether solution; concentration is 0.12 M.

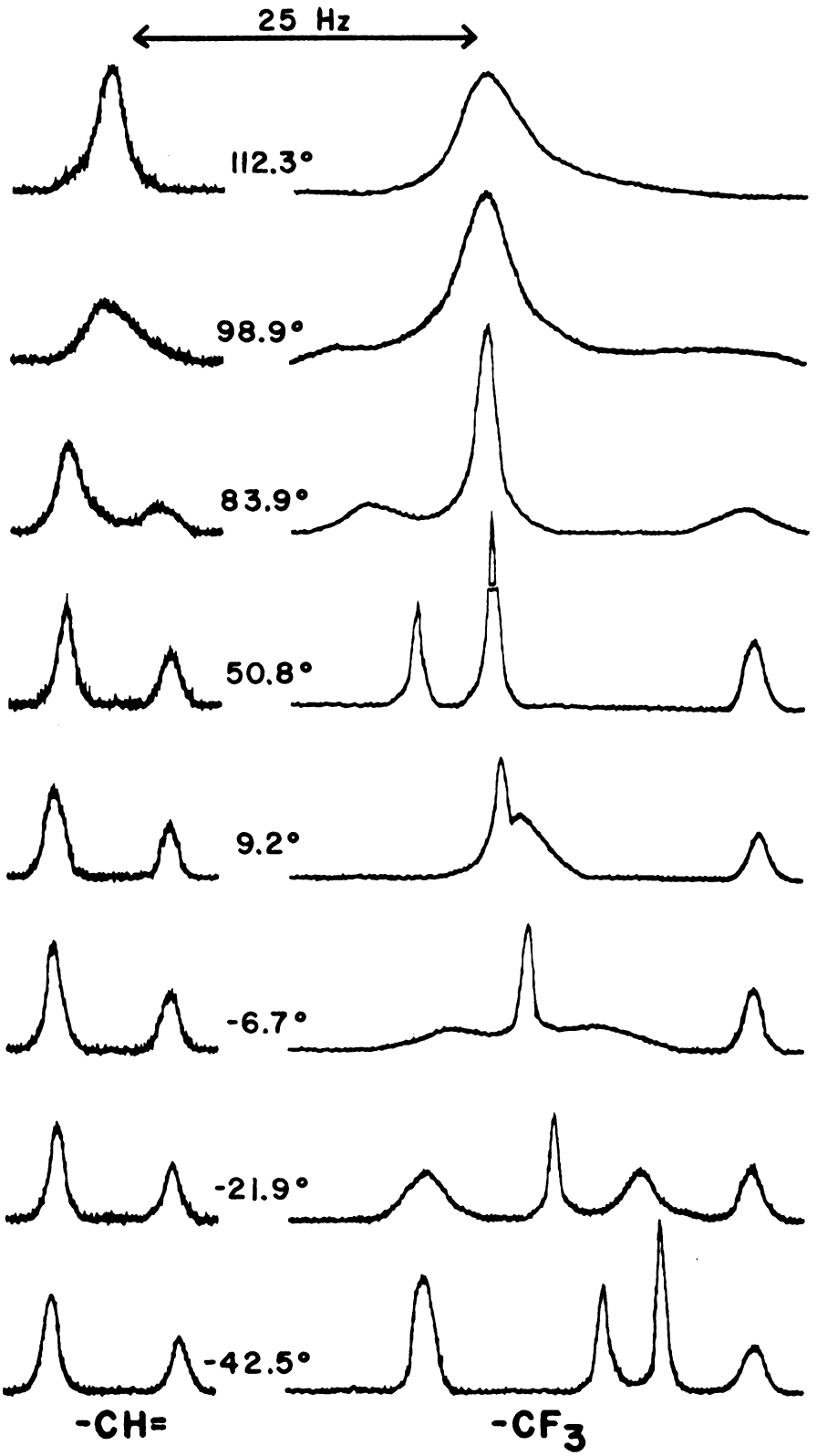


Figure 18.

less intense pair of CF_3 resonances broaden and merge into a single sharp line. Simultaneously, the two -CH= resonances broaden and coalesce.

The temperature dependence of the CF_3 and -CH= nmr line shapes indicates that two discrete types of stereochemical rearrangement processes occur for the $(\pi\text{-}C_5H_5)Zr(hfac)_3$ molecule, as suggested earlier by Elder, Evans, and Graham.[63] The faster process (process I), which is manifested in the CF_3 line broadening in the range -42.5 to 50.8°, interconverts the two nonequivalent pairs of CF_3 terminal groups ($R^{(A)}$ and $R^{(B)}$ in Figure 19) on the β-diketonate ligands which span equatorial edges of the pentagonal bipyramid. The slower process (process II) interchanges the unique β-diketonate ligand spanning the equatorial-axial edge with the two equatorial β-diketonate ligands and results in the simultaneous averaging of the two -CH= environments and all nonequivalent CF_3 environments.

Analogous rearrangement processes were observed for $(\pi\text{-}C_5H_5)Zr(dpm)_3$ and $(\pi\text{-}C_5H_5)Zr(acac)_3$. The temperature dependences of the tert-C_4H_9 and -CH= resonance lines of $(\pi\text{-}C_5H_5)Zr(dpm)_3$ in o-xylene solution, which are shown in Figure 20, are qualitatively similar to those described for the CF_3 and -CH= resonances of $(\pi\text{-}C_5H_5)Zr(hfac)_3$. The room temperature spectrum of two diketonate -CH= peaks in a 2:1 ratio and four tert-C_4H_9 peaks in a 1:2:2:1 ratio confirms that the coordination polyhedron of the dipivaloylmethanate derivative is also a pentagonal bipyramid. As the temperature is raised, the same qualitative stereochemical rearrangement processes occur. Process I occurs from room temperature to ca. 95°, and process II occurs above ca. 95°. Although $(\pi\text{-}C_5H_5)Zr(dpm)_3$ is appreciably less stereochemically labile than $(\pi\text{-}C_5H_5)Zr(hfac)_3$, the former complex is less thermally stable as evidenced by the appearance of several unidentified impurity lines in the

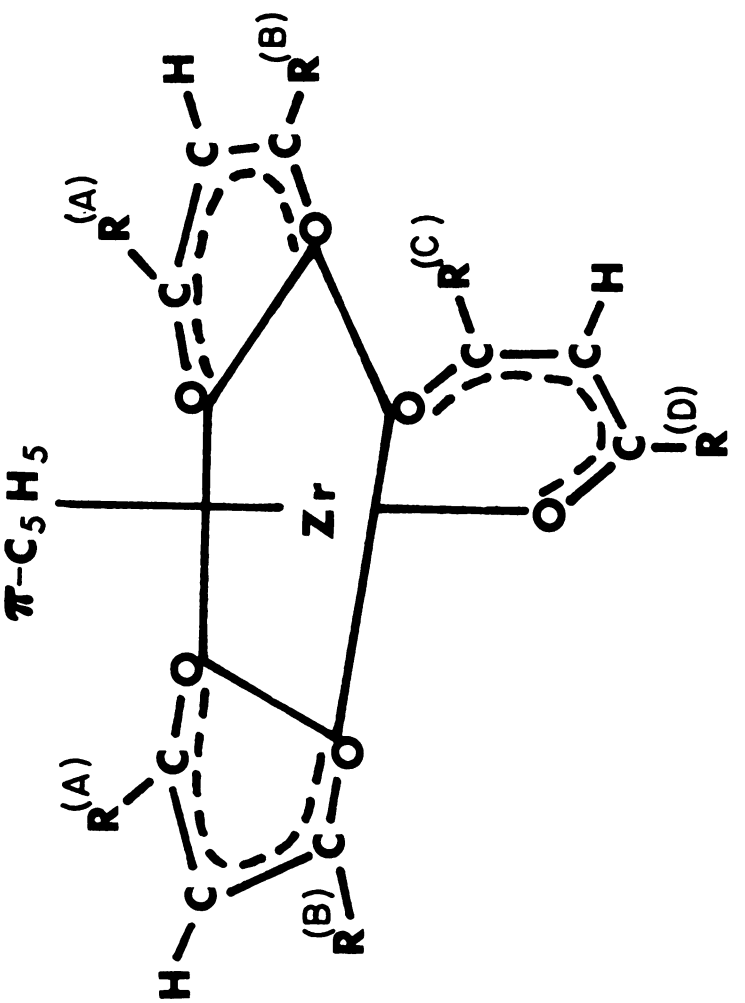


Figure 19. The molecular configuration for $(\pi\text{-}C_5H_5)Zr(dik)_3$ based on a simple pentagonal bipyramidal model.

Figure 20. Temperature dependence of the tert-C_4H_9 and -CH= proton nmr lines for (-C_5H_5)Zr(dpm)$_3$ in o-xylene; concentration is 0.21 M. The lines marked "X" in the tert-C_4H_9 region are due to unidentified thermal decomposition products.

tert-C_4H_9 region, especially at elevated temperatures. Since the widths of the tert-C_4H_9 resonance lines for $(\pi\text{-}C_5H_5)Zr(dpm)_3$ showed no dependence on the degree of thermal decomposition, the degradation products do not influence the rate of process I.

$(\pi\text{-}C_5H_5)Zr(acac)_3$ is stereochemically more labile than the hexafluoroacetylacetonate and dipivaloylmethanate derivatives as indicated by the temperature dependence of the nmr spectrum of $(\pi\text{-}C_5H_5)Zr(acac)_3$ in carbon disulfide and tetrachloroethylene (Figure 21). A pentagonal bipyramidal ground state configuration is suggested by the -100° spectrum, and the line-broadening phenomena at higher temperatures identify the two stereochemical rearrangement processes. The appearance of an impurity peak in the -CH= region indicates some thermal decomposition, but the onset of the degradation occurs at temperatures in excess of those used to obtain kinetic data for process II.

The asymmetry of the benzoylacetonate, trifluoroacetylacetonate, pivaloylacetonate, and pivaloyltrifluoroacetonate ligands can give rise to six possible geometric isomers based on a pentagonal bipyramidal configuration in which the $\pi\text{-}C_5H_5$ ring occupies an axial vertex. Therefore, in the absence of any stereochemical rearrangement, the nmr spectra for these derivatives are more complex than those of the symmetrical β-diketonate derivatives. Because of their mechanistic utility, a discussion of these derivatives will be discussed later. However, it should be noted that the temperature dependences of their nmr spectra indicate, in general, a stereochemical lability which is approximately equal to that for $(\pi\text{-}C_5H_5)Zr(hfac)_3$.

2. Process I. Mean lifetimes τ_A and τ_B for the nonequivalent terminal groups on the equatorial ligands of $(\pi\text{-}C_5H_5)Zr(hfac)_3$, $(\pi\text{-}C_5H_5)Zr(dpm)_3$ and $(\pi\text{-}C_5H_5)Zr(acac)_3$ were determined by comparing the

Figure 21. Temperature dependence of the CH_3 and -CH= proton nmr lines for $(\pi\text{-}C_5H_5)Zr(acac)_3$. The low temperature spectra (-58.9 to -94.9°) are in carbon disulfide solution; concentration is 0.22 M. At 42.7° and higher, the spectra are for a tetrachloroethylene solution; concentration, 0.32 M. The lines marked "X" are due to unidentified thermal decomposition products.

experimental CF_3, tert-C_4H_9, and CH_3 nmr line shapes with line shapes calculated for various trial values of τ, where $\tau = \tau_A/2 = \tau_B/2$. Although mean lifetimes for $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and $(\pi\text{-}C_5H_5)Zr(acac)_3$ could be determined in the region of exchange above and below the coalescence temperature, lifetimes for $(\pi\text{-}C_5H_5)Zr(dpm)_3$ were accessible only below the coalescence temperature. Above the coalescence temperature the time-averaged tert-C_4H_9 proton resonance for $(\pi\text{-}C_5H_5)Zr(dpm)_3$ is further broadened by the onset of process II, and the appearance of impurity lines prohibits accurate determination of line-shape parameters.

Curve A in Figure 22 indicates that for $(\pi\text{-}C_5H_5)Zr(hfac)_3$ the frequency separation between the CF_3 resonances in the region of slow exchange, $\delta\nu$, is temperature-dependent, presumably, because of temperature-dependent solvation effects. Therefore, values of $\delta\nu$ in the region of exchange were determined by linear least-squares extrapolation of the temperature dependence of $\delta\nu$ in the slow-exchange region. It is also apparent from curves B and C in Figure 22 that the widths of the two CF_3 resonances differ in the limit of slow exchange. Thus the apparent transverse relaxation times, T_{2A} and T_{2B}, are unequal. Values of T_{2A} and T_{2B} in the region of exchange were determined by estimating a small temperature dependence for each line width, as shown by the dashed lines connecting curves B and C with curve D. The estimated temperature dependences are based on the observed temperature dependences for the line widths of the CF_3 group on the unique ligand over the same temperature range: $-3.7 \pm 1.1 \times 10^{-3}$ Hz/°C for the narrower, low-field line and $2.0 \pm 0.6 \times 10^{-3}$ Hz/°C for the broader, high-field line.

A plot similar to that of Figure 22 indicates that the frequency separation and widths for the tert-C_4H_9 proton resonance components of $(\pi\text{-}C_5H_5)Zr(dpm)_3$ are also temperature dependent, but that the widths of

Figure 22. Temperature dependence of ^{19}F nmr line-shape parameters for the terminal CF_3 groups on the equatorial ligands of $(\pi\text{-}C_5H_5)Zr(hfac)_3$ in diisopropyl ether: curve A, frequency separation between the resonance components below coalescence; curves B and C, widths at half-maximum amplitude of the low- and high-field resonance components, respectively, below coalescence; curve D, width of the time-averaged resonance above coalescence. The significance of the extrapolated (dashed) lines is described in the text.

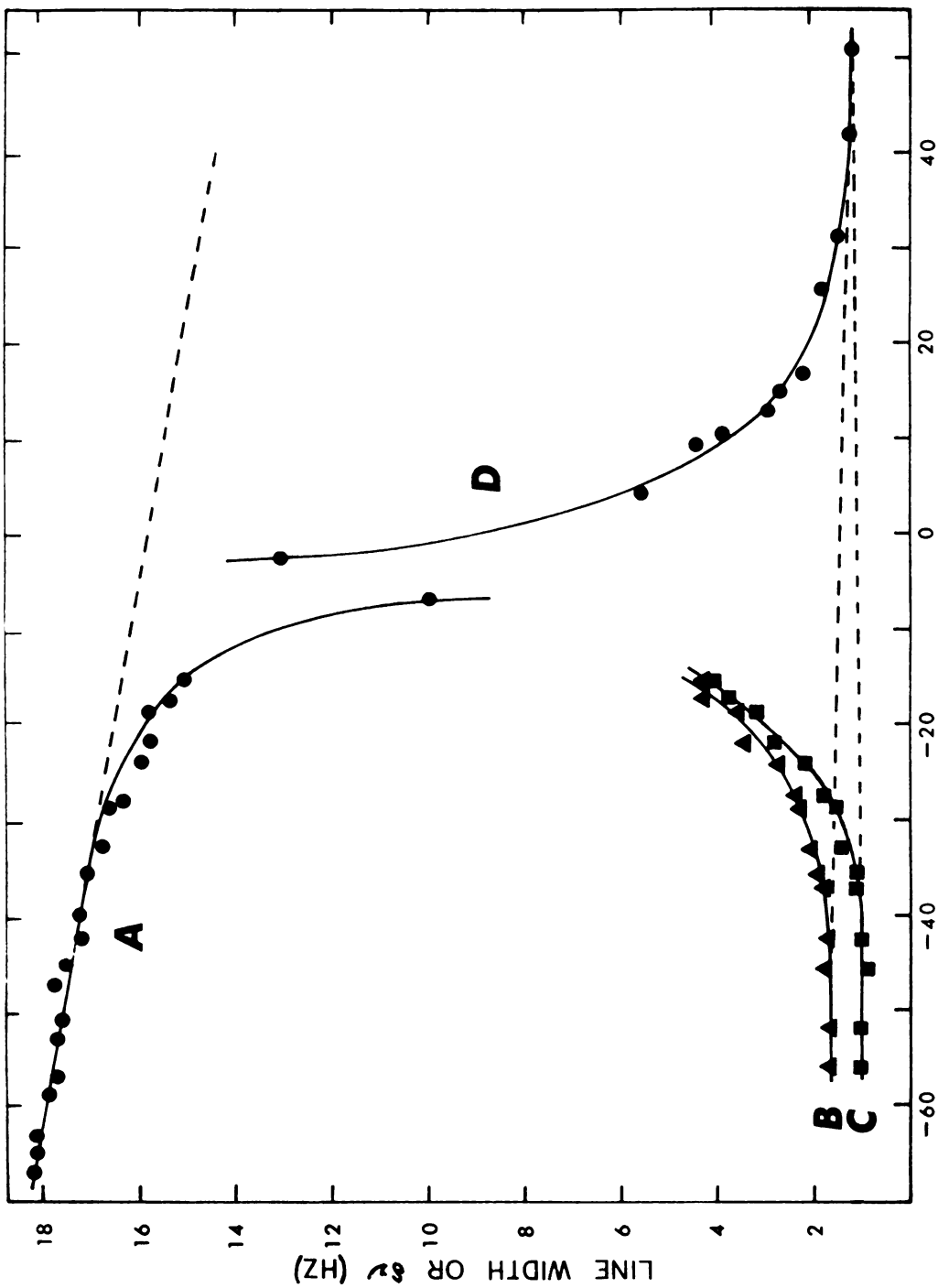

LINE WIDTH OR $\delta\nu$ (HZ)
18
16
14
12
10
8
6
4
2
A
B
C
D
-60
-40
-20
0
20
40
T (°C)

Figure 22.

the lines, and hence the transverse relaxation times, are equal in the region of slow exchange. In a manner exactly analogous to that depicted in Figure 22, values of $\delta\nu$ and the transverse relaxation times were determined from extrapolations of the appropriate lines.

The two low-field CH_3 lines of $(\pi\text{-}C_5H_5)Zr(acac)_3$ overlap in the region of slow exchange, and their accurate line widths are impossible to determine. However, in the region above the coalescence temperature for process I, the line-widths of the CH_3 resonances of the unique ligand are equal. Therefore, it was assumed that T_{2A} and T_{2B} for the CH_3 protons of the equatorial ligands were also equal. Values for T_{2A} and T_{2B} were determined by extrapolating the observed temperature-dependence of the CH_3 line-widths into the region of exchange. The extrapolation was aided by three data points in the region of exchange, -81.3, -73.7, and -58.9°, for which T_{2A} and T_{2B} were variables in total line shape analyses of the spectra. Finally, a temperature dependence was not observed for $\delta\nu$ in the region of slow exchange, i.e., below -94.9°, and therefore, a constant value for $\delta\nu$ was extrapolated into the region of exchange.

Values of the nmr line-shape parameters and the calculated values of τ for the terminal groups on the equatorial ligands of $(\pi\text{-}C_5H_5)Zr(hfac)_3$ in diisopropyl ether, $(\pi\text{-}C_5H_5)Zr(dpm)_3$ in o-xylene, and $(\pi\text{-}C_5H_5)Zr(acac)_3$ in carbon disulfide are given in Tables VIII, IX, and X, respectively. Shown in the Table XI are the Arrhenius activation energy, E_a, the frequency factor, A, the activation entropy, $\Delta S^{\ddagger}$, the activation enthalpy, $\Delta H^{\ddagger}$, and the extrapolated value of the first-order rate constant at 25°, $k_{25°}$, for the compounds. Values of E_a and A were determined from the slope and intercepts of graphs of log k vs. 1/T, where $k = (2\tau)^{-1}$. These graphs are shown in Figure 23. Graphs of log (k/T) vs. 1/T were used to determine $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

Table VIII. ^{19}F Nmr Line-Shape Parameters and Kinetic Data for the Interchange of Nonequivalent CF_3 Groups on the Equatorial Ligands of $(\pi\text{-}C_5H_5)Zr(hfac)_3$.[a]

Temp, °C	T_{2B}, sec[b]	T_{2A}, sec[c]	$\delta\nu$,[d] Hz	Line Widths,[e] Hz	$10^3\ \tau$, sec
-32.9	0.209	0.315	16.93	2.02,1.38	406
-28.8	0.211	0.312	16.79	2.25,1.54	283
-27.9	0.211	0.312	16.76	2.29,1.72	234
-24.2	0.214	0.309	16.62	2.72,2.15	145
-21.9	0.215	0.308	16.54	3.41,2.80	93.7
-18.8	0.217	0.307	16.43	3.51,3.17	83.6
-17.4	0.217	0.307	16.38	4.21,3.72	65.6
-15.6	0.218	0.306	16.32	4.26,4.03	62.1
4.1	0.231	0.298	15.63	4.50	5.09
9.2	0.234	0.295	15.44	4.36	3.95
10.3	0.234	0.295	15.41	3.88	3.40
12.7	0.236	0.295	15.32	2.94	2.28
14.8	0.238	0.292	15.25	2.65	1.92
16.6	0.239	0.292	15.18	2.19	1.33
25.4	0.247	0.289	14.87	1.79	0.838
31.0	0.251	0.287	14.67	1.51	0.444

[a]In diisopropyl ether; concentration is 0.12 M. [b]Transverse relaxation time for low-field CF_3 resonance. [c]Transverse relaxation time for high-field CF_3 resonance. [d]Frequency separation between the resonance components in absence of exchange. [e]Line widths in the range -32.9 to -15.6° refer to the widths at half-maximum amplitude of the low-field and high-field resonance components below the coalescence temperature; above -15.6°, the widths are for the time-averaged resonance above coalescence.

Table IX. ^{1}H Nmr Line-Shape Parameters and Kinetic Data for the Interchange of Nonequivalent tert-C_4H_9 Groups on the Equatorial Ligands of $(\pi\text{-}C_5H_5)Zr(dpm)_3$.[a]

Temp, °C	$\delta\nu$,[b] Hz	r[c]	Line widths, Hz[d]	$10^2\ \tau$, sec
65.2	11.60		1.16	27.0[e]
70.1	11.54		1.61	15.2
74.0	11.48		2.16	10.5
74.5	11.60	9.83	2.26	9.83
79.5	11.43	5.72	3.08	7.09
79.8	11.42	5.29	3.13	6.88
83.3	11.37	3.06	4.42	5.04
84.3	11.36	2.66	4.66	4.73
87.1	11.31	1.68		3.48

[a]In o-xylene at a concentration of 0.21 M. [b]Frequency separation between the resonance components in absence of exchange. [c]Ratio of the maximum to center minimum intensities. [d]Average width of the resonance components below the coalescence temperature. [e]The value of T_2 used in the calculation of all values of τ was 0.590 sec.

Table X. ^{1}H Nmr Line-Shape Parameters and Kinetic Data for the Interchange of Nonequivalent CH_3 Groups on the Equatorial Ligands of $(\pi\text{-}C_5H_5)Zr(acac)_3$.[a]

Temp, °C	sec[b]	r[c]	Line widths,[d] Hz	10^2 τ, sec
-85.8	.241		3.25	9.27
-85.6	.241	4.46	2.98	10.2
-81.3	.249	2.56	4.17	6.02
-80.3	.259	2.46	4.27	6.12
-76.0	.277	1.11		2.88
-75.0	.277	1.22		3.22
-74.9	.277	1.057		2.69
-73.9	.277		10.40	2.08
-72.1	.289		9.85	1.96
-72.0	.289		9.70	1.93
-69.7	.300		8.47	1.70
-67.1	.312		4.80	1.00
-64.8	.328		4.24	0.887
-6 .6	.328		4.45	0.904
-62.0	.346		3.40	0.694
-58.9	.364		2.52	0.473
-58.4	.370		2.38	0.439
-54.4	.393		1.81	0.291

[a]In carbon disulfide; concentration is 0.22 M. [b]Transverse relaxation time for the CH_3 resonances. [c]Ratio of the maximum to central minimum intensities. [d]Line widths in the range -85.8 to -80.3° refer to the widths at half-maximum amplitude of the high-field resonance component below the coalescence temperature; at -73.9° and above, the widths are for the time-averaged resonance above coalescence. [e]The value of $\delta\nu$ used in the calculation of all values of τ was 10.40 Hz.

Table XI. Activation Parameters for the Interchange of Nonequivalent Terminal Groups on the Equatorial Ligands of $(\pi\text{-}C_5H_5)Zr(dik)_3$.

Complex	$k_{25°}$, sec^{-1} [a]	E_a, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$ eu
$(\pi\text{-}C_5H_5)Zr(acac)_3$ [b]	4.44×10^{4}	9.2 ± 0.5 [c]	11.37 ± 0.50	8.8 ± 0.4	-7.7 ± 2.0
$(\pi\text{-}C_5H_5)Zr(hfac)_3$ [d]	6.46×10^{2}	15.7 ± 0.5	14.38 ± 0.38	15.2 ± 0.5	5.2 ± 1.8
$(\pi\text{-}C_5H_5)Zr(dpm)_3$ [e]	2.84×10^{-2}	21.3 ± 1.9	14.05 ± 1.19	20.7 ± 1.7	3.7 ± 4.9

[a]All first order rate constants at 25° are extrapolated values. [b]In carbon disulfide; concentration is 0.22 M. [c]All errors are estimated at the 95% confidence level. [d]In diisopropyl ether; concentration is 0.12 M. [e]In o-xylene; concentration is 0.21 M.

Figure 23. Arrhenius plots for the exchange of nonequivalent terminal groups on the equatorial ligands of $(\pi\text{-}C_5H_5)Zr(dpm)_3$ in o-xylene (line A), $(\pi\text{-}C_5H_5)Zr(hfac)_3$ in diisopropyl ether (line B), and $(\pi\text{-}C_5H_5)Zr(acac)_3$ in carbon disulfide (line C).

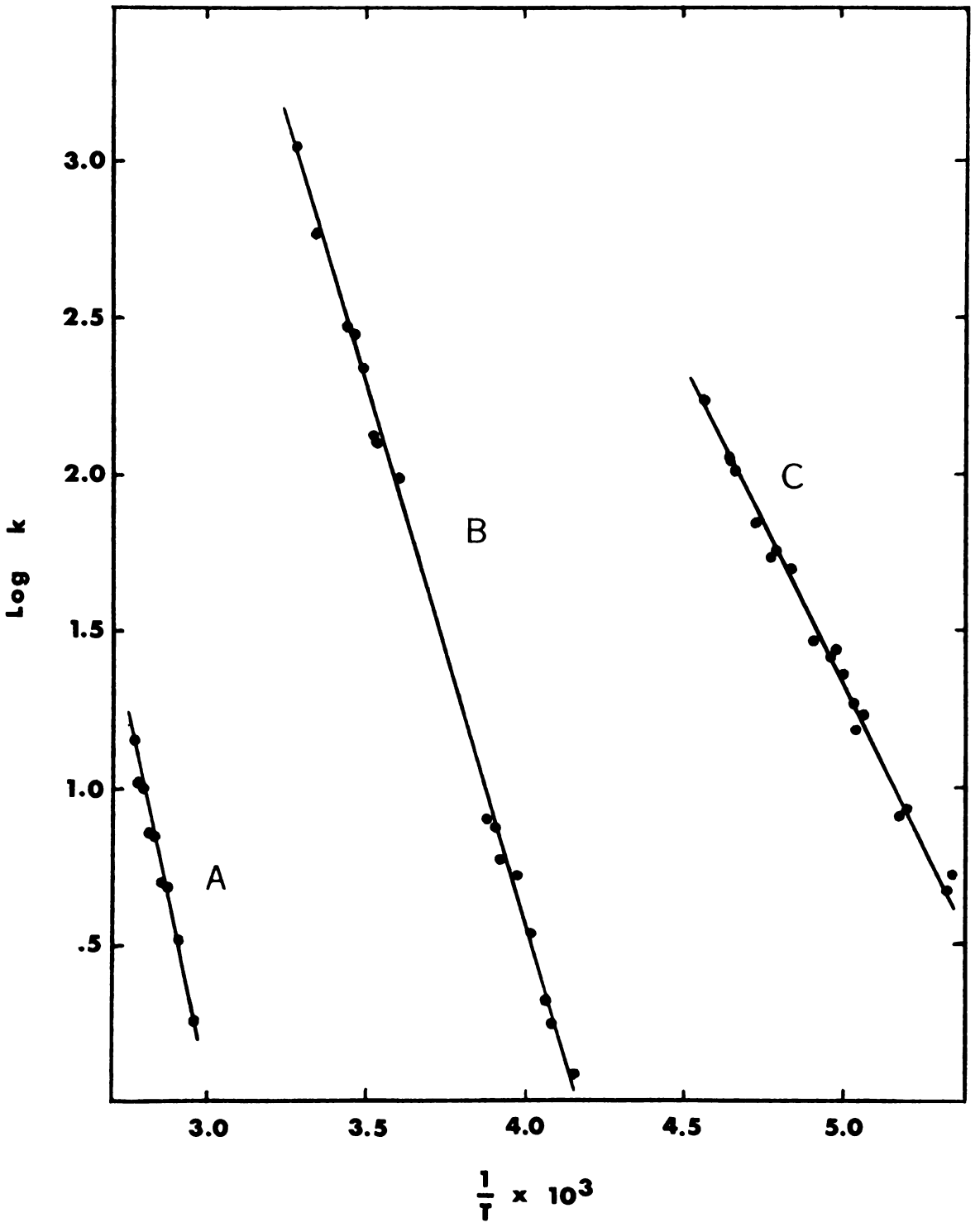


Figure 23.

The activation parameters for the exchange process are not appreciably dependent on the estimated temperature dependence for the relaxation times or $\delta\nu$. For example, and estimated error of 0.35 Hz in $\delta\nu$ for $(\pi\text{-}C_5H_5)Zr(acac)_3$ generates errors of only 0.1 kcal/mol and 0.13 in E_a and log A, respectively. An error of 0.15 Hz in calculating the T_2 values of $(\pi\text{-}C_5H_5)Zr(acac)_3$ produces errors of 0.5 kcal/mol in E_a and 0.52 in log A. These errors are within or nearly within the 95% confidence level estimates of error obtained by the above procedures.

A comparison of the activation parameters for $(\pi\text{-}C_5H_5)Zr(hfac)_3$, $(\pi\text{-}C_5H_5)Zr(dpm)_3$ and $(\pi\text{-}C_5H_5)Zr(acac)_3$ shows that the differences in stereochemical rigidity of the molecules is due primarily to differences in their activation energies. Solvent effects cannot account for the difference in activation energies. Rate constants for $(\pi\text{-}C_5H_5)Zr(dpm)_3$ in diisopropyl ether at five temperatures in the region 69.5 to 80.1°, as well as in toluene at four temperatures in the region 60.4 to 74.6°, gave estimated Arrhenius activation parameters which are equal within experimental error to the values found in o-xylene: $E_a = 22.1 \pm 1.1$ kcal/mol, log A = 14.68 $\pm$ 0.68 in diisopropyl ether; $E_a =$ 22.5 $\pm$ 1.3 kcal/mol, log A = 14.86 $\pm$ 0.81 in toluene. Likewise, the activation parameters for $(\pi\text{-}C_5H_5)Zr(acac)_3$ seem solvent-independent within the 95% confidence level of estimated error. Rate constants for four temperatures in the range -87.3 to -80.9° gave Arrhenius activation parameters in a 1:1 mixture of methylene chloride and trichloroethylene which fall within the limits of error expressed for the complex in carbon disulfide: $E_a = 11.1 \pm 4.8$ kcal/mol, log A = 13.84 $\pm$ 5.32.

The mean lifetimes of the terminal groups on the equatorial ligands of the three complexes are independent of concentration over the range 0.12-0.32 M, and also, are not affected by the presence of equal molar amounts of free ligand. Therefore, the rearrangement processes

are indeed first order, and an intramolecular mechanism operates.

Figure 24 shows four simple intramolecular mechanisms which would lead to the interchange of nonequivalent environments for the terminal groups on the equatorial ligands of a $(\pi\text{-}C_5H_5)Zr(dik)_3$ complex in which the diketonate ligands are symmetric. Mechanism A, which involves a sliding motion of the unique ligand, leads not only to the interchange of environments for the terminal groups on the equatorial ligands but, also, to the exchange of nonequivalent environments for the terminal groups on the unique ligand. Since coalescence of the nmr lines for the terminal groups on the unique ligand in these complexes does not accompany the collapse of the lines for the terminal groups on the equatorial ligands, mechanism A can be eliminated.

Mechanism B involves the bond rupture of a Zr-O bond on the unique ligand. The Zr-O bond of $R^{5,C}$, adjacent to $R^{4,B}$, ruptures on the front side of the pentagonal bipyramid and re-forms by attacking the back side of the octahedral intermediate. Terminal group $R^{5,C}$ is now adjacent to R^3 and R^1 thereby exchanging the A and B environments on the equatorial ligands while retaining the identity of $R^{5,C}$ and $R^{6,D}$ of the unique ligand.

In mechanism C, a Zr-O bond of an equatorial ligand ruptures on one equatorial edge of the pentagonal bipyramid and re-forms along a different equatorial edge. Again R^A and R^B environments of the equatorial ligands are interchanged without interchanging the R^C and R^D environments of the unique ligands.

The fourth mechanism (D) invokes a diagonal twist motion[92] of the equatorial ligands. This motion also results in the desired effects.

The relative merits of these last three mechanisms, the unique ligand bond rupture, the equatorial ligand bond rupture, and the

Figure 24. Possible intramolecular mechanisms for the interconversion of nonequivalent environments for the terminal group on the equatorial ligands of a $(\pi\text{-}C_5H_5)M(dik)_3$ complex. The superscripts label and identify the environments of each R group. Mechanisms C and D are degenerate in energy with analogous processes for the equatorial ligand containing terminal groups R^3 and R^4.

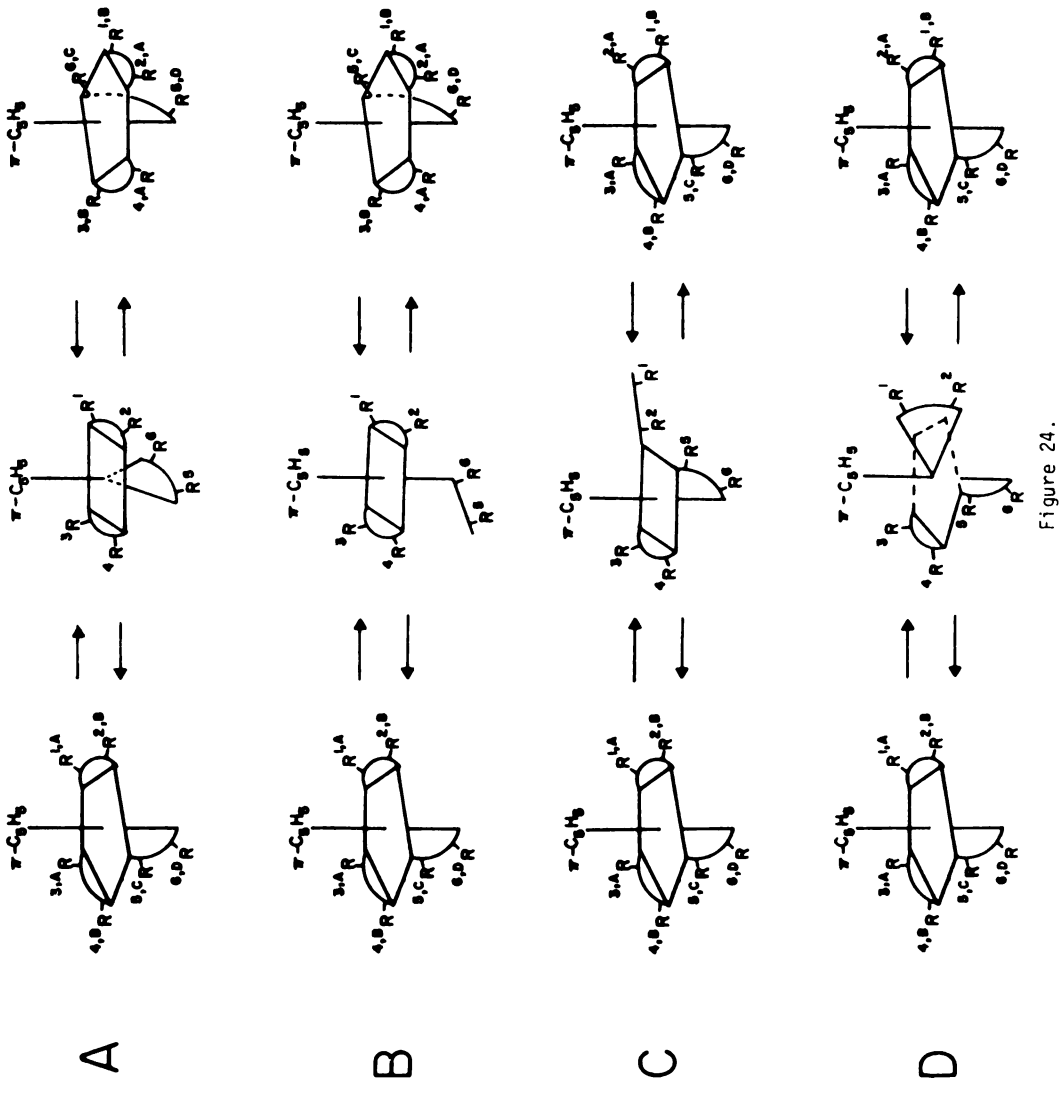


Figure 24.

equatorial ligand diagonal twist mechanisms, can be evaluated, in part, by the investigation of a $(\pi\text{-}C_5H_5)Zr(dik)_3$ derivative which contains asymmetric β-diketonate ligands. Because of the asymmetry of the β-diketonate ligands, $(\pi\text{-}C_5H_5)Zr(dik)_3$ may give rise to the six geometric isomer shown in Figure 25. In the absence of any exchange processes, an equilibrium mixture of all six isomers should give six C_5H_5, fourteen -CH=, fourteen R, and fourteen R' nmr lines.

The proton nmr spectrum of the trifluoroacetylacetonate derivative, $(\pi\text{-}C_5H_5)Zr(tfac)_3$, consists at room temperature of two sets of 1:2 methyl doublets, four -CH= lines, and two C_5H_5 resonances. The spectrum has been interpreted previously[63] in terms of a stereochemical rearrangement process which averages the terminal groups on the equatorial ligands in the set of three isomers in which one of the distinguishable terminal groups on the unique ligand is axial (I← →II← →III) and in the other set in which the distinguishable terminal groups is equatorial (IV← →V← →VI). However, the existence of all six isomers in solution has not yet been demonstrated. Elder[64] has found that the bond between zirconium and the axial oxygen atom in $(\pi\text{-}C_5H_5)Zr(hfac)_3$ is substantially shorter, and presumably stronger, than the five equatorial Zr-O bonds in the molecule. One might expect, therefore, that only one set of three $(\pi\text{-}C_5H_5)Zr(tfac)_3$ isomers (e.g., I, II and III) may exist, because of the potentially different donor properties of the two carbonyl oxygen atoms on the asymmetric trifluoroacetylacetonate ligand. In the presence of only one set of isomers, a bond-rupture mechanism involving the bond to the equatorial oxygen on the unique ligand (mechanism B) would interchange the two isomer with apparent C_s symmetry (e.g., I⟷II) and interconvert the environments of the nonequivalent "equatorial" terminal methyl groups on the isomer with C_1 symmetry (III).

Figure 25. Possible geometric isomers for (π-C_5H_5)Zr(dik)$_3$ having asymmetric ß-diketonate ligands. R and R' represent the distinguishable terminal groups on the asymmetric ß-diketonate ligand.

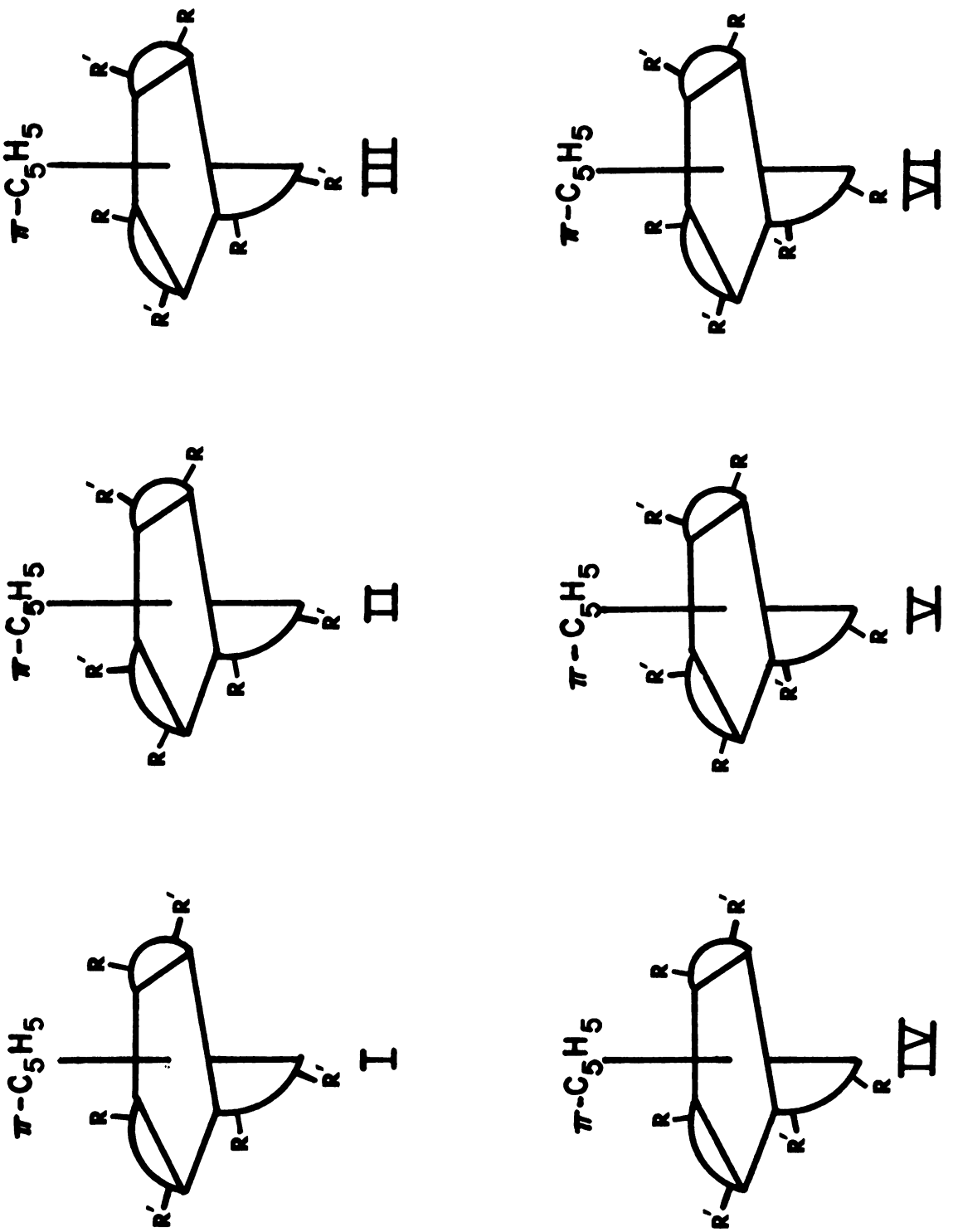


Figure 25.

Thus the expected number of proton nmr lines in the region of fast exchange would be in agreement with that observed. On the other hand, if all six isomers were present, then either rupturing of a bond to oxygen on the equatorial ligands to give a lower coordination number intermediate (mechanism C) or a digonal twisting motion of the equatorial ligands (mechanism D) would interchange the three isomers in each set and would give rise to the observed number of proton nmr lines in the fast-exchange limit. Mechanism B in the presence of all six isomers would give rise to twice the number of observed nmr lines at room temperature.

The temperature dependence of the nmr spectra of $(\pi\text{-}C_5H_5)Zr(tfac)_3$ in dichloromethane is illustrated in Figure 26. In contrast to the room-temperature spectrum, the proton spectrum in the range -90 to -75°, where the exchange process is slow, contains three C_5H_5 lines, five broad -CH= resonances, and seven broad CH_3 lines. The widths of the -CH= and CH_3 lines lie in the range 1.5-4.0 Hz. The ^{19}F spectrum at -80° showed at least seven rather sharp lines. Although the number of nmr lines supports the presence of only one set of three isomers, the relative intensities of the CH_3 resonances cannot be explained on this basis. It must be assumed that more than three isomers, probably all six isomers, are indeed present, and that the ^1H and ^{19}F chemical shiftsfor many of the isomers are nearly coincident. This assumption is also supported, in part, by the broadness of the CH_3 and -CH= lines.

The pivaloyltrifluoroacetonate derivative, $(\pi\text{-}C_5H_5)Zr(pvtf)_3$, is stereochemically less labile than the trifluoroacetylacetonate complex, hence the region of slow exchange for the former complex is the more accessible of the two. At -48.1° (Figure 27), nine CF_3 lines are resolved in the ^{19}F spectrum, and three C_5H_5 and six <u>tert</u>-C_4H_9 lines

Figure 26. Temperature dependence of the CH_3 and π-C_5H_5 proton nmr lines for $(\pi\text{-}C_5H_5)Zr(tfac)_3$ in dichloromethane. Concentration is 5.0 g/100 ml solvent.

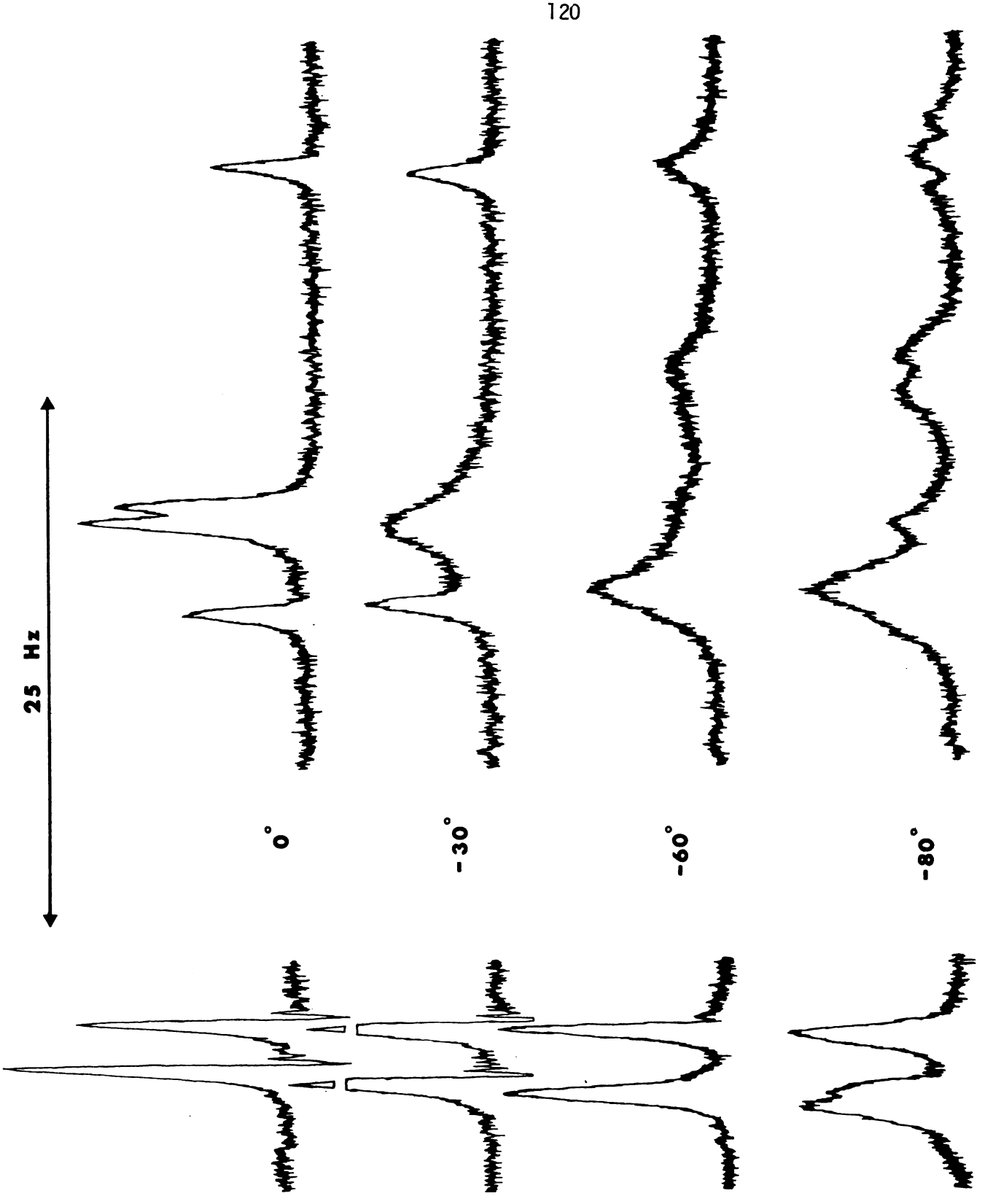


Figure 26.

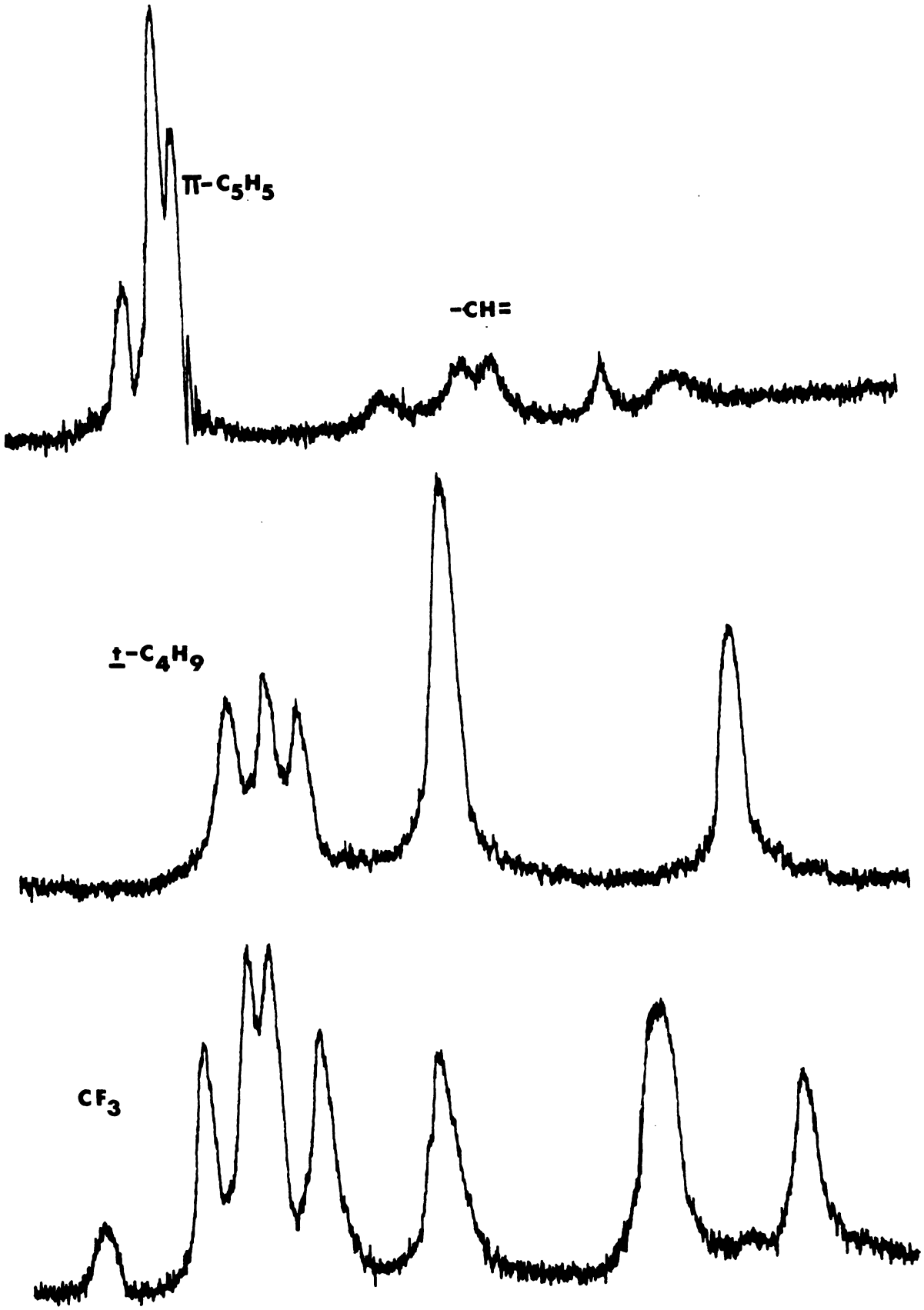


Figure 27. ^{1}H and ^{19}F nmr spectrum of $(\pi\text{-}C_5H_5)Zr(pvtf)_3$ at -48.1°. Concentration is 16.0 g/100 ml dichloromethane.

are observed in the ^1H nmr spectrum. Integration of the CF_3 peaks does not reveal even a single set of peaks in the 1:2 ratio expected for an isomer. Again, it must be concluded that more than three isomers are present, and that the chemical shifts for many of the isomers are nearly coincident.

It should be noted that the benzoylacetonate and pivaloylacetonate derivatives are more labile than $(\pi\text{-}C_5H_5)Zr(tfac)_3$ and $(\pi\text{-}C_5H_5)Zr(pvtf)_3$. Either their regions of slow exchange are not readily accessible or, if they are accessible, the nmr resonances are broad and poorly resolved.

The nmr data for $(\pi\text{-}C_5H_5)Zr(tfac)_3$ and $(\pi\text{-}C_5H_5)Zr(pvtf)_3$ are believed to be consistent with either a bond-rupture or a digonal-twist mechanism involving the equatorial ligands (e.g., either mechanism C or D), but not mechanism B as the sole pathway. Digonal-twist mechanisms have been regarded as unlikely processes in the isomerization of octahedral complexes,[92] but in rearrangements of higher coordination number metal complexes, such twists could be favored and cannot be ruled out.

It may be argued that since the bulkiness of the terminal groups increases in the order $CH_3 < CF_3 <$ tert-C_4H_9, the corresponding increase in activation energies for the complexes would be more consistent with a twist mechanism than a bond-rupture mechanism. However, it is possible that steric effects could predominate in a rearrangement subsequent to the initial rupture of a Zr-O bond, and therefore the activation parameters would not reflect the relative strengths of the Zr-O bonds. Thus, neither mechanism can yet be eliminated.

It should be noted that among the dipivaloylmethanate complexes, the stereochemical lability increases with decreasing coordination number of zirconium in the following order: $(\pi\text{-}C_5H_5)Zr(dpm)_3 <$

$(\pi\text{-}C_5H_5)Zr(dpm)_2Cl < [(\pi\text{-}C_5H_5)Zr(dpm)_2]^+$. A decrease in coordination number is expected to cause an increase in the Arrhenius energy of activation in which bond-rupture is an important part of the activation process. On the other hand, just the opposite result is expected for a twisting mechanism.

3. Process II. The exchange of the unique β-diketonate ligand with the two equivalent equatorial ligands on $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and $(\pi\text{-}C_5H_5)Zr(acac)_3$ was examined in diisopropyl ether and tetrachloroethylene solutions, respectively, by observing the temperature dependence of the -CH= proton resonances. A similar study was not attempted for $(\pi\text{-}C_5H_5)Zr(dpm)_3$ because of the rapid thermal decomposition of the complex at temperatures above 100°.

In the study of process II for $(\pi\text{-}C_5H_5)Zr(hfac)_3$ it was found that the frequency separation of the -CH= lines decreases linearly with temperature in the region of slow exchange from -2 to 50° (Curve A, Figure 28). Curves B and C in Figure 28 indicate that the line widths are unequal and temperature-dependent over the same temperature range. Therefore, values of $\delta\nu$, T_{2A}, and T_{2B} for the -CH= protons at temperatures in the region of exchange were determined by extrapolation into the region of exchange as shown by the dashed lines in Figure 28. Similar temperature dependences were observed for the -CH= lines of $(\pi\text{-}C_5H_5)Zr(acac)_3$, and values of $\delta\nu$, T_{2A}, and T_{2B} were obtained by analogous extrapolations.

The nmr line-shape parameters and values of τ for $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and $(\pi\text{-}C_5H_5)Zr(acac)_3$ are given in Tables XII and XIII, respectively. Since the population ratio of -CH= protons in the two nonequivalent sites is 1:2, the parameter τ is related to the mean lifetimes for the

Figure 28. Temperature dependence of the nmr line-shape parameters for the -CH= protons on the β-diketonate ligands of $(\pi\text{-}C_5H_5)Zt(hfac)_3$ in diisopropyl ether: curve A, frequency separation of the resonance components below coalescence; curve B, width at half-maximum amplitude of the resonance of relative intensity 1; curve C, width at half-maximum amplitude of the resonance of relative intensity 2; curve D, width at half-maximum amplitude of the time-averaged resonance above coalescence. The significance of the extrapolated (dashed) lines is described in the text.

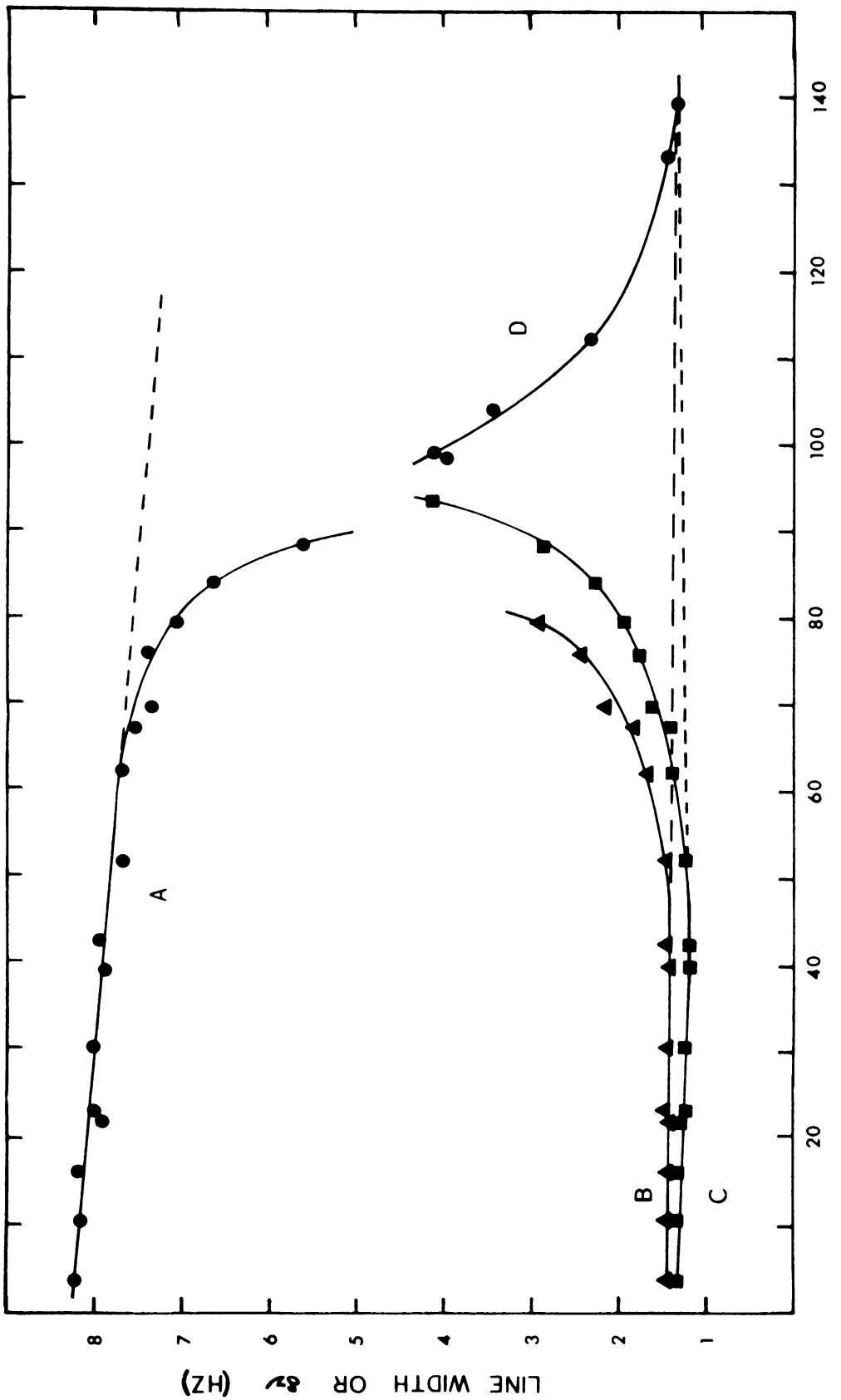

LINE WIDTH OR $\pi\delta\nu$ (HZ)
T (°C)
A
B
C
D
1
2
3
4
5
6
7
8
20
40
60
80
100
120
140

Figure 28.

Table XII. ^{1}H Nmr Line-Shape Parameters and Kinetic Data for the Interchange of the Unique and Equatorial Ligands on $(\pi\text{-}C_5H_5)Zr(hfac)_3$.[a]

Temp, °C	T_{2A}[b] sec	T_{2B}[c] sec	$\delta\nu$, Hz[d]	r[e]	Line widths, Hz[f]	$10^2\ \tau$, sec
74.4	0.255	0.230	7.48		1.78,2.35	25.2
78.4	0.254	0.230	7.44	9.36	2.03,2.99	16.6
82.2	0.253	0.231	7.40	5.40	2.25,3.90	12.2
85.3	0.252	0.231	7.37	4.23	2.68	8.88
89.3	0.251	0.232	7.33	2.90	3.38	5.88
92.5	0.250	0.232	7.30		4.45	4.42
95.6	0.250	0.232	7.27		4.69	2.39
100.0	0.249	0.233	7.22		4.07	1.86
103.1	0.248	0.234	7.19		3.38	1.38
106.3	0.247	0.234	7.16		3.05	1.17

[a]In diisopropyl ether; concentration is 0.32 M. [b]Transverse relaxation time for the low-field -CH= resonance. [c]Transverse relaxation time for the high-field -CH= resonance. [d]Frequency separation between the -CH= resonances in absence of exchange. [e]Ratio of the maximum to central minimum intensities. [f]Widths in the range 69.4-89.3° refer to the low-field and high-field lines below coalescence; above 89.3°, the widths are for the time-averaged line above coalescence.

Table XIII. ^{1}H Nmr Line-Shape Parameters and Kinetic Data for the Interchange of the Unique and Equatorial Ligands on $(\pi\text{-}C_5H_5)Zt(acac)_3$.[a]

Temp, °C	T_{2B},[b] sec	$\delta\nu$,[c] Hz	r[d]	Line widths,[e] Hz	$10^2\ \tau$, sec
68.6	.663	9.48		1.18	31.1
74.5	.667	9.42			19.4
80.6	.692	9.36		1.47,2.84	10.0
85.9	.692	9.31	5.96	2.19,5.23	6.11
52.2	.707	9.25		3.93	3.23
97.7	.723	9.20		4.60	2.60
99.4	.723	9.18		4.80	2.30
104.5	.723	9.13		4.10	1.62
111.5	.723	9.07		2.68	.973
115.8	.740	9.02		2.25	.712

[a]In tetrachloroethylene; concentration is 0.32 M. [b]Transverse relaxation time for the high-field -CH= resonance component. [c]Frequency separation between the -CH= resonances in absence of exchange. [d]Ratio of the maximum to central minimum intensities. [e]Widths in the range 68.6-92.2° refer to the low-field and high-field lines below coalescence; above 92.2°, the widths are for the time-averaged line above coalescence. [f]The value for the transverse relaxation time for the low-field resonance component, T_{2A}, used in the calculation of all values of τ was 0.802 sec.

unique ligand, τ_A, and the two equatorial ligands, τ_B, by $\tau = 2\tau_A/3 = \tau_B/3$. The activation parameters in Table XIV were determined from graphs of log k_A *vs.* 1/T (Figures 29 and 30, respectively) and log (k_A/T) *vs.* 1/T, where $k_A = 2(3\tau)^{-1}$.

As for process I, the activation parameters for process II are not extremely sensitive to choices of $\delta\nu$, T_{2A}, and T_{2B}. For example, a 0.30 Hz error in $\delta\nu$ of $(\pi\text{-}C_5H_5)Zr(acac)_3$ generates errors of only 0.1 kcal/mol and 0.2 eu in E_a and $\Delta S^{\ddagger}_{25°}$ respectively. A 10% error in T_{2A} and T_{2B} causes equally small errors of 0.3 kcal/mol in E_a and 0.9 eu in $\Delta S^{\ddagger}_{25°}$.

The differences in the activation enthalpy and activation entropy between process I and process II are essentially identical for the two complexes: $\Delta(\Delta H^{\ddagger}) = 10.3 \pm 3.6$ kcal/mol and $\Delta(\Delta S^{\ddagger}) = 11.1 \pm 13.3$ eu for $(\pi\text{-}C_5H_5)Zr(hfac)_3$; $\Delta(\Delta H^{\ddagger}) = 11.6 \pm 1.3$ kcal/mol and $\Delta(\Delta S^{\ddagger}) = 11.3 \pm 4.0$ eu for $(\pi\text{-}C_5H_5)Zr(acac)_3$. This would seem to support the assumption that the rearrangement processes for the two complexes occur *via* analogous mechanisms. Furthermore, since the mean lifetimes of the -CH= protons are independent of concentration for both compounds, process II is also first order.

In contrast to process I, the exchange of coordinated and free ligand accompanies process II. For example, at 98° in a solution containing a 1:3 molar ratio of $(\pi\text{-}C_5H_5)Zt(hfac)_3$ and free hexafluoroacetylacetone, the widths of the time-averaged -CH= lines for the coordinated ligands and the -CH= resonance of the free ligand are *ca.* 1.0 Hz larger than the line widths observed in the absence of the second component. Detailed kinetic studies of ligand exchange between $(\pi\text{-}C_5H_5)Zt(hfac)$ and free diketone have been attempted. The rate of intermolecular exchange was studied at 135° as a function of $[(\pi\text{-}C_5H_5)Zr(hfac)_3]$ *vs.* constant [H(hfac)] and *vice versa*. However, the resultant data were too widely

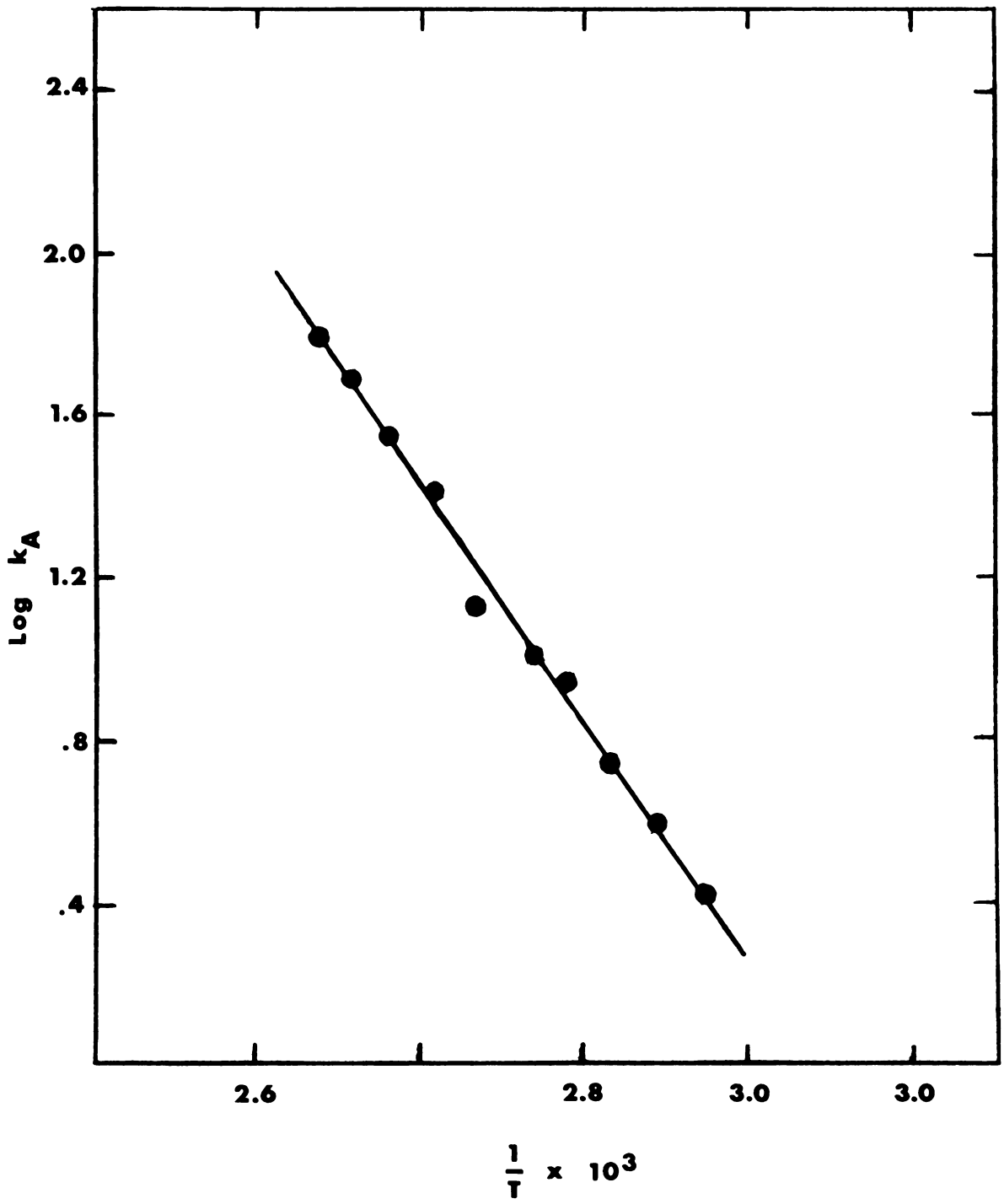


Figure 29. Arrhenius plot for the interchange of the unique diketonate ligand and the equatorial diketonate ligands on $(\pi\text{-}C_5H_5)Zr(hfac)_3$ in diisopropyl ether solution.

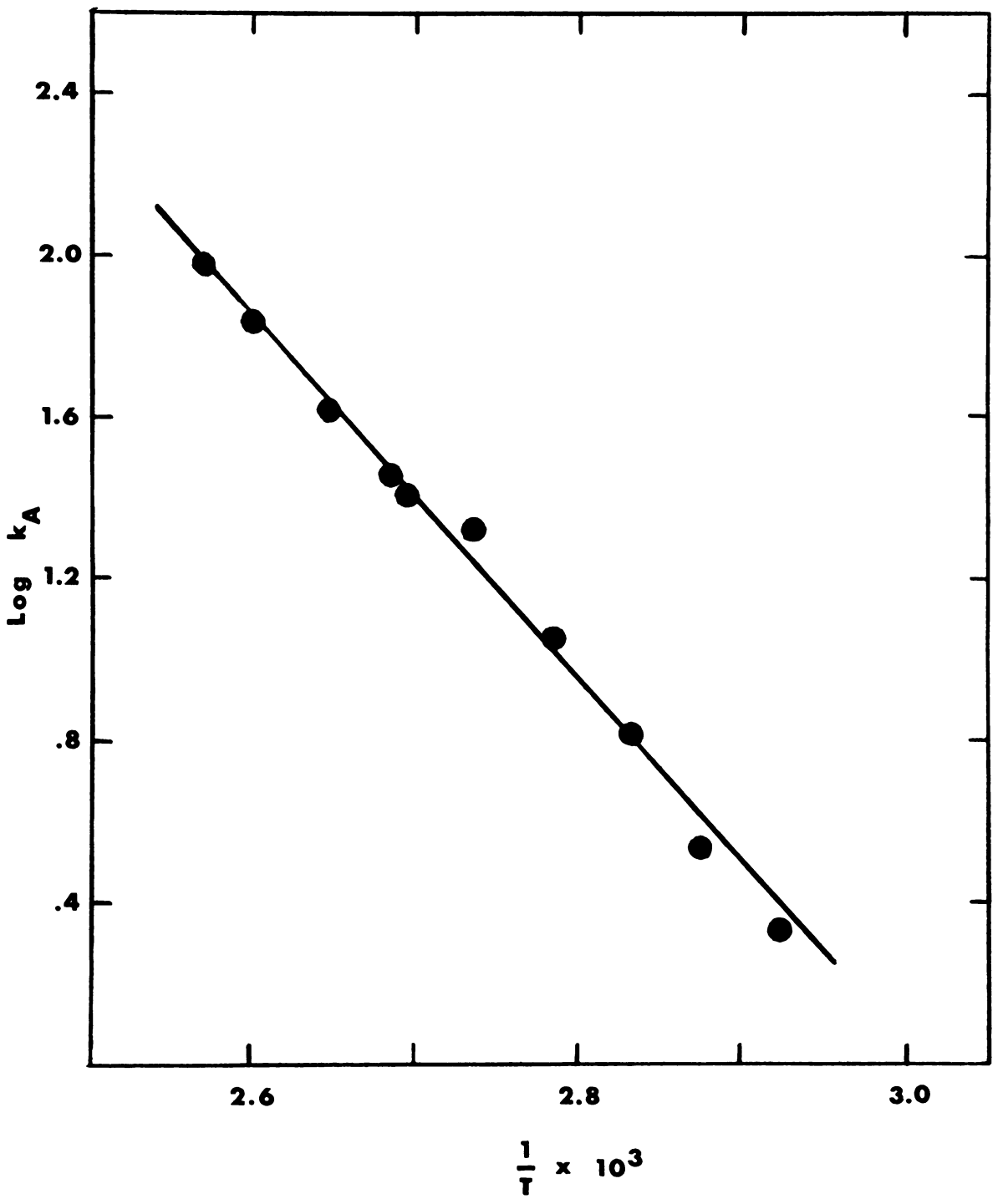


Figure 30. Arrhenius plot for the interchange of the unique diketonate ligand and the equatorial diketonate ligands on $(\pi\text{-}C_5H_5)Zr(acac)_3$ in tetrachloroethylene solution.

Table XIV. Kinetic Parameters for Exchange of the Unique and Equatorial Ligands on $(\pi\text{-}C_5H_5)Zr(hfac)_3$[a] and $(\pi\text{-}C_5H_5)Zr(acac)_3$.[b]

Complex	$k_{A\ 25°}$,[c] sec^{-1}	E_a, kcal/mol	log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$(\pi\text{-}C_5H_5)Zr(hfac)_3$	4.51×10^{-3}	26.4 ± 1.9[d]	16.97 ± 1.06	25.5 ± 3.6	16.3 ± 9.6
$(\pi\text{-}C_5H_5)Zr(acac)_3$	24.1×10^{-3}	21.1 ± 1.2	13.84 ± 0.74	20.4 ± 1.2	2.4 ± 3.4

[a]In diisopropyl ether; concentration is 0.32 M. [b]In tetrachloroethylene; concentration is 0.32 M. [c]All first order rate constants at 25° are extrapolated values. [d]All errors are estimated at the 95% confidence level.

scattered to permit making any conclusions about the rate law. A separate experiment, conducted over a 48 hr period, indicated a large time-dependence for the rate of intermolecular exchange between free diketone and the coordinated ligands. This would help explain the inconsistency of the earlier data. Also, it suggests that the intermolecular exchange is catalyzed by disproportionation products and/or decomposition products of the complex. Alternatively, a series of competing reactions may occur in the presence of the free diketone. It can be stated, however, that the rate of exchange between equimolar amounts of free diketone and complex in a freshly prepared solution is initially about ten times slower than the rate of process II at the same temperature. It is possible that the exchange of free and coordinated ligand occurs by a mechanism similar to that for halogen exchange in the $(\pi\text{-}C_5H_5)Zr(acac)_2X$ complexes since a great time-dependency is observed in both cases. Previous studies have shown that ligand exchange between zirconium β-diketonates and free diketones can occur <u>via</u> first-order as well as second-order paths.[91] In the case of $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes, the formation of a square-pyramidal $(\pi\text{-}C_5H_5)Zr(dik)_2^+$ intermediate in the rate-limiting step should lead to comparable rates for process II and the exchange of free and coordinated ligand, providing that the transfer of the enolic proton between the free ligand and its conjugate base in the latter process is fast. Thus it would seem that the formation of a $(\pi\text{-}C_5H_5)Zr(dik)_2^+$ intermediate is not an important pathway in process II. Furthermore, the magnitude of the activation energy favors an intramolecular mechanism for process II rather than a complete ligand-dissociation mechanism.

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APPENDIX

A. Nmr Chemical Shifts in Benzene-d_6 and Chloroform-d_1

Table XV presents ^1H chemical shifts in benzene-d_6 and chloroform-d_1 for the β-diketones which were used as ligands in this study. Table XVI presents ^1H and ^{19}F chemical shifts for the complexes which were studied in this investigation.

Table XV. ^{1}H Chemical Shifts for β-Diketones in Benzene-d_6 and Chloroform-d_1.[a]

Ligand	Solvent	C_6H_6	-CH=	CH_3	tert-C_4H_9
H(acac)[b]	C_6D_6		-5.00	-1.62	
	$CDCl_3$		-5.50	-2.05	
H(dpm)	C_6D_6		-5.71		-1.06
	$CDCl_3$		-5.72		-1.16
H(hfac)	C_6D_6		-5.67		
	$CDCl_3$		-6.36		
H(bzbz)	C_6D_6	-7.85, -7.13[c]	-6.61		
	$CDCl_3$	-7.97, -7.47[c]	-6.80		
H(tfac)	C_6D_6		-5.30	-1.34	
	$CDCl_3$		-5.91	-2.20	
H(pvac)[b]	C_6D_6		-5.37	-1.70	-1.03
	$CDCl_3$		-5.64	-2.08	-1.16
H(pvtf)	C_6D_6		-5.85		-0.81
	$CDCl_3$		-6.06		-1.22
H(bzac)	C_6D_6	-7.78, -7.13[c]	-5.82	-1.75	
	$CDCl_3$	-7.90, -7.45[c]	-6.17	-2.18	

[a]Shifts are given in ppm relative to TMS as an internal standard (1% by volume). The probe temperature is 42° and all concentrations are 10.0 g/100 ml solvent. [b]Enol form. [c]C_6H_6 resonances are broad multiplets.

Table XVI. ^{1}H and ^{19}F Chemical Shifts for Some Zirconium Complexes in Benzene-d_6 and Chloroform-d_1.[a]

Complex	Solvent	C_6H_6[b]	C_5H_5	-CH=	CH_3	tert-C_4H_9	CF_3[c]
$(\pi\text{-}C_5H_5)ZrCl_2$	C_6D_6[d]		-5.91				
	$CDCl_3$[e]		-6.48				
$(C_5H_5)_4Zr$	C_6D_6[f]		-5.57				
	$CDCl_3$[f]		-5.83				
$(\pi\text{-}C_5H_5)Zr(acac)_3$	C_6D_6		-6.48	-5.31, -5.16	-1.92, -1.80, -1.50		
	$CDCl_3$		-6.11	-5.40, -5.22	-1.97, -1.89, -1.63		
$(\pi\text{-}C_5H_5)Zr(dpm)_3$	C_6D_6		-6.34	-5.86, -5.66		-1.33, -1.32, -1.12, -0.93	
	$CDCl_3$		-5.94	-5.61, -5.43		-1.16, -1.14, -0.97, -0.71	
$(\pi\text{-}C_5H_5)Zr(hfac)_3$	C_6D_6		-5.89	-6.10, -6.07			+0.22, +0.29, +0.60
	$CDCl_3$		-6.42	-6.25, -6.12			+0.06, +0.27, +0.57
$(\pi\text{-}C_5H_5)Zr(bzbz)_3$	C_6D_6	-8.13, -7.12	-6.72	-6.89, -6.81			
	$CDCl_3$	-8.00, -7.35	-6.48	-6.83, -6.78			
$(\pi\text{-}C_5H_5)Zr(tfac)_3$	C_6D_6		-6.23, -6.20	-5.72, -5.64, -5.60, -5.57	-1.73, -1.61, -1.58, -1.31		-0.86, -0.39, -0.35, -0.23
	$CDCl_3$		-6.25, -6.22	-5.98, -5.81, -5.60, -5.57	-2.18, -2.11, -2.09, -1.80		-1.04, -0.62, -0.56, -0.39
$(\pi\text{-}C_5H_5)Zr(pvac)_3$	C_6D_6		-6.46, -6.42	-5.59, -5.55, -5.42, -5.40	-1.97, -1.86, -1.83, -1.50	-1.28, -1.20, -1.18, -0.93	
	$CDCl_3$		-6.11, -6.09	-5.51, -5.43, -5.35, -5.29	-1.98, -1.92, -1.88, -1.59	-1.19, -1.08, -1.07, -0.80	
$(\pi\text{-}C_5H_5)Zr(pvtf)_3$	C_6D_6		-6.20	-6.05, -5.99, -5.97, -5.93		-1.10, -0.98, -0.74	-1.11, -0.80, -0.61
	$CDCl_3$		-6.19	-5.98, -5.96, -5.85, -5.81		-1.24, -1.14, -0.86	-0.86, -0.77, -0.53
$(\pi\text{-}C_5H_5)Zr(bzac)_3$	C_6D_6	-8.07, -7.20	-6.63, -6.62	-6.16, -6.01, -5.90, -5.88	-2.15, -1.95, -1.93, -1.51		
	$CDCl_3$	-7.94, -7.40	-6.32	-6.19, -6.02, -5.88	-1.38, -1.28, -1.21, -0.87		
$(\pi\text{-}C_5H_5)Zr(dpm)_2Cl$	C_6D_6		-6.47	-5.84, -5.76		-1.15, -1.12, -1.01, -0.94	
	$CDCl_3$		-6.33	-5.81, -5.79		-1.19, -1.03, -0.99	

[a]Shifts are given in ppm relative to TMS as an internal standard (1% by volume). The probe temperature is 42° and all concentrations are 10.0 g/100 ml solvent unless otherwise noted. [b]C_6H_6 resonances are multiplets. [c] ^{19}F chemical shifts are given in ppm relative to the free diketone as an internal standard (1% by volume) [d]Concentration is 7.4 g/100 ml solvent. [e]Concentration is 6.7 g/100 ml solvent. [f]Saturated solution.

B. Linear Least-Squares Analysis, Computer Program

This least-squares Fortran program, written by Charles Sokol for a CDC 3600 computer, was used for linear extrapolations of nmr line-shape parameters and for determining the best straight lines for the Arrhenius and Eyring plots of kinetic data. The program calculates the slope and intercept for a straight line along with their standard deviations. The data cards are prepared as explained by the comment cards in the program itself.

```
      PROGRAM LORENTZ
      REAL K1,K2,NUA,NUAX,LL,HMAX
      DIMENSION OMEGA(600),HERTZ(600),AMP(600),IDENT(10)
      NMRD=60 $ NMWR=61 $ TWOPI = 2.*3.1415927
      WRITE (NMWR,1)
    1 FORMAT(*0EVALUATION OF THE TWO-SITE NMR LINE SHAPE EQUATION*)
      WRITE(NMWR,2)
    2 FORMAT(* SEE ROGERS AND WOODBREY,J.PHYS.CHEM., 66, 540 (1962)*)
    3 READ(NMRD,8)(IDENT(I),I=1,10)
    8 FORMAT(10A8)
      READ(NMRD,4) NUAX,T2A,T2B,PA,PB
    4 FORMAT(5F10.5)
      IF (T2A) 5,5,6
    6 READ(NMRD,7) N1,N2,K1,K2,TLL,LL
    7 FORMAT (2I10,4F10.5)
      WRITE(NMWR,9)(IDENT(I),I=1,10)
    9 FORMAT(*1*,10A8)
      WRITE(NMWR,10) NUAX,T2A,T2B,PA,PB
   10 FORMAT(*0ABSEP =*,F8.4,5X,*T2A =*,F8.4,5X,*T2B =*,F8.4,5X,*PA =*,
     1F7.3,5X,*PB =*,F7.3)
      WRITE(NMWR,11) N1,K1,TLL
   11 FORMAT(*0THIS RUN GENERATES*,I8,5X,*TAU VALUES IN*,F10.5,3X,
     1*INCREMENTS WITH A LOWER LIMIT OF*,F10.5)
      WRITE(NMWR,12) N2,K2,LL
   12 FORMAT(*0THIS RUN GENERATES*,I8,3X,*OMEGA VALUES IN*,F10.5,3X,
     1*INCREMENTS WITH A LOWER LIMIT OF*,F10.5)
      TAU=TLL-K1 $ NUA=NUAX*3.1415927
      DO 13 IA=1,N1
      TAU=TAU + K1
      WRITE(NMWR,14) TAU
   14 FORMAT(*1TAU =*,F12.6)
      OMEGAX=LL-K2
      DO 15 M=1,N2
      OMEGAX=OMEGAX+K2
      OMEGA(M)=TWOPI*OMEGAX
```

```
 20 FORMAT(* *,*SUMX=*,F15.6,5X,*SUMY=*,F15.6,5X,*SUMXSQ=*,F15.6,5X,*SOPTIONAL
    1UMYSQ=*,F15.6,/,* SUMXY=*,F15.6,5X,*SUMX SUMY=*,F15.6,5X,*(SUMX)SQOPTIONAL
    2=*,F15.6,5X,*(SUMY)SQ=*,F15.6)                                    OPTIONAL
     WRITE(61,22)SUMXYN,B,EN,F,FSQ,G,SSQN,SSQ,H                        OPTIONAL
 22 FORMAT(* *,*(SUMX SUMY)/N=*,F15.6,5X,*(SUMX)SQ/N=*,F15.6,5X,*(SUMYOPTIONAL
    1)SQ/N=*,F15.6,5X,*SUMXY-(SUMX SUMY)/N=*,F15.6,/,* (SUMXY-(SUMX SUMOPTIONAL
    2Y)/N)SQUARED=*,F15.6,5X,*SUMXSQ-(SUMX)SQ/N=*,F15.9,5X,*(N-2)S SQUAOPTIONAL
    3RED=*,F15.6,5X,/,* S SQUARE=*,F15.6,5X,*(SUMXY-SUMX SUMY/N)SQ/(SUMOPTIONAL
    4XSQ-(SUMX)SQ/N))=*,F15.6)                                         OPTIONAL
     WRITE (61,8)
  8 FORMAT (*-*,*POINT NUMBER*,11X,*X*,18X,*Y*)
     WRITE (61,9)(I,X(I),Y(I),I=1,N,1)
 9   FORMAT(* *,I3,11X,2(F15.7,2X))
     WRITE (61,10)SLOPE,STDEVSLO,ANTERCPT,STDEVINT
 10 FORMAT(*-*,*SLOPE=*,F15.7,*PLUS OR MINUS*,F15.5,/,*INTERCEPT=*,F15
    1.7,*PLUS OR MINUS*,F15.7)
     GO TO 99
100 CONTINUE
     END
```

C. Nmr Line-Shape Analysis, Computer Program

This program has evolved into its present status through several minor modifications in a program originally written by John M. Sebeson, II. It is used to calculate nmr line shapes by use of the Rogers-Woodbrey modification[15] of the Gutowski-Holm equation.[16] The program indexed here has been used with a CD 3600 computer, but minor changes will permit it to be used with CDC 6500 and IBM 1130 computers. The input for the program is as follows:

Card #1	ol	1-80	Identification of the run
Card #2	col	1-10	separation in absence of exchange of the two resonance components, in Hz
	col	1-20	T_{2A} in seconds where A is the low-field peak
		21-30	T_{2B} in seconds where B is the high-field peak
		31-40	P_a, decimal fractional population of the low-field peak
		41-50	P_b, decimal fractional population of the high-field peak
Card #3	col	1-10	N1, number of tau values (right justified)
		11-20	N2, number of frequency values/spectrum
		21-30	increment in tau, in seconds
		31-40	increment in omega (frequency), in Hz
		41-50	lower limit of tau, in seconds
		51-60	lower limit omega (frequency) in Hz

Repeating this sequence of three card may be done for another data set. After the last card of the last data set, there should be two blank cards.

```
      PROGRAM LINEARLS
      DIMENSION X(200),Y(200),IDENT(10)
C THIS PROGRAM WILL CALCULATE THE LEAST SQUARES SLOPE,INTERCEPT AND THE STANDARD
C DEVIATIONS OF THE SLOPE AND INTERCEPT FOR A STRAIGHT LINE CONTAINING 200 OR
C FEWER EXPERIMENTAL POINTS.THIS PROGRAM CAN BE USED TO CALCULATE MULTIPLE RUNS.
C THE FIRST DATA CARD SHOULD HAVE THE NUMBER OF EXPERIMENTAL POINTS IN COLUMNS 1
C TO 3.THE SECOND DATA CARD SHOULD IDENTIFY THE RUN USING COLUMNS 1 TO 80.THEN
C YOU SHOULD HAVE ONE DATA CARD FOR EACH EXPERIMENTAL POINT USING COLUMNS 1 TO
C 10 FOR THE VALUE OF X AND COLUMNS 11 TO 20 FOR THE VALUE OF Y. THEN YOU CAN
C HAVE ANOTHER SET OF CARDS FOR THE NEXT RUN, ETC. AFTER THE LAST DATA CARD OF
C THE LAST RUN, THERE SHOULD BE ONE BLANK DATA CARD.
   99 READ (60,1) N
    1 FORMAT (I3)
      SUMX=0 $ SUMY=0 $ SUMXSQ=0 $ SUMYSQ=0 $ SUMXY=0
C N IS THE NUMBER OF DATA POINTS ON THE STRAIGHT LINE.ANTERCPT IS THE INTERCEPT.
      IF (N) 100,100,2
    2 READ (60,11)(IDENT(I),I=1,10,1)
   11 FORMAT (10A8)
      DO 4 I=1,N,1
      READ (60,3) X(I),Y(I)
    3 FORMAT (2F10.0)
      SUMX=SUMX+X(I) $ SUMXSQ=SUMXSQ+X(I)**2 $ SUMXY=SUMXY+X(I)*Y(I)
      SUMY=SUMY+Y(I) $ SUMYSQ=SUMYSQ+Y(I)**2
    4 CONTINUE
      Q=N $ SLOPE=(Q*SUMXY-SUMX*SUMY)/(Q*SUMXSQ-SUMX**2)
      ANTERCPT=(SUMXSQ*SUMY-SUMX*SUMXY)/(Q*SUMXSQ-SUMX**2)
      C=SUMX*SUMY $ D=SUMX**2 $ E=SUMY**2 $ SUMXYN=C/Q $ B=D/Q $ EN=E/Q
      F=SUMXY-SUMXYN $ FSQ=F**2 $ G=SUMXSQ-B $ SSQN=SUMYSQ-EN-FSQ/G
      SSQ=SSQN/(Q-2) $ H=FSQ/G $ STDEVSLO=SQRTF(SSQ/G)
      STDEVINT=SQRTF(SSQ*SUMXSQ/(Q*SUMXSQ-D))
      WRITE (61,12)(IDENT(I),I=1,10,1)
   12 FORMAT (*-*,10A8)
      WRITE (61,7) N
    7 FORMAT(*-*,*THE NUMBER OF DATA POINTS ON THE STRAIGHT LINE =*,I3)
      WRITE(61,20)SUMX,SUMY,SUMXSQ,SUMYSQ,SUMXY,C,D,E                    OPTIONAL
```

```
      HERTZ(M)=OMEGAX
      P=TAU*(1./(T2A*T2B)-OMEGA(M)**2+NUA**2)+PB/T2B+PA/T2A
      Q=TAU*(OMEGA(M)-NUA*(PA-PB))
      R=OMEGA(M)*(1.+TAU*(1./T2A+1./T2B))+TAU*NUA*(1./T2B-1./T2A)
     1+NUA*(PA-PB)
      AMP(M)=(P*(1.+TAU*(PB/T2A+PA/T2B))+Q*R)/(P**2+R**2)
   15 CONTINUE
      DO 16 IC=2,N2
      IF(AMP(IC).GT.AMP(IC-1)) AMPMAX=AMP(IC)
   16 CONTINUE
      HMAX=AMPMAX/2.
      WRITE(NMWR,17)AMPMAX,HMAX
   17 FORMAT(*0MAXIMUM AMPLITUDE =*,F10.5,3X,*HALF-MAXIMUM =*,F10.5///)
      WRITE(NMWR,18)
   18 FORMAT(*0*,8X,2(*HERTZ*,10X,*AMPLI*,25X),*HERTZ*,10X,*AMPLI*///)
      LIMIT=N2/3
      DO 19 ID=1,LIMIT
      LIMIT1=ID+LIMIT
      LIMIT2=LIMIT1+LIMIT
      WRITE(NMWR,20)HERTZ(ID),AMP(ID),HERTZ(LIMIT1),AMP(LIMIT1),
     1HERTZ(LIMIT2),AMP(LIMIT2)
   20 FORMAT(* *,3(2F15.5,15X))
   19 CONTINUE
   13 CONTINUE
      GO TO 3
    5 WRITE(NMWR,21)
   21 FORMAT(*1FUNCTION COMPLETED*)
      CALL EXIT
      END
```