STEREOCHEMISTRY, LABILITY, AND INFRARED SPECTRAL STUDIES OF CHLOROBIS (2,4-PENTANEDIONATO) PENTAHAPTOCYCLOPENTADIENYLZIRCONIUM

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ABSTRACT

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By

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The stereochemistry of chlorobis(2,4-pentanedionato)-pentahaptocyclopentadienyl zirconium, $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$, has been investigated in solution by nuclear magnetic resonance spectroscopy. The simplest configuration consistent with the results is based on an octahedron in which the C_5H_5 ring occupies one stereochemical position and the chlorine atom is positioned cis to the ring. A superior description based on a dodecahedron is also discussed. Four geometric isomers have been observed for the benzoylacetonate analogue. This latter result supports the stereochemical assignment for $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$.

At elevated temperatures $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ undergoes a rapid, first order, stereochemical rearrangement process. The kinetics of the rearrangement have been studied by nmr line broadening techniques. Also, infrared vibration frequencies in the region 1600-155 cm^{-1} have been assigned for $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$. Assignments for $(h^5\text{-}C_5H_5)Zr(acac\text{-}d_7)_2Cl$ and $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$ are included for comparison.

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E. Dean Butler

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To Brendii

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Graduate work has at least two results: it leaves an indelible mark on the psyche of the student, and it leaves him with a debt of gratitude to many people. I acknowledge three distinct types of assistance. First, the ideas that represent the nucleus of this thesis were provided by Dr. T. J. Pinnavaia, who is not only an academician and practitioner in the highest sense, but a patient, understanding mentor as well. Second, I thank Dr. J. B. Kinsinger for allowing me to hold a teaching assistantship in the Department of Chemistry while I pursued an MBA as well as the degree for which this work is partial fulfillment. Finally, for the inspiration that has made the agony of this graduate student more than worthwhile, I thank Brendii.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

Coordination compounds containing both cyclopentadienyl and β-diketonate ligands are known for only a few transition metal elements. The chromium compound bromo(acetylacetonato)pentahaptocyclopentadienylchromium, $(h^5\text{-}C_5H_5)Cr(acac)Br$,* was the first known compound of this class. The compound was synthesized by Thomas[1] in 1956 by reaction of $Cr(acac)_3$ and C_5H_5MgBr in benzene solution. Thomas suggested that a class of compounds of this type should exist. The discovery of a mixed β-diketonato-cyclopentadienyl complex of zirconium by Freidlina, Brainina, and Nesmeyanov[2] followed in 1961. Recently, mixed complexes of titanium and vanadium have been reported by Doyle and Tobias[3,4].

The titanium and vanadium complexes are cations of the general type $(h^5\text{-}C_5H_5)_2M(dik)^+$, where dik can be the conjugate base of various β-diketones (eg., acetylacetone, benzoylacetone, dibenzoylmethane, etc.)[3,4]. The analogous cationic complexes with tropolonate and ethylacetoacetate[5] and a

*The nomenclature used in this thesis to describe the connexity of the C_5H_5 moiety is after F. A. Cotton, J. Amer. Chem. Soc., 90, 6230 (1968). Trivial names, however, will often be used for convenience (eg., dichlorobis(pentahaptocyclopentadienyl)zirconium will be referred to as zirconcene dichloride.)

neutral complex with squarate[5], $[C_4O_4]^{2-}$, have also been prepared. It is interesting to note that in the case of ethyl acetoacetate, coordination to vanadium is normal, whereas coordination to titanium occurs via one keto oxygen and the "ether" oxygen. The complex cations can be precipitated readily as salts with ClO_4^- by reaction of $(h^5\text{-}C_5H_5)_2M(ClO_4)_2$ with the conjugate base of the diketone in aqueous solutions. Salts with other large uninegative anions have been isolated from aqueous solution by reaction of $(h^5\text{-}C_5H_5)_2MCl_2$ and the diketonate in presence of the desired anion[4,5].

Zirconium compounds containing β-diketonate and cyclopentadienyl ligands are of special interest in the present work. The first reported compounds, chlorobis(acetylacetonato)cyclopentadienylzirconium, $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$, and the benzoylacetonate analogue, $(h^5\text{-}C_5H_5)Zr(bzac)_2Cl$, were prepared by reaction of $(h^5\text{-}C_5H_5)_2ZrCl_2$ and the diketone[2]. Other synthetic routes to $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ included (a) reaction of $Zr(acac)_2Cl_2$ and C_5H_5Na in tetrahydrofuran[2], (b) metathesis reaction between $(h^5\text{-}C_5H_5)_2ZrCl_2$ and $Zr(acac)_4$[6] in toluene and (c) reaction of $[(h^5\text{-}C_5H_5)_2ZrCl]_2O$ or $(h^5\text{-}C_5H_5)_2Zr(OC_2H_5)Cl$ with acetylacetone[7]. It was also reported[6] that $(h^5\text{-}C_5H_5)Zr(acac)_2Br$ could be obtained from metathesis reaction of $(h^5\text{-}C_5H_5)_2ZrBr_2$ and $Zr(acac)_4$, although a product of suitable purity could not be isolated from the reaction when it was repeated in this laboratory. Brainina, Freidlina and Nesmeyanov

suggested that the structure of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ may be based on an octahedron with the chloride atom positioned cis or trans to the h^5-bonded cyclopentadienyl ring. However, evidence in support of either structure was lacking.

A second type of mixed ligand zirconium complex reported by the Russian chemists is a zirconoxane of the type $[(h^5\text{-}C_5H_5)Zr(acac)_2]_2O$. The compound was prepared by hydrolysis of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in presence of an alcohol or an amine[8].

Zirconium compounds of the type $(h^5\text{-}C_5H_5)Zr(dik)_3$ (dik = benzoylacetonate or dibenzoylmethanate), wherein zirconium achieves an inert gas configuration, are also known[9]. A similar compound has been prepared with 8-hydroxyquinoline[9]. The general method of synthesis involved the interaction of $Zr(C_5H_5)_4$ and the free ligand in benzene. The method may have some practical limitations, because the authors report that reaction of $Zr(C_5H_5)_4$ and acetylacetone yielded a viscous oil which, according to analysis, was a binary compound of $(h^5\text{-}C_5H_5)Zr(acac)_3$ with benzene.

The present research deals primarily with a characterization of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in solution. The main objectives were (a) to deduce the stereochemistry of the molecule in solution by nuclear magnetic resonance spectroscopy, (b) to define quantitatively the stereochemical lability of the molecule by nmr line broadening techniques, and (c) to assign the infrared vibrational spectrum of the molecule, especially in the low energy region where Zr-Cl, Zr-O,

and Zr-(h^5-C_5H_5) stretching modes should be infrared active. Previous attempts to determine the stereochemistry and lability of six-, seven-, and eight-coordinate zirconium acetylacetonate complexes of the type $Zr(acac)_2Cl_2$, $Zr(acac)_3Cl$, and $Zr(acac)_4$, respectively, have been unsuccessful[11,12]. At temperatures even as low as -130°, these latter molecules undergo rapid configurational rearrangement processes which average the expected nonequivalent methyl proton and -CH= proton environments. Recent proton and fluorine magnetic resonance studies also failed to provide stereochemical information for tetrakis(1,1,1,5,5,5-hexafluoroacetylacetonato)zirconium(IV)[13].

II. EXPERIMENTAL

A. Preparation of Compounds

1. Reagents and Solvents

Zirconocene dichloride was purchased from Arapahoe Chemicals, Incorporated, and used without further purification.

Zirconocene dibromide and hafnocene dichloride were prepared by reaction of stiochiometric amounts of cyclopentadienylsodium with the appropriate metal tetrahalide in tetrahydrofruan under a dry nitrogen atmosphere. The general procedure has been described by Wilkinson and Birmingham[14]. The crude zirconocene dibromide was purified by treatment with Norit "A" alkaline decolorizing carbon in chloroform solution. A Fisher burner was used to dry the carbon which was kept under a stream of dry nitrogen. Both compounds were recrystallized from chloroform carbon-tetrachloride solution and dried at 80^0 under reduced pressure for two hours. The melting points of the compounds were checked against literature values[6,10]. The cyclopentadienylsodium used in these syntheses was prepared according to the method of King and Stone[15].

Anhydrous hafnium(IV) chloride was purchased in high purity (spectrographic grade) from Wah Chang Corporation.

Anhydrous zirconium(IV) bromide was prepared by reaction of the elements according to the general procedure of Young and Fletcher[16] as their method of preparation from the oxide works equally well when zirconium metal chunks are substituted for zirconium dioxide and carbon.

Acetylacetone was purchased from Matheson, Coleman and Bell. The ligand was freshly distilled before use, and the absence of organic impurities was checked by nmr spectroscopy.

Acetylacetone deuterated in all eight positions was obtained in the following manner. Anydrous sodium carbonate (4 g) was added to a mixture of 100 ml of freshly distilled acetylacetone and 250 ml of deuterium oxide (99.5+ %). The mixture was placed in a 500 ml round bottom flask, to which was attached a 15 in. vigreaux column and a distillation head. The mixture was refluxed for eight hours, and the product which distilled below 101^0 was collected. The distillate separated into two layers on cooling to room temperature. The less dense layer was mostly acetylacetone, and the more dense layer was a solution of heavy water and acetylacetone. The heavy water - acetylacetone layer was redistilled, and again the product distilling below 101^0 was collected. This second distillate also separated into two layers on cooling to room temperature. The process of redistilling the heavy water-acetylacetone layer was repeated until the distillate yielded insufficient heavy water-acetylacetone to carry on the operation. The acetylacetone layers

obtained from each distillation were combined, and the entire process was repeated three additional times, each time starting with a fresh supply of deuterium oxide and anhydrous sodium carbonate. The deuterated acetylacetone was distilled three times from anhydrous magnesium sulfate to ensure dryness. The product was better than 99% deuterated, as judged by nmr spectroscopy.

Trifluoroacetylacetone was purchased from Columbia Organic Chemicals Company, and was freshly distilled before use.

Benzoylacetone was obtained from Eastman Organic Chemicals Company and was sublimed at 60^0 in vacuo before use.

All organic solvents used in the synthesis and purification of products were reagent grade and were dried over suitable desiccants. Toluene, carbon tetrachloride, benzene, and hexane were refluxed over calcium hydride. When benzene was used as an nmr solvent, it was further distilled from lithium aluminum hydride. Chlorobenzene was distilled from phosphorus pentoxide and tetrahydrofuran was distilled from lithium aluminum hydride.

Deuterochloroform was prepared according to a slight modification of the procedure described by Paulsen and Cooke[17]. Freshly distilled hexachloroacetone (151 ml, 1.00 mole) and 99.5+ % deuterium oxide (10 g, 1.0 mole) were placed in a 500 ml round bottom flask. The mixture was cooled in an ice bath, and 10 ml of pyridine was added dropwise with stirring. The mixture darkened immediately

and became quite warm. After the reaction had subsided, the solution was refluxed for two hours. Then the deuterochloroform was distilled and dried over anhydrous calcium sulfate in a glass-stoppered erlenmeyer flask in the freezer section of a refrigerator. It was not necessary to add ethanol-d_1 as a stabilizing agent when the deuterochloroform was stored in this manner. When used as a solvent for ir and nmr studies, the solvent was freshly distilled from phosphorus pentoxide. The chloroform was more than 99% deuterated, as judged by nmr spectroscopy.

Nitrogen used as a purging agent was "Hi-Pure" nitrogen purchased from the Liquid Carbonic Division of General Dynamics and is referred to herein as "dry nitrogen".

2. General Techniques

Any preparation involving the reaction of hydroscopic compounds was conducted in a side-arm erlenmeyer flask or a three-necked flask. The reactions were carried out under a stream of dry nitrogen or *in vacuo*. Readily hydrolyzable metal tetrahalides were transferred to the reaction vessel in a glove bag, and the weight of material delivered to the flask was determined by difference. A magnetic stirrer was used to stir the solution. All glassware was washed with detergent and water, rinsed with distilled water and acetone, dried at 180^0, and cooled in a calcium sulfate desiccator whenever possible. Ground glass joints were usually greased with silicone grease.

Filtrations were carried out with a specially designed glass frit Buchner funnel similar to that described by Holah[18]. Recrystallizations were performed in a glass stoppered erlenmeyer flask fitted with a side-arm and stopcock. While solutions were being heated during recrystallization, dry nitrogen was passed through the side-arm and over the solution to prevent contact with air.

Compounds were stored in screw-cap vials fitted with Teflon liners and were kept in a calcium sulfate desiccator. Hafnium and zirconium tetrahalides are especially hydrolyzable; therefore, they were stored in screw-cap vials sealed with paraffin wax.

3. Chlorobis(2,4-pentanedionato)pentahaptocyclopentadienylzirconium

A modification of the method of Freidlina, Brainina, and Nesmeyanov[2] was used to synthesize this compound. Zirconocene dichloride (5.0 g, 0.017 mole) was placed in a 250 ml side-arm erlenmeyer flask to which was attached a dropping funnel containing 50 ml of freshly distilled acetylacetone. The flask was evacuated through the side-arm and heated at 80^0 in an oil bath for thirty minutes to ensure dryness. Then the acetylacetone was added to the erlenmeyer flask, and the solution was stirred at 80^0 for 15 min. During the heating period the connection to the vacuum pump was opened every two minutes to remove volatile products from the very slightly yellow, clear solution. The excess acetylacetone

was then removed under reduced pressure to leave a white powder. The total heating time was approximately twenty-five minutes. It may be noted that longer heating times gave a less pure, yellow product. Also, a yellow product was obtained if the volatile products were removed in a stream of dry nitrogen rather than under reduced pressure. The white powder was recrystallized under anhydrous conditions from benzene (6.3 g, 95% yield). Melting point is 189-190° d; lit.[2] 188-190° d.

Anal. Calcd for $C_5H_5Zr(C_5H_7O_2)_2Cl$: C, 46.20; H, 4.91. Found: C, 46.01; H, 5.00.

4. Chlorobis(2,4-pentanedionato-d_7)pentahaptocyclopentadienylzirconium

Zirconocene dichloride (2.0 g, 0.0068 mole) and acetylacetone-d_8 (50 ml, 0.5 mole) were reacted as was described for preparation of the protonated analogue, except that the reaction time was 55 min. The pale yellow crude product was recrystallized twice from benzene-hexane. The yield was 0.30 g (11%). Melting point is 188-190° d.

5. Chlorobis(2,4-pentanedionato)pentahaptocyclopentadienylhafnium

This compound was prepared by reaction of hafnocene dichloride (5.79 g, 0.0152 mole) and acetylacetone (50 ml, 0.50 mole) according to the method described for the zirconium analogue, except that the reaction time was 30 min.

Anal. Calcd for $C_5H_5Zr(C_{10}H_9O_2)_2Cl$: C, 58.40; H, 4.51. Found: C, 58.47; H, 4.60.

B. Attempted Preparation of Chlorobis(1,1,1-trifluoro-2,4-pentanedinato)pentahaptocyclopentadienylzirconium

Zirconocene dichloride (1.0 g, 0.0034 mole) and trifluoroacetylacetone (20 ml) were reacted at 90° for 45 min. according to the general procedure described for preparation of $(\eta^5\text{-}C_5H_5)Zr(acac)_2Cl$. The excess trifluoroacetylacetone was removed under reduced pressure. The resulting brown, viscous oil yielded yellow crystals on further pumping at room temperature. The crystals were dissolved in a minimum amount of benzene. Addition of a small amount of hot hexane to the hot benzene solution and cooling produced a mixture of a dark yellow, flocculant precipitate and colorless crystals. The precipitate and crystals were filtered under anhydrous conditions and discarded. Addition of more hot hexane to the hot filtrate and cooling yielded clear, colorless crystals. The crystals were dried at room temperature in vacuo; the yield was 1.0 g (48%). The melting point was 91.0-93.6°. The compound gave a negative test for chloride ion with acidic silver nitrate solution. The reaction has been repeated by J. J. Howe and the product purified by vacuum sublimation. Chemical analysis indicated the product to be $(C_5H_5)Zr(C_5H_4O_2F_3)_3$[19].

C. Attempted Preparations of Bromobis(2,4-pentadionato)-pentahaptocyclopentadienylzirconium

Brainina and Friedlina[6] have reported that metathesis reaction of equimolar amounts of zirconocene dibromide and zirconium acetylacetonate in toluene yields $(h^5\text{-}C_5H_5)Zr(acac)_2Br$ (yield 39%, melting point 203.5-205° d). Attempts by this author to duplicate their results were unsuccessful. Also, the reaction of zirconocene dibromide and acetylacetone, which is analogous to the reaction found successful for preparation of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$, did not yield the desired product. Both reactions are described here.

1. Reaction of Zirconocene Dibromide and Tetrakis-(2,4-pentanedionato)zirconium

Zirconocene dibromide (1.14 g, 0.00299 mole) and $Zr(acac)_4$ (1.46 g, 0.00299 mole) were placed in a 250 ml side-arm erlenmeyer flask to which was attached a dropping funnel containing 15 ml of toluene. The solid reactants were heated in vacuo at 100° C for 30 min. to ensure dryness. Then the toluene was added to the flask; the reactants dissolved immediately to give a yellow-orange solution. After the solution had been heated at 100° for 3 hours, the solvent was removed under reduced pressure. A brown, oily substance remained. The substance was dissolved in benzene, and the solution was filtered to remove a small amount of insoluble brown material. Addition of hot hexane to the hot

filtrate and cooling gave brownish crystals. Recrystallization from benzene-hexane gave colorless crystals which melted at 190°. These crystals were regarded as being zirconium acetylacetonate; melting point was 194-196°.

The reaction was repeated in tetrahydrofuran solution under a slight positive pressure of dry nitrogen. After a 2 hour reaction time at 50°, the solvent was removed under reduced pressure. A fine, deep yellow solid was obtained. This yellow solid turned green after it had aged at room temperature for 0.5 hour in the evacuated reaction flask. After aging 2 hours the product was brown, and after aging 24 hours it was a brown oil.

2. Reaction of Zirconocene Dibromide and Acetylacetone

Zirconocene dibromide (2.5 g, 0.0066 mole) and acetylacetone (25 ml, 0.25 mole) were reacted at 80° according to the procedure described for preparation of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$. After reaction times of 5 min. and 30 min., white crystals, which had a melting point near the melting point of $(h^5\text{-}C_5H_5)_2ZrBr_2$, were recovered from the reaction mixture. After a reaction time of 1 hour a brown powder was obtained. This brown powder was insoluble in benzene, hexane, acetone, and methylene chloride and did not melt below 300°.

The reaction was repeated in carbon tetrachloride solution. Zirconocene dibromide (1.0 g, 0.0026 mole), acetylacetone (5.4 ml, 0.0052 mole), and 50 ml of CCl_4 which had

been dried over calcium hydride were placed in a 125-ml, side-arm erlenmeyer flask to which was attached a condenser and a P_2O_5 drying tube. The apparatus was swept with a slow stream of dry nitrogen while the solution was heated to just below reflux temperature for twelve hours. No reaction was observed as all the zirconocene dibromide was recovered unchanged from the reaction solution.

D. Physical Measurements

1. Molecular Weight Determinations

The freezing point depression method was used to determine molecular weights. Benzene was chosen as the solvent, and its molal freezing point depression constant was found to be 5.410^0 per molal solution when benzil was used as the calibrating solute of known molecular weight. The benzene was dried over lithium aluminum hydride before use. Freezing point depressions were measured for solutions in the concentration range 0.0062-0.0131 molal with a Beckman differential thermometer graduated at intervals of 0.01^0. Temperature readings, however, were estimated to $\pm\ 0.001^0$ with the aid of a magnifying lens.

2. Conductance Measurements

The conductivity bridge used in this study has been described previously[20]. It was operated at a frequency of 1000Hz. The conductivity cell was a Freas-type solution

cell with bright platinum electrodes. The temperature of the cell was maintained at 25.00 ± 0.02° by a Sargent 5-84805 thermostatic bath assembly filled with light mineral oil. The cell constant at 25.00° was found to be 0.214 cm^{-1}. An aqueous solution of potassium chloride was used as the calibrating solution of known specific conductance[21]. The nitrobenzene used for the conductance measurements was washed successively with 1:1 H_2SO_4, water, and 1M NaOH. Washing with 1M NaOH was repeated until the wash solution was no longer colored. The nitrobenzene was then washed with water, allowed to stand over molecular sieves for one day, and finally vacuum distilled from a fresh supply of molecular sieves.

3. Melting Points Determinations

A Thomas-Hoover 6406-H capillary melting point apparatus containing G. E. Silicone Oil SF96(40) was used to determine melting points. Thermometers graduated in increments of 0.2° were used, and they were calibrated using an appropriate standard such as vanillin (melting point 81-83°), sulfapyridine (melting point 190-193°), or caffeine (melting point 235-237°).

4. Infrared Spectra

Infrared spectra in the region 400-625 cm^{-1} were recorded with a Perkin-Elmer Model 237B grating infrared spectrophotometer. Polystyrene film was used to calibrate the

instrument. The accuracy of the reported frequencies in this range is estimated to be ± 5 cm^{-1}. Solution spectra were obtained in 0.1 mm matched KBr cells with amalgam seals. The KBr pellet method was used to obtain spectra of solids.

Spectra in the range 700-150 cm^{-1} were recorded on a Perkin-Elmer Model 301 grating spectrophotometer, which was calibrated with the pure rotational bands of water vapor. The estimated accuracy in this region is ± 2 cm^{-1}. The instrument was purged with dry nitrogen for recording spectra in the 310-150 cm^{-1} region. Solution spectra were obtained in 0.4 mm and 1.0 mm polyethylene molded cells; the Nujol mull technique was used to obtain solid spectra.

Nujol mulls of each compound were carefully examined in the region 3800-3000 cm^{-1} to verify the absence of water and hydroxyl groups. All solutions were prepared in a glove bag purged with dry nitrogen. Deuterochloroform and benzene were dried as described in section II.A.1.

5. Nuclear Magnetic Resonance Spectra

Variable temperature proton nuclear magnetic resonance spectra were obtained with a Varian A-60 high resolution spectrometer operated at 60 MHz. The probe temperature was controlled to within ± 0.5^0 by a Varian temperature controller, Model V-6040. Temperatures were determined by measuring the chemical shift differences for methanol (low temperatures) and ethylene glycol (elevated temperatures). The

audiofrequency side-band technique or a standard sample containing seven non-interacting compounds with chemical shifts uniformly distributed over a magnetic sweep width of 500 Hz was used to calibrate the magnetic sweep width.

In the case of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$, relative signal intensities were determined by planimetric integration. The temperature dependence of the nmr line shapes were determined in benzene solution at a concentration of 15 g/100 ml of solvent. Small radiofrequency fields were employed to avoid saturation effects. Because of the small radiofrequency fields employed, the -CH= proton spectra had a low signal to noise ratio, especially at temperatures above 65^0. It was necessary to resort to low filter band width settings and high spectrum amplitude settings.

Although $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ and $(h^5\text{-}C_5H_5)Zr(bzac)_2Cl$ were found to be insensitive to atmospheric moisture when in the solid state, these compounds were extremely sensitive to moisture in solution. Therefore, prolonged exposure of the crystals to the atmosphere was avoided. Preparation of solutions was done in a dry-nitrogen-filled glove bag. The compound was weighed into a small glass vial, and the solvent added with a one milliliter syringe. The vial was heated gently to effect dissolution, and the solution was transferred to an nmr tube with the syringe. The nmr tube was stoppered and removed from the glove bag. Then the solution was frozen in liquid nitrogen, and the tube was sealed with a flame. The benzene, chlorobenzene, and

deuterochloroform used to prepare the solutions were dried as described in section II.A.1.

III. RESULTS AND DISCUSSION

A. Preparative Chemistry

Chlorobis(acetylacetonato)pentahaptocyclopentadienylzirconium, $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$, and the benzoylacetonate derivative, $(h^5\text{-}C_5H_5)Zr(bzac)_2Cl$, are readily obtained by reaction of zirconocene dichloride and the free diketone as originally reported by Freidlina, Brainina, and Nesmeyanov[2]. An analogous reaction between $(h^5\text{-}C_5H_5)_2HfCl_2$ and acetylactone gives $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$. The volatile products of these reactions are presumably HCl and cyclopentadiene, although no attempt has yet been made to confirm their identity.

Zirconocene dibromide is considerably less reactive than zirconocene dichloride toward acetylacetone. For example, reaction of the dichloride and neat acetylacetone affords $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in essentially quantitative yield within 15 min at 80^0. Under similar conditions reaction with the dibromide is incomplete after 30 min. Furthermore, the product obtained from the dibromide reaction is an intractable brown powder and not the desired $(h^5\text{-}C_5H_5)Zr(acac)_2Br$. Also, no reaction was observed on heating a 1:2 molar mixture of $(h^5\text{-}C_5H_5)ZrBr_2$ and acetylacetone in carbon tetrachloride solution for 12 hours.

Brainina and Freidlina[6] have reported that metathesis reaction of equimolar amounts of zirconocene dibromide and zirconium acetylacetonate in toluene yields crystalline $(h^5\text{-}C_5H_5)Zr(acac)_2Br$. When the reaction was repeated by this investigator, a brown oily substance was obtained as a crude product. The only crystalline compound that could be isolated from the crude product was unreacted zirconium acetylacetonate. A yellow solid was obtained when the reaction was conducted in tetrahydrofuran. However, this yellow solid was apparently thermally or photochemically unstable as it decomposed to a brown oil within 25 hours when stored in vacuo at room temperature.

Attempts to prepare chlorobis(trifluoroacetylacetonato)-pentahaptocyclopentadienylzirconium, $(h^5\text{-}C_5H_5)Zr(tfac)_2Cl$, by reaction of zirconocene dichloride and trifluoroacetylacetone under conditions found successful for preparation of the acetylacetonate derivative did not yield the desired compound. The reaction afforded instead crystalline $(h^5\text{-}C_5H_5)Zr(tfac)_3$. The identity of the compound was established by J. J. Howe.[19] The only compound of this type reported previously is a binary compound of $(h^5\text{-}C_5H_5)Zr(acac)_3$ with benzene[9]; however, this binary compound is a viscous oil.

B. Characterization of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$, $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$, and $(h^5\text{-}C_5H_5)Zr(bzac)_2Cl$

Conductivity and molecular weight data for $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$, $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$, and $(h^5\text{-}C_5H_5)Zr(bzac)_2Cl$ are collected in Table I. The compounds are very weak electrolytes in nitrobenzene solution.

Table I. Conductivity and molecular weight data for $(h^5\text{-}C_5H_5)M(dik)_2Cl$ complexes.

	Conductivity[a]		Molecular Weight[b]		
	Molarity x 10^3	, ohm^{-1} cm^2 mole^{-1}	Molarity x 10^3	Found	Calcd
$(h^5\text{-}C_5H_5)Zr(acac)_2Cl$	7.3	<0.014	22.1	407	390
$(h^5\text{-}C_5H_5)Hf(acac)_2Cl$	10.0	<0.014	6.19	517	514
$(h^5\text{-}C_5H_5)Zr(bzac)_2Cl$	10.0	<0.014	33.1	454	477

[a] In nitrobenzene at 25°.

[b] In benzene.

A typical 1:1 electrolyte, such as $[Ti(acac)_3][SbCl_6]$, would exhibit a molar conductivity of ca. 25 $ohm^{-1}cm^2mole^{-1}$ at a concentration of 1.0×10^2 M.[12] In benzene solution the compounds are monomeric.

Infrared spectra indicate that all four carbonyl groups are coordinated to the central metal in $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ and $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$. Both compounds exhibit a bond due to a symmetric carbonyl stretching vibration near 1595 cm^{-1}. No bonds were found in the region 1626-1695 cm^{-1} where ketonic carbonyl modes have been reported for silicon (IV)[22] and platinum (II)[23,25,26] acetylacetonates containing uncoordinated carbonyl groups. Infrared data also indicate h^5-bonding of the C_5H_5 ring to the central metal. Huggins and Kaesz[27] note that an h^5-bonded C_5H_5 group can be differentiated from a h^1-bonded ring by its simpler infrared spectrum. The most noteworthy differences are the multiple C-H stretching frequencies and the presence of the free double bond absorptions near 1600 cm^{-1} in the spectrum of the h^1-bonded C_5H_5 group. $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ and the hafnium analogue show only one C-H stretching vibration and no vibrations due to a free double bond in the C_5H_5 group. More cogent evidence for an h^1-bonded C_5H_5 ring has been obtained by Stezowski and Eick[28]. Their single crystal X-ray diffraction analysis shows that the C_5H_5 group is centrosymmetrically bonded to the zirconium atom. Since the infrared spectrum of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in solution is essentially identical to the spectrum obtained

for the solid state, the C_5H_5 ring must be h^5-bonded to zirconium in solution also. Infrared frequency assignments will be assigned and discussed in detail later.

The proton nmr spectrum of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in benzene solution is shown in Figure 1. The resonance line at τ 3.50 is assigned to protons on the cyclopentadienyl ring. The remaining six lines are due to -CH= and methyl protons on the acetylacetonate ligands. The two -CH= lines at τ 4.75 and τ 4.82 have relative intensities 1:1.03 ± 0.03. Four methyl lines occur in the region τ 8.31 to τ 8.45. Relative to the methyl proton line at τ 8.31, the two lines of equal intensity at τ 8.37 and τ 8.38 have a combined intensity of 2.03 ± 0.05, and the line at τ 8.45 has an intensity of 0.99 ± 0.03. The intensities were determined by planimetric integration of five spectra; errors are estimated at the 95% confidence level.

The nmr data connot be interpreted in terms of an equilibrium mixture of compounds of different stoichiometries arising from disproportionation of the $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ complex. Equal molar mixtures of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ and $Zr(acac)_2Cl_2$, $Zr(acac)_3Cl$, $Zr(acac)_4$, Hacac, or $(h^5\text{-}C_5H_5)ZrCl_2$ gave spectra characteristic of the individual compounds initially mixed[19]. That is, the relative intensities of resonance lines found in the spectrum of a solution containing only $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ are not altered by varying the ligand composition. Therefore, it must be concluded that the observed methyl and -CH= proton resonances

Figure 1. Proton nmr spectrum of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in benzene solution at 36^0 (60 MHz); concentration is 7.5 g/100 ml of solvent.

result from nonequivalent environments for these groups in the $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ 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 methyl and -CH= groups in nonequivalent environments is based on an octahedron with the C_5H_5 ring at one stereochemical position and the chlorine atom at a position cis to the ring (Figure 2). It may be noted that a trans configuration (Figure 2), 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. Configurations somewhat similar to the cis configuration may be derived from a D_{2d} dodecahedron and a D_{4d} square antiprism (Figure 3). In these higher polyhedra it is assumed that the ring occupies a triangular face in forming three bonds to zirconium. For example, in the case of dodecahedron, the C_5H_5 ring may occupy an AAB face with the two ligands spanning a g-g pair of edges and the chlorine atom at a B position. An analogous anti-prismatic configuration may be readily visualized with the acetylacetonates spanning an s-s pair of edges. It is of interest to note that a configuration identical to that described in terms of the simplest octahedral model is possible based on a bicapped prism (cf., Figure 4). The advantage of the bicapped prism over the octahedral model is that the three bonds between zirconium and the C_5H_5 ring are more readily visualized.

Figure 2. Possible <u>cis</u> and <u>trans</u> configurations for $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ based on a simple octahedral model.

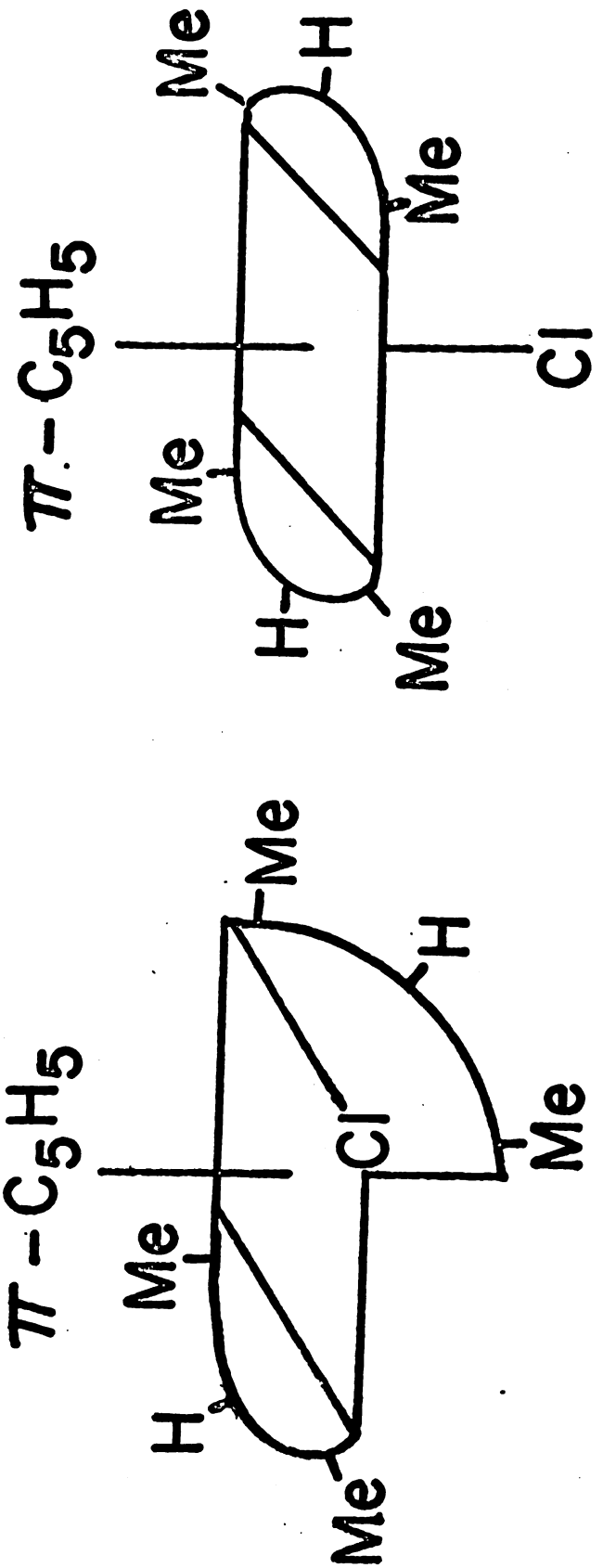
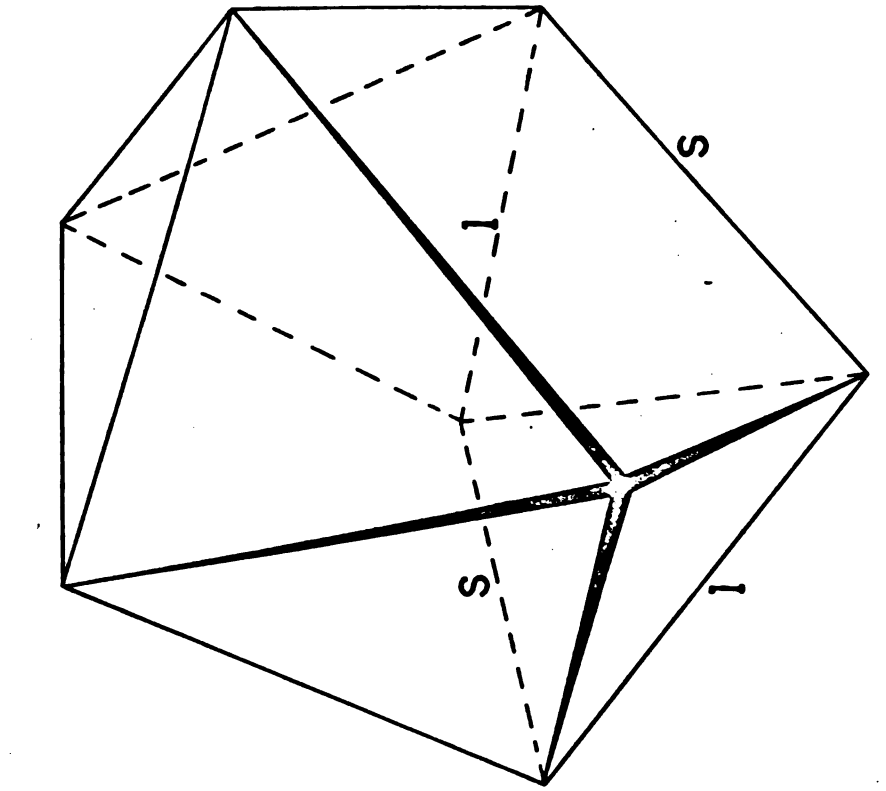


Figure 2.

Figure 3. The D_{2d} dodecahedron (a), and the D_{4d} square antiprism (b). Edge and vertex notation for (a) and (b) is from J. L. Hoard and J. V. Silverton, Inorg. Chem., 2, 235 (1963).



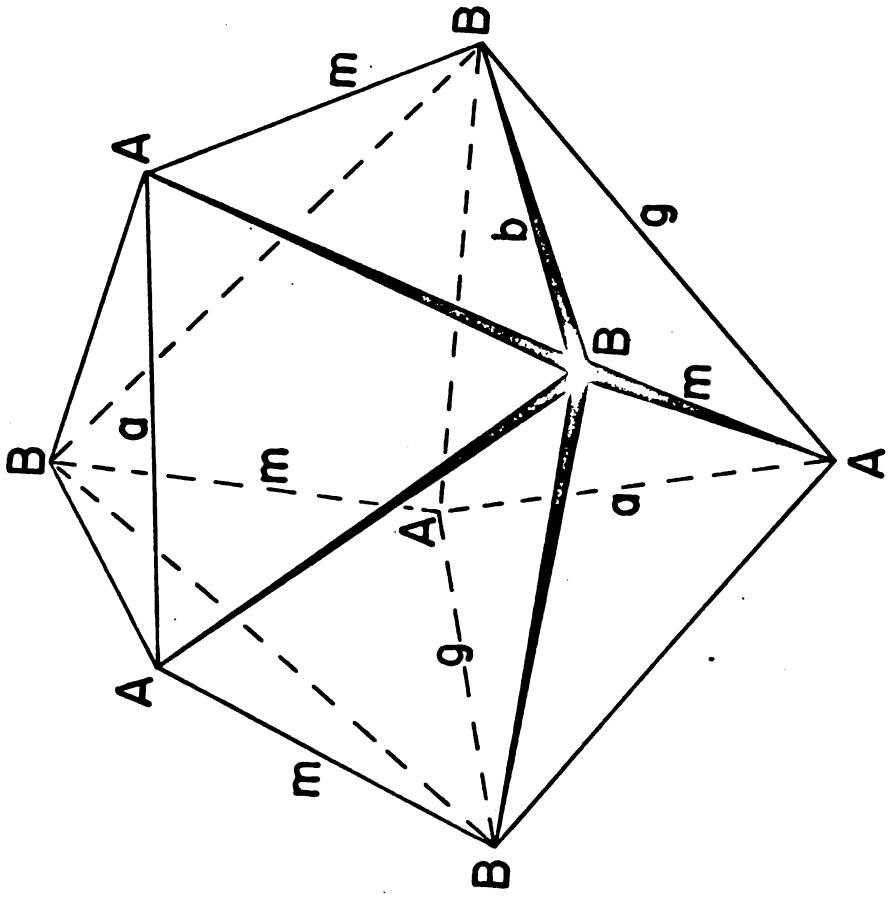


Figure 3.

Figure 4. Two views of the C_{2h} bicapped prism. A configuration identical to that described in terms of a simple octahedron (cf., Figure 2) is achieved if the C_5H_5 ring occupies the triangular face XYZ.

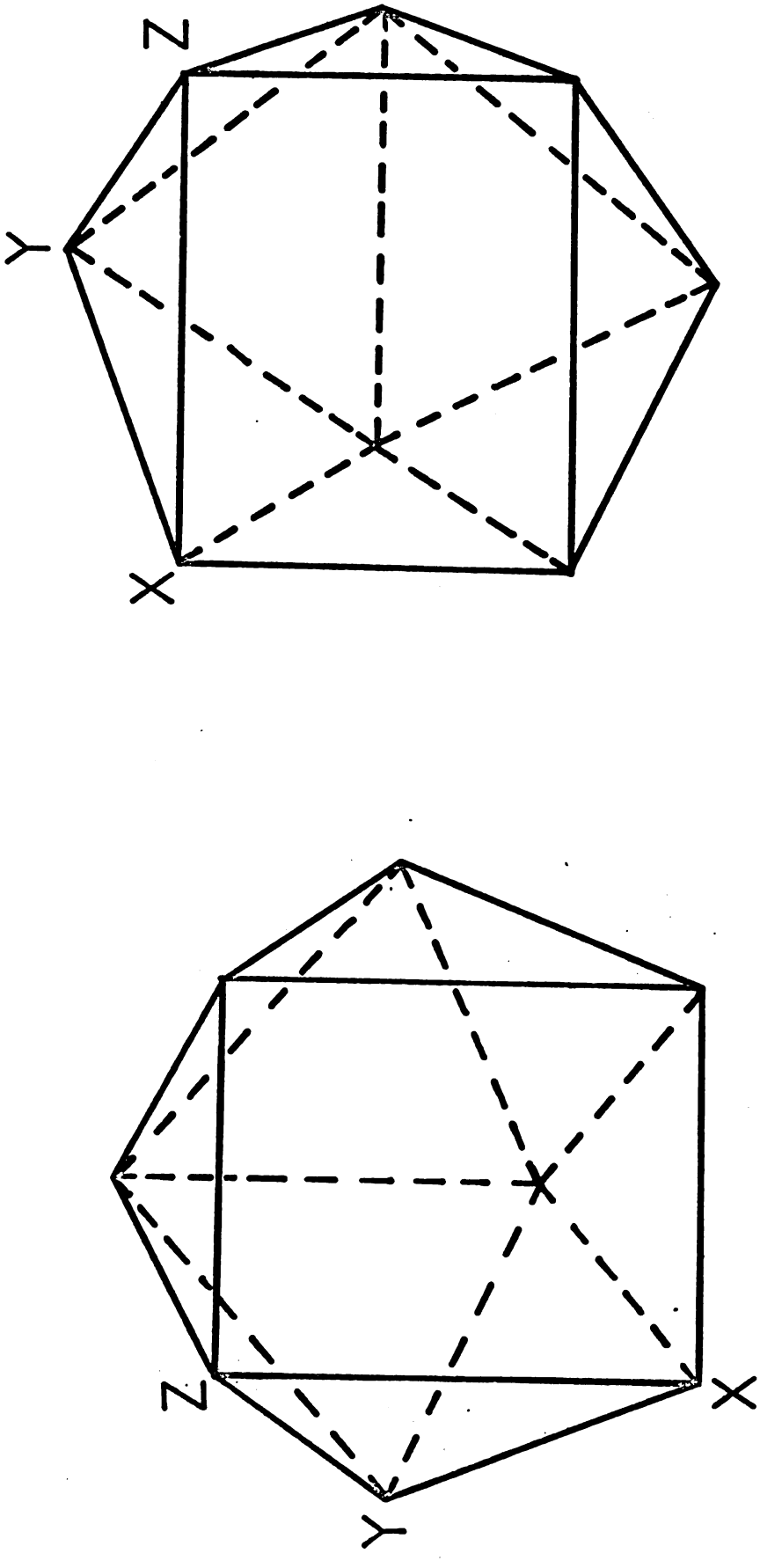


Figure 4.

Stezowski and Eick (28), in their single crystal X-ray diffraction structure determination, have shown that the molecule is more nearly dodecahedral than octahedral or antiprismatic in the solid state. In view of this result one might have hoped to observe more than one stereoisomer in solution because at least five potentially detectable stereoisomers are possible for the dodecahedral model. Seven additional isomers are possible if the C_5H_5 ring is capable of bonding through an ABB triangular face. Four stereoisomers are possible for the antiprism model. Table II lists the stereoisomers possible for dodecahedral and antiprismatic configurations. However, no isomerization could be detected even after the compound was heated in benzene solution for 24 hours at 80^0.

The proton nmr spectrum of $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$ in benzene contains the same number of C_5H_5, -CH= , and CH_3 resonance lines as the zirconium analogue. Presumably the two compounds have the same molecular structure in solution.

The proton nmr spectrum of the benzoylacetonate derivative, $(h^5\text{-}C_5H_5)Zr(bzac)_2Cl$, however, is considerably more complex than that described for the acetylacetonate derivative. In deuterochloroform solution at room temperature the compound exhibits a complex set of phenyl proton lines in the region τ1.9 to τ 2.8, two C_5H_5 lines near τ 3.4, two -CH= lines near τ 3.7, and at least eight CH_3 lines in the region τ 7.7 to τ 8.1. The methyl proton lines are better resolved in benzene solution and are shown in

Table II. Possible stereoisomers for $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ based on a dodecahedron and a square antiprism.

Dodecahedral Isomers	Ligand Positions C_5H_5	acac	Cl
I_d	AAB[a]	g,b[b]	A[c]
II_d	AAB	g,g	B
III_d	AAB	g,m	B
IV_d	AAB	b,a	B
V_d	AAB	g,b	A
VI_d	ABB	m,a	B
VII_d	ABB	g,a	B
$VIII_d$	ABB	b,a	A
IX_d	ABB	m,g	A
X_d	ABB	g,g	A
XI_d	ABB	m,m	A
XII_d	ABB	g,g	A
Antiprismatic Isomers			
I_a	-	s,s	-
II_a	-	s,l	-
III_a	-	l,l	-
IV_a	-	l,l	-

[a]Face notation.

[b]Edge Notation.

[c]Vertex notation. See Figure 3 for definition of edge and vertex notations.

Figure 5. The existence of eight methyl lines is consistent with a single stereochemical coordination geometry or stereoisomer, such as the dodecahedral stereoisomer II_d in Table II. Because of the asymmetry of the diketonate ligand, a total of four geometric isomers are possible when the chlorine atom is positioned cis to the C_5H_5 ring and the benzoylacetonate ligands span a set of dodecahedral edges. The four geometric isomers are illustrated in Figure 6. Each isomer is expected to give rise to two methyl proton lines, two -CH= lines, and a single C_5H_5 line in presence of rapid rotation of the C_5H_5 ring about the metal-ring axis. The existence of only two -CH= and two C_5H_5 lines in deuterochloroform indicates that the chemical shifts of these protons are less sensitive to differences in chemical environment than the terminal methyl protons. In benzene solution one C_5H_5 line and four rather broad -CH= lines are observed.

The chemical shift difference for the two non-equivalent protons in $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ is also dependent on the nature of the solvent. At a concentration of 7.5 g/100 ml of solvent, for example, the -CH= lines are separated by ca. 0.07 ppm and ca. 0.01 ppm in benzene and deuterochloroform, respectively, whereas in chlorobenzene solution a single, sharp line is observed over the temperature range -20^0 to 36^0. Another interesting feature of the spectrum of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ is the temperature dependence of the chemical shifts for the methyl protons in benzene and chlorobenzene below 60^0. Near room temperature only three

Figure 5. Methyl proton resonance lines of $(h^5\text{-}C_5H_5)Zr(bzac)_2Cl$ in benzene solution at 36^0 (60 MHz); concentration is 7.5 g/100 ml of solvent.

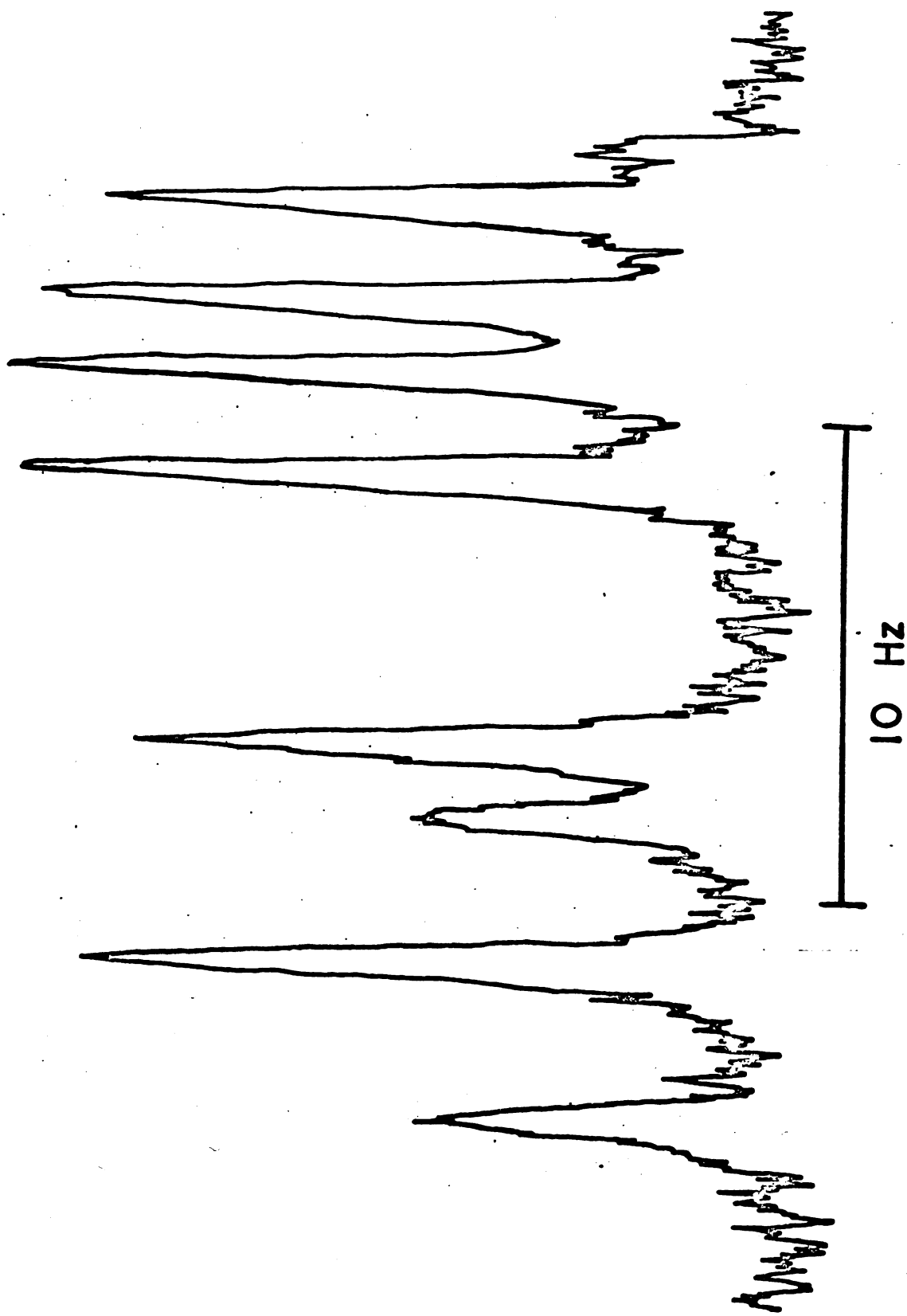


Figure 5.

Figure 6. Geometric isomers of $(h^5\text{-}C_5H_5)Zr(bzac)_2Cl$ based on a D_{2d} dodecahedron in which the chlorine atom is positioned <u>cis</u> to the C_5H_5 ring and the diketone ligands span the same pair of edges. Only the four edges which define the equatorial plane in a hard sphere model of the dodecahedron are shown.

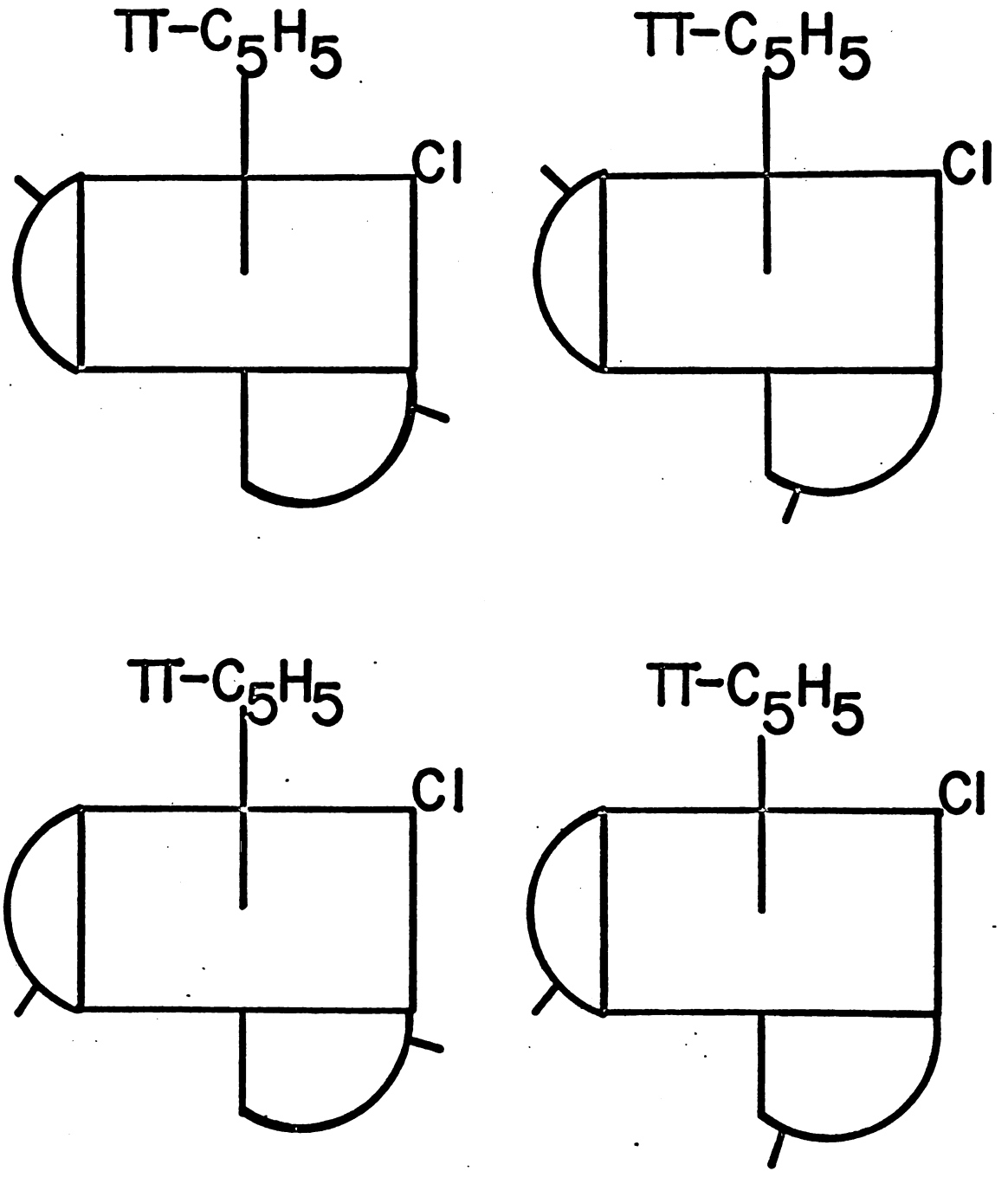


Figure 6.

of the expected four methyl lines are observed, because of temperature dependent solvation effects which result in identical chemical shifts for two of the resonance lines. The temperature dependence of the relative chemical shifts of the methyl protons in chlorobenzene is shown in Figure 7. Above 60^0 the methyl lines broaden and then coalesce into a single broad line at ca. 80^0. A similar line broadening phenomenon is observed for the -CH= resonance lines above 60^0. The line broadening is due to a rapid configurational rearrangement process which averages the nonequivalent methyl or -CH= proton environments. The determination of the kinetics of the exchange process from the line broadening behavior is described below.

C. Kinetics of Configurational Rearrangement for $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$.

As described above, $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ is sufficiently stereochemically rigid at room temperature to permit observation of non-equivalent -CH= and CH_3 proton environments by nmr spectroscopy. As the temperature is increased above ca. 60^0 in benzene, however, the set of two -CH= lines and the set of four CH_3 lines each collapse into a single broad line, which then sharpens as the temperature is increased above the coalescence temperature of ca. 80^0. The temperature dependence for both types of proton resonance lines is illustrated in Figure 8. The line broadening is attributed to a rapid configurational rearrangement

Figure 7. Temperature dependence of the relative chemical shifts for the methyl protons of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in chlorobenzene; concentration is 7.5 g/100 ml of solvent. The shifts are plotted relative to the methyl line which appears at lowest field.

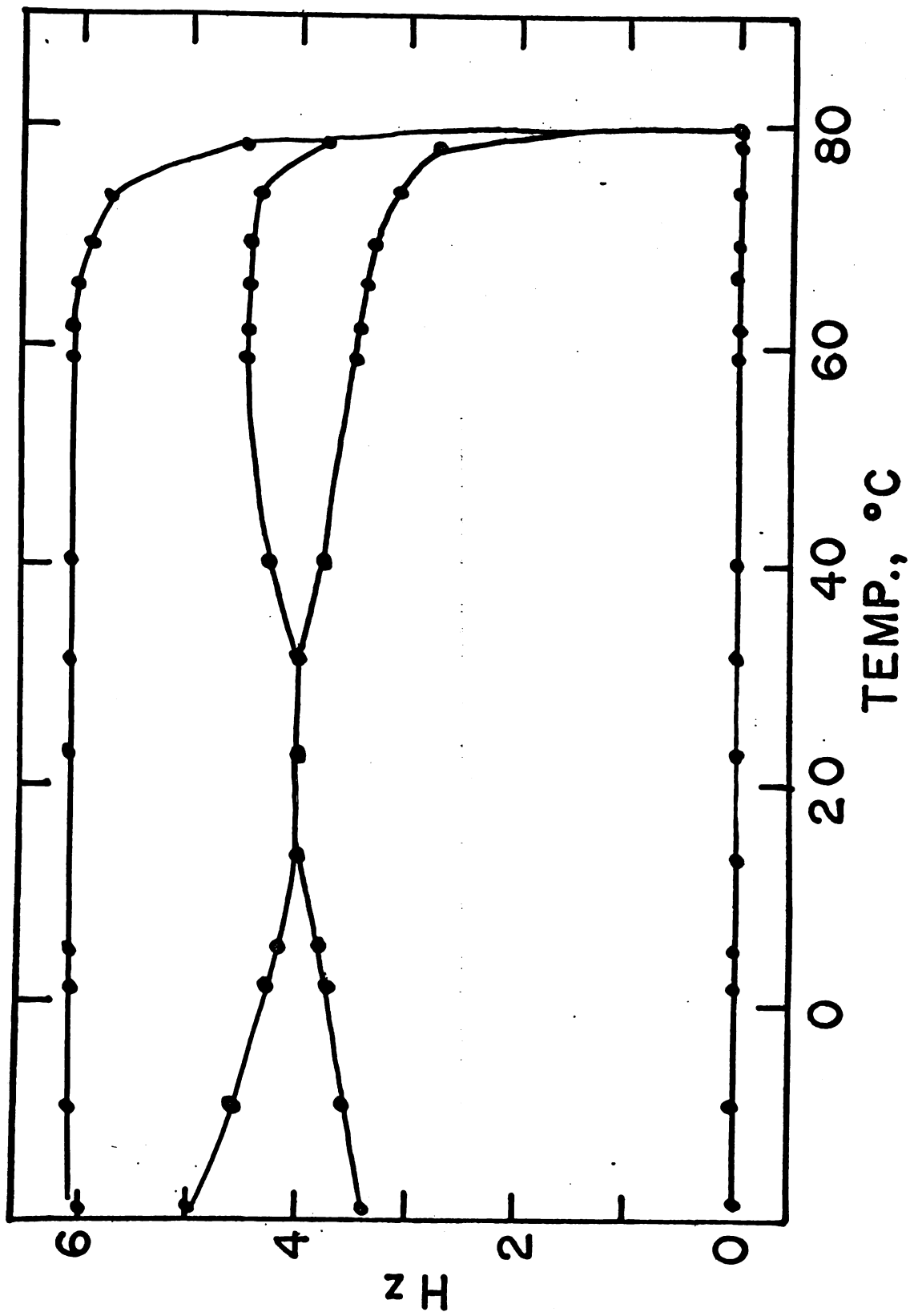


Figure 7.

Figure 8. Temperature dependence of the -CH= and CH_3 proton resonance lines for $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in benzene.

Concentration is 15 g/100 ml of solvent. The spectrum amplitude used to record the spectra was larger for the -CH= lines.

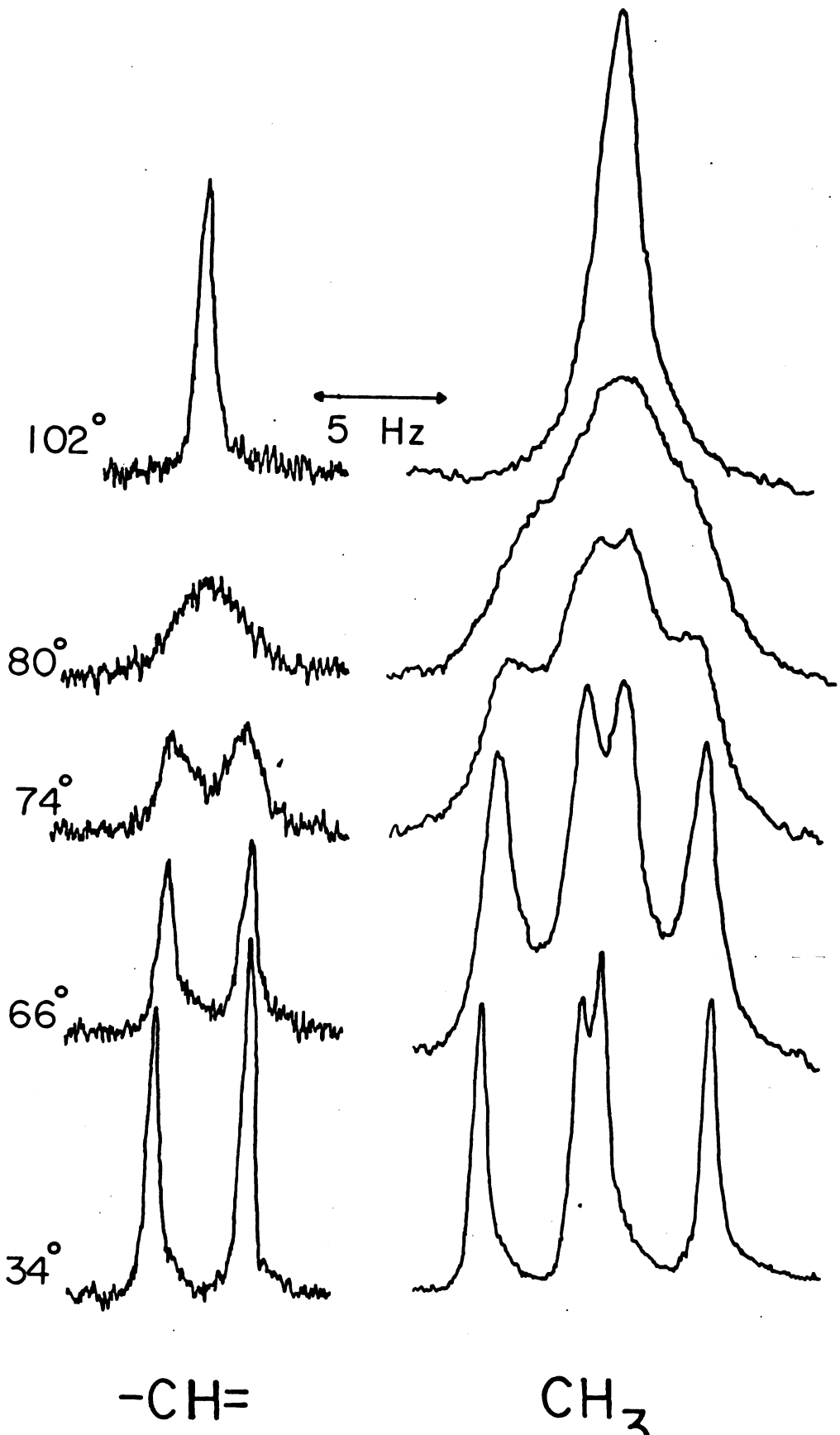


Figure 8.

process which averages the nonequivalent environments for the -CH= and CH_3 groups on the acetylacetonate ligands.

The exchange of -CH= group environments represents an exchange of nuclei between two nonequivalent sites of equal population. For processes of this type, Gutowsky and Holm[29] have derived the dependence of the nmr line shape on (1) $\delta\nu$, the frequency of separation between the resonance components assuming no exchange and no overlap of the components, (2) T_2, the transverse relaxation time, and (3) the quantity τ, which is given by $\tau_A\tau_B/(\tau_A + \tau_B)$, where τ_A and τ_B are the mean lifetimes of protons at each site. When the two sites are equally populated, $\tau_A = \tau_B = 2\tau$.

Normally, a limiting value of the experimentally observed frequency separation, $\delta\nu_e$, is reached as the temperature is lowered, and this limiting value of $\delta\nu_e$ is taken as $\delta\nu$. As can be seen in Figure 9, $\delta\nu_e$ for the -CH= protons of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in benzene is temperature dependent over the entire temperature range investigated. The observed dependence of $\delta\nu_e$ below 55^0 cannot be attributed to exchange effects. Within experimental error, the widths of the resonance components remain constant over the temperature range from $31\text{-}55^0$. Above 55^0 the resonance components broaden markedly as the rate of -CH= group exchange increases. Therefore, the exchange is slow below 55^0, and the observed temperature dependence of $\delta\nu_e$ must be due mainly to temperature dependent solvent effects which cause the chemical shift difference between the two

Figure 9. Temperature dependence of the frequency separation between the -CH= proton resonance lines of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in benzene. Concentration is 15 g/100 ml of benzene.

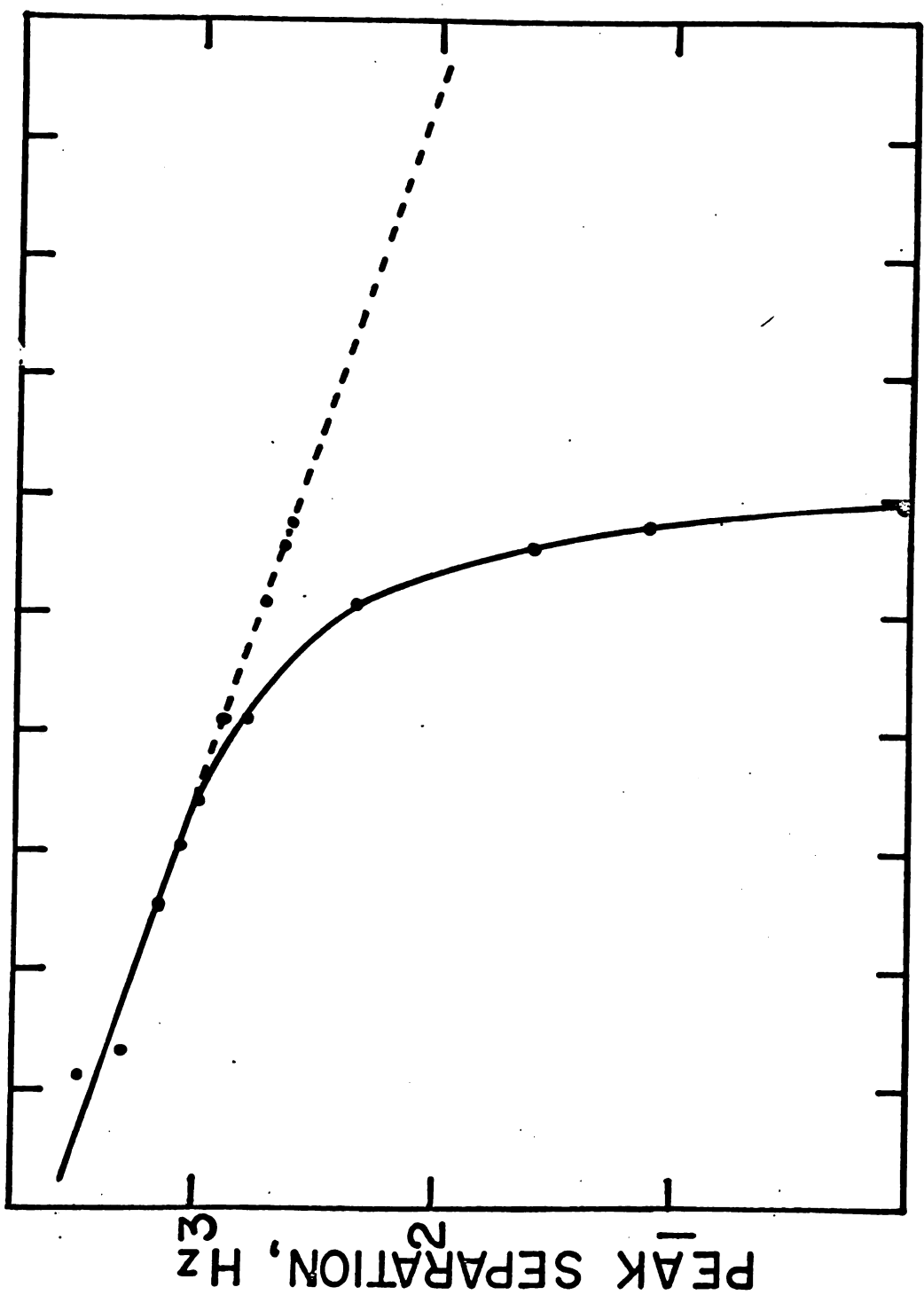


Figure 9.

resonance components to decrease with increasing temperature. Thus $\delta\nu$ will take on a different value for every temperature. The appropriate values of $\delta\nu$ in region of fast exchange were found by extrapolating the linear portion of the $\delta\nu_e$ vs T curve to the region of fast exchange (cf., dashed line in Figure 9). The extrapolated line was assumed to represent the temperature dependence of the frequency of separation that would be observed in the absence of exchange. Since the ratio of the line width at half-maximum amplitude to the frequency of separation is less than 0.3, no correction for $\delta\nu$ due to the slight overlap of the two resonance components was necessary[29].

The resonance components for the -CH= groups in the region of slow exchange do not have equal widths; therefore $T_{2A} \neq T_{2B}$. In benzene solution at a concentration of 15 g/100 ml of solvent, the average values for the line width at half-maximum amplitude were 0.62 Hz and 0.55 Hz, respectively, for the low field and high field line in the region of slow exchange (36^0). Corresponding values of the transverse relaxation times, $2/2\pi \times$ half width, are 0.513 sec and 0.579 sec, respectively. These values of T_2 were assumed to be independent of temperature over the entire region of exchange. It is interesting to note, however, that the line widths are apparently dependent on concentration. Values of T_2 at a concentration of 7.5 g/100 ml of solvent were 0.624 sec for the low field -CH= line and 0.965 sec for the high field -CH= line at 36^0.

With the appropriate values of $\delta\nu$ and T_2, values of the mean lifetimes for the -CH= groups in $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in benzene solution were obtained by comparison of the observed nmr line shapes in the region of exchange with the line shapes calculated from the full Gutpwsky-Holm equation. The complexity of the Gutowsky-Holm equation necessitated use of the Control Data Corporation 3600 computer of the Michigan State University Computer Laboratory. The program used is presented in the Appendix. Six line shape parameters were used for comparing the observed nmr spectra with the computer-calculated spectra. Below the coalescence temperature the spectra were compared with regard to $\delta\nu_e$, the frequency separation between the two C-H resonance lines and the quantities r and r', which are defined as the ratio of the maximum amplitude of the low and high field resonance lines, respectively, to the between-peak minimum amplitude at $(\nu_A + \nu_B)/2$. At coalescence and above the line widths at one-fourth, one-half, and three-fourths maximum amplitude were compared. At each temperature three copies of the spectrum were recorded and the shape parameters averaged. The calculated spectra consisted of 100 coordinate pairs spaced at intervals of 0.36 radians/sec about the mean frequency of the spectrum. The reliability of the shape parameter method was checked by comparison of 24 coordinate pairs for spectra obtained at two temperatures below coalescence (81.2^0, 94.7^0). The observed shape parameters for the -CH= resonance components

are given in Table III.

Values of τ for the interchange of -CH= group environments are given in Table IV along with values of log k, where k, the first order rate constant, is given by $1/2\tau$. Within experimental error the coalescence temperature for the -CH= proton lines at a concentration of 7.5 g/100 ml of benzene was the same as that observed at a concentration of 15 g/100 ml (79.2^0). The mean lifetime at the coalescence temperature for the -CH= protons at the former concentration was determined from a line shape analysis in which appropriate values of T_2 (0.965 sec for the low field line, 0.628 sec for the high field line) and $\delta\nu$ (2.90 Hz) were used. The value of τ for the 7.5% solution (0.118 sec) was in good agreement with the value of τ obtained at a concentration of 15 g/100 ml of solvent (0.124). Therefore, the exchange is indeed a first order process.

The Arrhenius activation energy, E_a, the frequency factor, A, and the activation entropy, ΔS^*, are also included in Table III. The activation energy and the frequency factor were determined from the least squares straight line of a log k vs. 1/T plot (see Figure 10). The activation entropy was calculated at 25^0 from the expression

$$\Delta S^* = R \ln A - R[1 + \ln \frac{kT}{h}]$$

where R, T, k, and h have their usual meanings.

Table III. Observed line shape parameters for the -CH= proton resonance components of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$[a]

Temp. °C	Average Values[b] $\delta\nu_e$[c]	$\delta\nu$[d]	r[e]	r'[f]	$W_{1/4}$[g]	$W_{1/2}$[h]	$W_{3/4}$[i]
31.2	3.48	3.48	6.00	6.40	---	---	---
33.3	3.30	3.30	4.38	5.15	---	---	---
45.3	3.15	3.15	4.71	5.25	---	---	---
50.3	3.07	3.07	3.22	3.88	---	---	---
54.3	3.00	3.00	2.90	3.34	---	---	---
61.0	2.80	2.88	1.88	2.33	---	---	---
70.9	2.35	2.72	1.33	1.75	---	---	---
75.4	1.60	2.64	1.14	1.33	---	---	---
77.3	1.10	2.62	1.07	1.21	---	---	---
79.2	---	2.58	---	---	4.80	3.67	2.45
81.1	---	2.55	---	---	4.48	3.05	1.96
86.7	---	2.45	---	---	3.78	2.40	1.32
89.2	---	2.41	---	---	3.30	2.10	1.18
94.7	---	2.32	---	---	2.60	1.50	0.88
103.5	---	---	---	---	1.98	1.18	0.68
116.0	---	---	---	---	1.98	1.16	0.60

[a] 15 g/ml of benzene.

[b] Average shape parameters obtained from three spectral measurements.

[c] Observed frequency of separation between the two resonance components, in Hz.

[d] Frequency of separation between the two resonance components in absence of exchange (Hz).

[e] Ratio of the low-field-peak maximum to the between-peak-minimum.

[f] Ratio of the high-field-peak maximum to the between-peak minimum.

[g] Line width at one-quarter maximum amplitude, Hz.

[h] Line width at one-half maximum amplitude, Hz.

[i] Line width at three-quarters maximum amplitude, Hz.

Table IV. Kinetic data for the interchange of nonequivalent -CH= group environments in $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$.[a]

Temp, ^0C	τ, sec	log k
61.0	0.217	0.3625
70.9	0.176	0.4535
75.4	0.142	0.5467
77.3	0.130	0.5850
79.2	0.124	0.6055
81.1	0.101	0.6946
86.7	0.0791	0.8008
89.2	0.0730	0.8356
94.7	0.0550	0.9587

E_a = 10.4 ± 0.8 kcal/mole

log A = 7.126 ± 0.497

ΔS^* = -27.9 ± 2.3 eu

k_{250} = 0.293 sec^{-1}

[a] In benzene; concentration is 15 g/100 ml solvent.

Figure 10. Log k *vs.* 1/T plot for the exchange of non-equivalent -CH= group environments in $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in benzene solution.

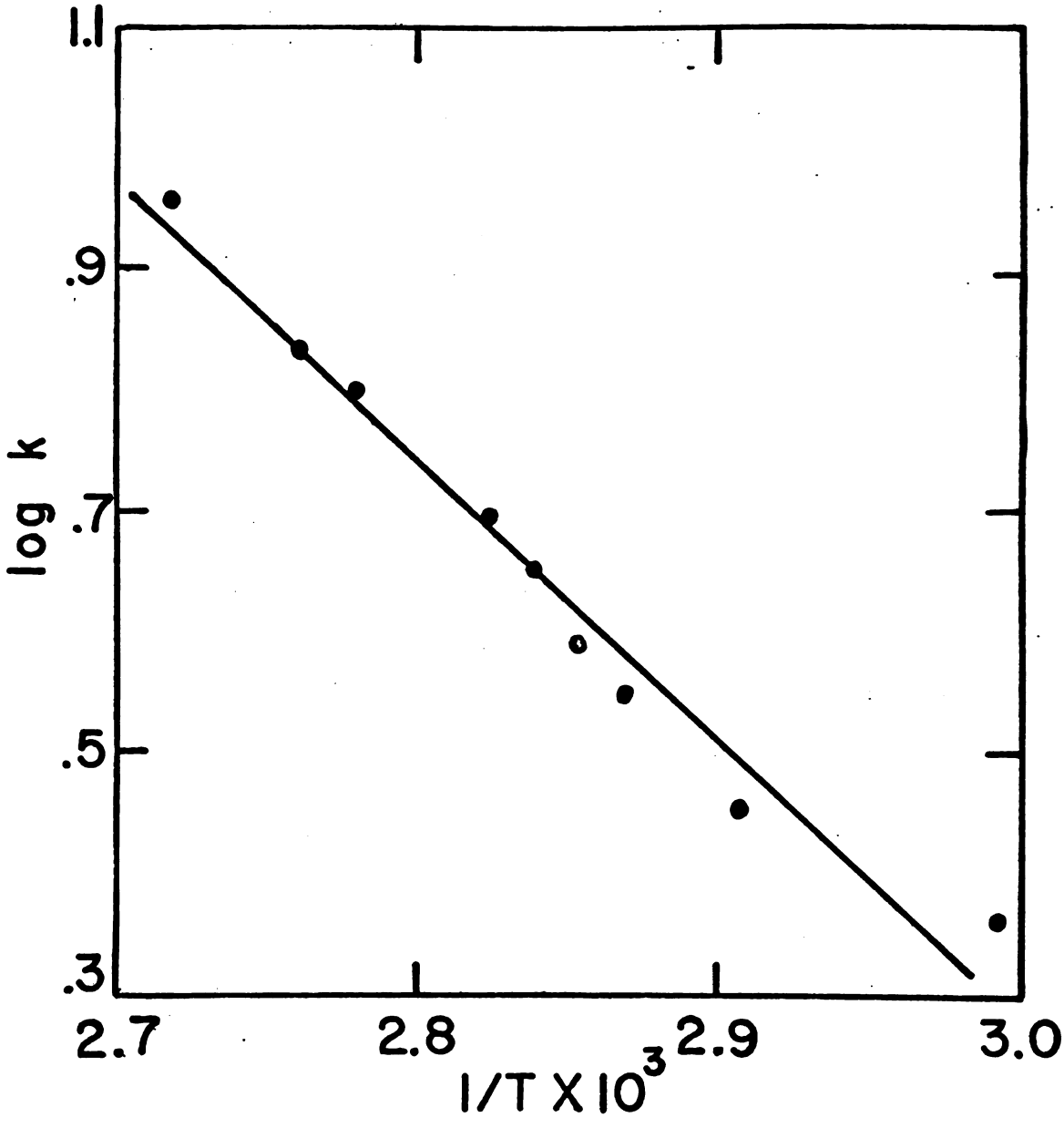


Figure 10.

The activation energy of 10.4 kcal/mole falls in the range of values reported for first order configurational rearrangement processes of a variety of six coordinated metal β-diketonates[30-32]. The value obtained for the activation entropy (-27.9 eu) is the most negative value among the reliable determinations of ΔS^* for first order rearrangement processes of metal β-diketonates. It should be noted, however, that the signal-to-noise ratio for the -CH= proton lines, on which the values of E_a and ΔS^* are based, was limited by the solubility of the compound. In order to obtain useable spectra, it was necessary to record the spectra at progressively lower filter band width levels as the temperature of the sample was increased. It is well known that very low filter band width levels can lead to apparent broadening of resonance lines[33]. The lowest filter band width setting of 0.1 cps was used in the region above coalescence. Consequently, the values of log k above coalescence would tend to be too low relative to the values obtained below coalescence. A systematic error of this type would cause the observed activation energy to be too low and the activation entropy to be too negative. Therefore, the reported values of E_a and ΔS^* should be regarded as lower limits for these activation parameters.

D. Assignment of Infrared Vibrational Frequencies for $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$, $(h^5\text{-}C_5H_5)Zr(acac\text{-}d_7)_2Cl$, and $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$

The infrared spectrum of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ was recorded in the region 4000-155 cm^{-1}. Spectra of the acetylacetonate-d_7 analogue and of $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$ were recorded for comparison. The frequencies are listed in Tables V and VI. Except for a sharp weak band due to a C-H stretching vibration of the C_5H_5 group near 3100 cm^{-1} and broad, weak bands in the region 3000-2900 cm^{-1} due to C-H stretching modes of acetylactonate, no bands were observed above 1600 cm^{-1}. The C-H stretching vibrations are not of interest in the present work and will not be discussed further. In general, bands observed in solid spectra were only slightly shifted from bands observed in solution spectra. However, several bands observed in solution were split in the solid; the splittings will be discussed later. A Nujol mull of each compound was carefully investigated in the 3500-3000 cm^{-1} region to verify the absence of water or hydroxyl groups in the samples.

Bands appearing in the 1600-480 cm^{-1} region are expected to be due mainly to vibrational modes localized in the acetylacetonate and cyclopentadienyl ligands. The vibrational modes of acetylacetonate assigned in Table V are based mainly on the normal coordinate calculations of Benke and Nakamoto[26] for $Pt(acac)Cl_2^-$ and its deuterium analogues. The fundamental vibrations of the C_5H_5 group are assigned on the basis of the normal coordinate treatment for ferrocene by Lippincott and Nelson[34] and on the extensive

Table V. Infrared vibrational frequencies for some $(h^5\text{-}C_5H_5)M(acac)_2Cl$ complexes in the region 1600-480 cm^{-1} [a]

$(h^5\text{-}C_5H_5)Zr(acac)_2Cl$		$(h^5\text{-}C_5H_5)Zr(acac\text{-}d_7)_2Cl$		$(h^5\text{-}C_5H_5)Hf(acac)_2Cl$	Predominant Mode
Solution	Solid	Solution	Solid	Solid	
1597 s[b]	1600 s	1587 s	1597 s	1598 s	(acac) C···O sym str.
1577 s	1586 s	1561 s	1562 s	1585 s	
	1570 s		1553 s	1568 s	
1524 s	1536 s	1526 s	~1529 s	1534 s	(acac) C···C asym str
	1526 sh	1494 s	1493 s	1524 sh	
N.R. [c]	N.R.	1451 w	1450 sh	N.R.	$(h^5\text{-}C_5H_5)$ C···C str
1427 m	1431 m	1087 vw	1081 vw	1424 m	(acac) CH_3 deg def
1373 sh	1377 sh	1376 s	1373	1374 sh	(acac) C···O asym str
			1361 s		
1360 s	1362 s	1044 sh	1040 sh	1360 s	(acac) CH_3 sym def
1275 s	1280 s	1303 m	1304 m	1280 s	(acac) C···C sym str
		1242 w	1242 w		+ C-CH_3 str
1185 w	1189 w	-	-	1188 w	(acac) C-H in-plane bend
1131 vw	1131 vw	1131 vw	1131 vw	1131 vw	$(h^5\text{-}C_5H_5)$ ring def
-	-	1112 vw	1110 vw	-	?
1069 vw	1071 vw	1069 vw	1064 vw	1075 vw	$(h^5\text{-}C_5H_5)$?
1023 s	1029 s	975 m	976 m	1027 s	(acac) CH_3 rock
		965	969		

Table V. (Continued)

$(h^5\text{-}C_5H_5)Zr(acac)_2Cl$		$(h^5\text{-}C_5H_5)Zr(acac\text{-}d_7)_2Cl$		$(h^5\text{-}C_5H_5)Hf(acac)_2Cl$	Predominant Mode
Solution	Solid	Solution	Solid	Solid	
1023 s	1020	1021 m	1031 m	1017 s	(h^5-C_5H_5) C-H in-plane
			1019 m		bend
-	945 sh	d	900 w	947 sh	(acac) sym C-CH_3 str
934 m	935 m	950 m	949 m	937 m	(acac) asym C-CH_3 str
d	906 vw	d	912 sh	908 vw	(h^5-C_5H_5) ?
d	831 m	d	832 m	832 m	(h^5-C_5H_5) C-H out-of-plane bend
814 s	820 s	817 s	821 s	821 s	(h^5-C_5H_5) C-H out-of-plane bend
	810 s		809 s	810 s	
d	796 m	d	607 m	800 m	(acac) C-H out-of-plane bend
665 m	665 m	d	618 m	664 m	(acac) ring def or C-CH_3 in-plane bend + M-O str
d	557 m	d	500 s	557 m	(acac) ring def ?
538 s	536 s		481 m	539 s	

[a]Solution spectra were obtained in deuterochloroform, except for the bands below 600 cm^{-1}, which were obtained in benzene; concentration is 5 g/100 ml solvent. Spectra of solids were obtained by the KBr pellet method. [b]s, strong; m, medium; w, weak; v, very; sh, shoulder. [c]N.R., not resolved. [d]Bands in this region were obscured by solvent.

Table VI. Infrared vibrational frequencies for some $(h^5\text{-}C_5H_5)M(acac)_2Cl$ complexes in the region 480-155 cm^{-1} [a]

$(h^5\text{-}C_5H_5)Zr(acac)_2Cl$		$(h^5\text{-}C_5H_5)Zr(acac\text{-}d_7)_2Cl$	$(h^5\text{-}C_5H_5)Hf(acac)_2Cl$		Predominant Mode
Solution	Solid	Solid	Solution	Solid	
437 s	439 s	417 sh	439 s	441 s	M-O str + ?
424 s	428 s	409 s	424 s	428 s	
403 s	403 s	381 s	408 s	406 s	
318 s	330 s	330 s	294	296 sh	M-Cl str.
				287 s	
318 s	314 s	312 s	276 s	270 s	M-O str.
	306 sh	304 sh			
~280 w	281 w	277 w			
	262 sh				
~237 sh	254 sh	254 sh			
241 m	244 m	245 m	237 m	241 m	
	221 m	210 w		223 w	
				207 w	
	195 w	194 w	195 sh	194 w	

[a] Solution spectra were obtained in benzene, concentration is ca 8 g/100 ml solvent. Solid spectra were obtained in Nujol mulls.

data compiled by Fritz[35] for various cyclopentadienyl metal compounds.

The spectrum of solid $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$ in the 1600-480 cm^{-1} region is virtually identical to the spectrum of the zirconium analogue (cf., Table V). Little mass dependence is consistent with assignment of the frequencies in this region to modes which involve primarily motion of the ligand atoms. The assignments for $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$ follow directly the assignments made for the zirconium analogue.

Several features of the frequencies and assignments given in Table V for $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ and the corresponding acetylacetonate-d_7 derivative merit special comment. A considerable number of metal acetylacetonates exhibit a single, strong band in the region 1600-1550 cm^{-1}.[36] Based on Nakamoto's most recent calculations for a C_{2v} one-ring model[A], the band in this region is due to a nearly pure symmetric carbonyl stretching vibration. In deuterochloroform solution $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ exhibits two strong bands at 1597 and 1577 cm^{-1}. Furthermore, the 1577 cm^{-1} band split into two bands at 1586 and 1570 cm^{-1} in the solid. More than one carbonyl vibration could arise from coupling of the carbonyl vibrations of the two different chelate rings. It is of interest to note that Shimarouchi and coworkers[37] have assigned an extra band in the carbonyl region of $Cu(acac)_2$ and $Pd(acac)_2$ to a combination band between an infrared active C-H out-of-plane vibration and an infrared

inactive C-H out-of-plane vibration. A similar assignment is not possible for the 1577 cm^{-1} band in $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$, because this band is shifted only slightly to lower energy in the acetylacetonate-d_7 derivative.

The band at 1524 cm^{-1} in the solution spectrum of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ is assigned to the asymmetric C---C stretching mode of acetylacetonate coupled slightly with the C-H in-plane bending mode. In the deuterated compound these vibrations are decoupled, and the band splits into two bands at 1526 and 1496 cm^{-1}. The origin of the splitting, however, is not clear.

Acetylacetonate is expected to give rise to three bands in the region between 1500 and 1300 cm^{-1} due to degenerate and symmetric methyl deformation modes and an asymmetric carbonyl stretching vibration. Since the rather broad band of medium intensity at 1427 cm^{-1} is absent in the acetylacetonate-d_7 derivative, it is reasonable to assign this band to the degenerate methyl deformation. The shoulder that appears at 1450 cm^{-1} in the deuterated compound is assigned to the C---C stretching mode of C_5H_5. This shoulder could not be resolved from the 1427 cm^{-1} band in the protonated compound in solution or in the solid. The shoulder at 1373 cm^{-1} and the strong band at 1360 cm^{-1} in $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ are assigned to the asymmetric carbonyl stretching and symmetric methyl deformation modes, respectively. These latter assignments are supported by the spectrum of the deuterated compound, in which the 1360 cm^{-1} band is

absent. It should be noted that Doyle and Tobias have assigned a strong band at 1321 cm^{-1} in $[(h^5\text{-}C_5H_5)_2Ti(acac)]ClO_4$[3] and a shoulder at 1360 cm^{-1} in $[(h^5\text{-}C_5H_5)_2V(acac)]ClO_4$[4] to a C_5H_5 ring stretching vibration. A similar band may be superimposed on the band at 1360 cm^{-1} in $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$, because the 1376 cm^{-1} band observed in the solution spectrum of the acetylacetonate-d_7 derivative is resolved into two bands at 1373 and 1361 cm^{-1} in the solid spectrum. Based on the compilations of Fritz, however, a band near 1360 cm^{-1} would not be expected to represent a fundamental vibration of an h^5-bonded C_5H_5 group.

The next band at 1280 cm^{-1} is due to the C===C symmetric stretches of acetylacetonate coupled slightly with the C-CH_3 stretching mode. As was observed by Benke and Nakamoto for $Pt(acac)Cl_2$, this band splits into two bands at 1304 cm^{-1} and 1242 cm^{-1} upon deuteration of acetylacetonate.

The band at 1185 cm^{-1} is assigned to the C-H in-plane bend of acetylacetone. This latter band is expected to shift below 900 cm^{-1} upon deuteration of the -CH= group. However, no band in either the solution or solid spectrum of the acetylacetonate-d_7 compound could be unambiguously assigned to the C-D in-plane bend. Perhaps the band corresponding to this mode is superimposed on the bands in the C_5H_5 bands in the 834-800 cm^{-1} region. It is also possible that the band may be too weak and broad to observe at room temperature. For example, Benke and Nakamoto[26], observed

the C-D in-plane bending mode in $[Pt(acac\text{-}d_1)Cl_2]^-$ and the corresponding acetylacetonate-d_7 complex only at liquid nitrogen temperature.

Two very weak bands near 1130 and 1070 cm^{-1} are present in both the protonated and deuterated acetylacetonate compounds. The 1130 cm^{-1} band is in the region where the antisymmetric ring breathing mode of C_5H_5 should be observed, and the band is assigned accordingly. However, we are unable to assign the 1070 cm^{-1} band to an infrared active fundamental vibration of the C_5H_5 group.

The band at 1023 cm^{-1} in the solution spectrum of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ consists of two overlapping bands, one due to a methyl rocking mode of acetylacetonate and the other due to an in-plane C-H bending vibration of the C_5H_5 group. The assignment is supported by the fact that the band is approximately one half as intense in the deuterated compound. The two overlapping bands in $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ are apparently resolved in the solid. The C-D in-plane bending frequency of the C_5H_5 group, however, is split in the solid, which accounts for the qualitative similarities between the spectra of the solid samples.

With the exception of the very weak band near 906 cm^{-1} band assignments in the region 1000-600 cm^{-1} are quite straight forward. It is interesting to note, however, that the two types of C-CH_3 stretching modes of acetylacetonate are resolved partially in the solid sample but not in solution. Also, the lower energy C-H out-of-plane

bending mode of the C_5H_5 group appears as a single band in solution, but the band is split in the solid phase.

The two bands at 557 cm^{-1} and 536 cm^{-1} in the spectrum of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ are sensitive to deuteration of acetylacetonate. These bands are tentatively assigned to out-of-plane deformation vibrations of the acac ring.

Bands due to metal-oxygen, metal-halogen and metal-$h^5\text{-}C_5H_5$ stretching modes are expected to occur in the region 480-155 cm^{-1}. Bands in this region are given in Table VI. In solution, the band at 318 cm^{-1} in $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ which is assigned to both Zr-O and Zr-Cl stretching vibrations, and the corresponding band at 294 cm^{-1} in the hafnium analogue are further resolved in the solid state. Spectra in the region 350 cm^{-1} to 155 cm^{-1} are shown in Figures 11-13.

Fay and Pinnavaia[38] have assigned zirconium-oxygen stretching modes in both seven coordinate $Zr(acac)_3Cl$ and eight coordinate $Zr(acac)_4$ to strong absorption in the regions 450-421 cm^{-1} and 314-301 cm^{-1}. Zirconium-chlorine vibration in $Zr(acac)_3Cl$[38] and $ZrCl_4 \cdot 2$Diarsine[39] have been assigned to bands at 314 cm^{-1} and near 300 cm^{-1}, respectively. Similar assignments have been made for the analogous hafnium compounds at somewhat lower absorption frequencies. No assignments have yet been made for zirconium- or hafnium-$h^5\text{-}C_5H_5$ stretching vibrations. The assignments in Table VI are based on the above data.

Figure 11. Infrared spectrum of $(h^5\text{-}C_5H_5)Zr(acac)_2Cl$ in the region 350-155 cm^{-1}. Dashed line, solid in Nujol mull; solid line, in benzene solution at a concentration of ca. 8 g/100 ml solvent.

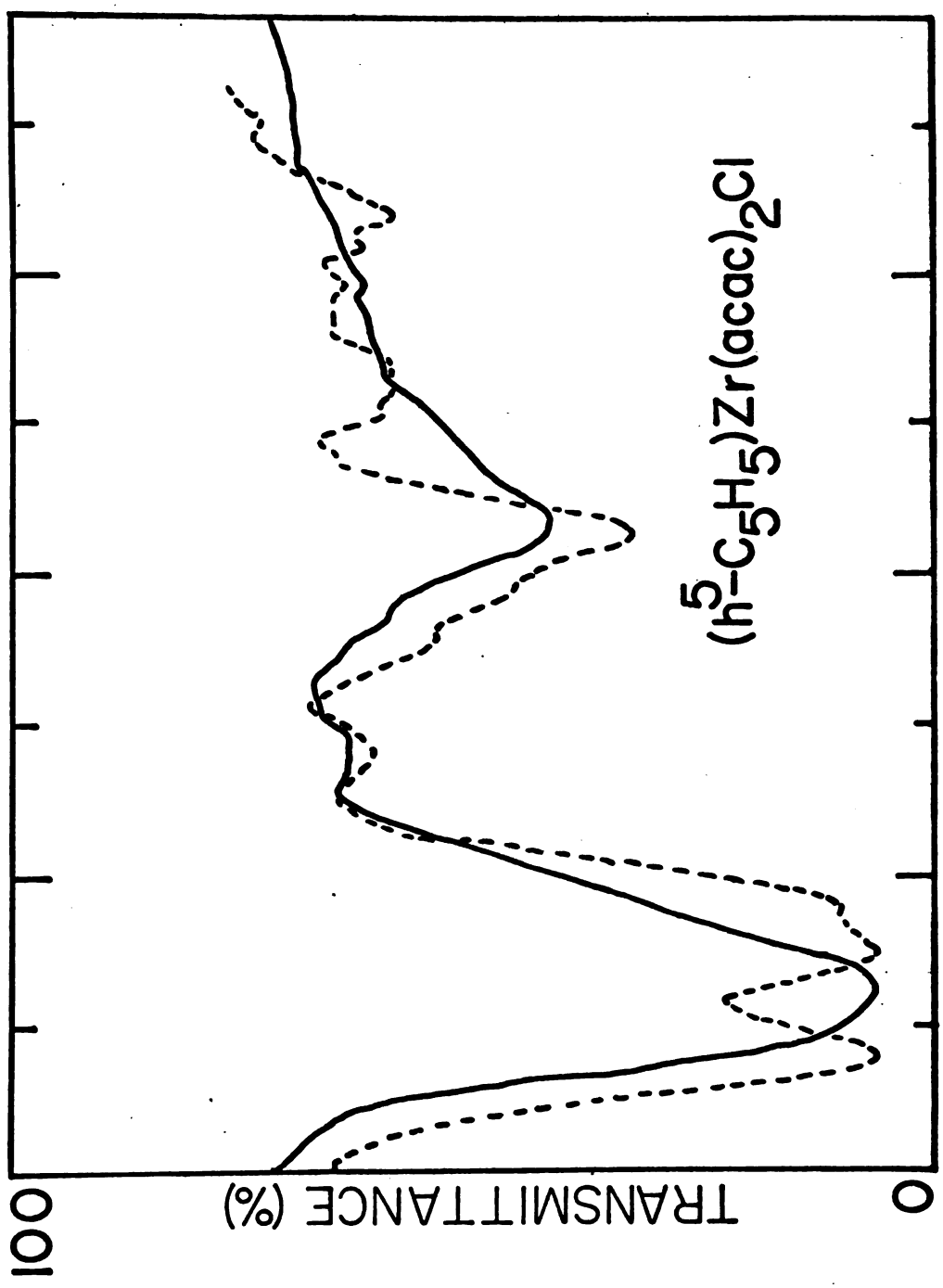

100
0
TRANSMITTANCE (%)
300
250
200
FREQUENCY, cm⁻¹
$(h^5\text{-}C_5H_5)Zr(acac)_2Cl$

Figure 11.

Figure 12. Infrared spectrum of $(h^5\text{-}C_5H_5)Zr(acac\text{-}d_7)_2Cl$ in the region 350-155 cm^{-1}; the spectrum was obtained in a Nujol mull.

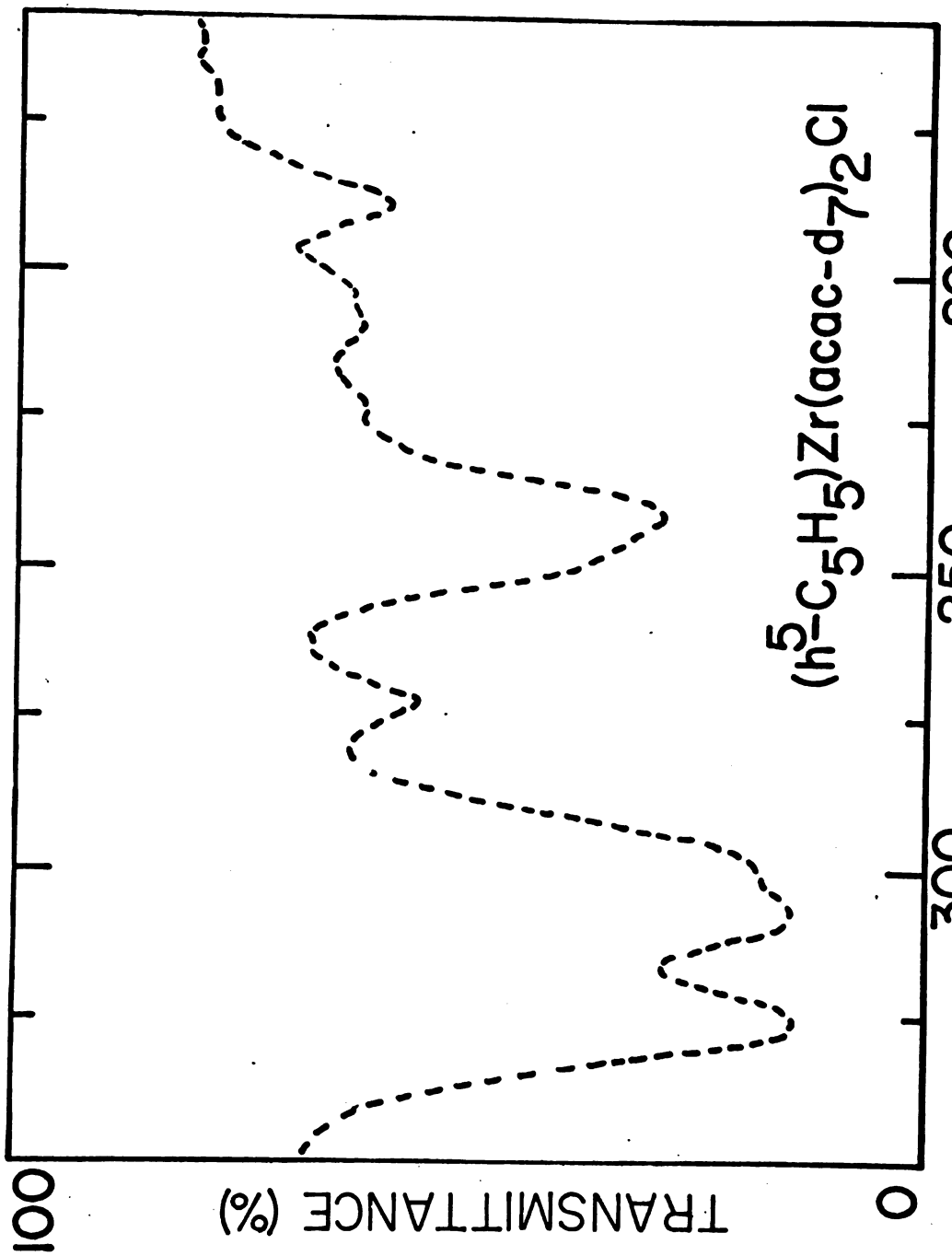

100
0
TRANSMITTANCE (%)
300
250
200
FREQUENCY, cm⁻¹
$(h^5\text{-}C_5H_5)Zr(acac\text{-}d_7)_2Cl$

Figure 12.

Figure 13. Infrared spectrum of $(h^5\text{-}C_5H_5)Hf(acac)_2Cl$ in the region 350-155 cm^{-1}. Dashed line, solid in Nujol mull; solid line, in benzene solution at a concentration of ca. 8 g/100 ml of solvent.

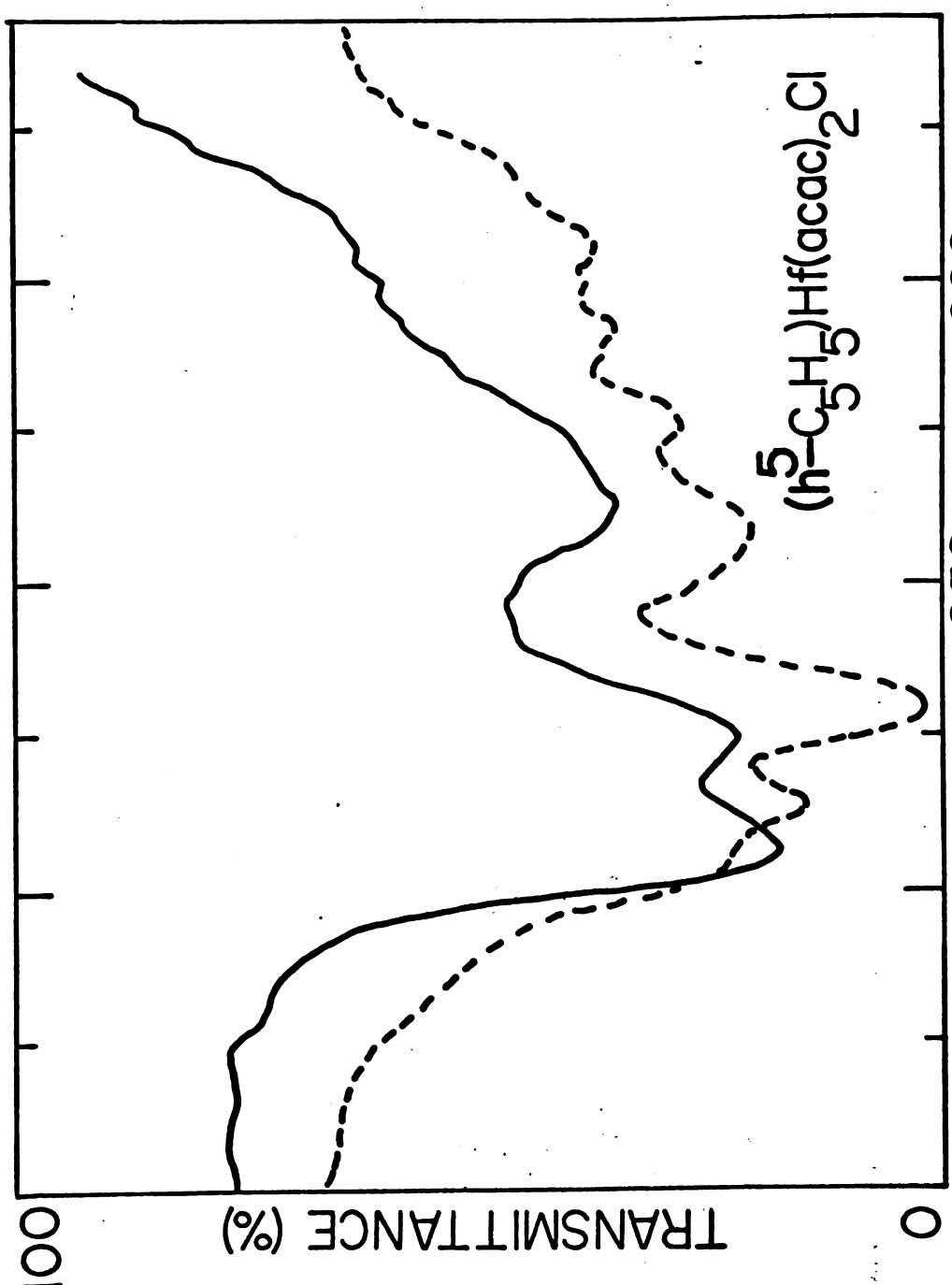

100
TRANSMITTANCE (%)
0
300
250
200
FREQUENCY, cm⁻¹
(h⁵-C₅H₅)Hf(acac)₂Cl

Figure 13.

Unfortunately, it is not possible to assign unambiguously the metal-$h^5C_5H_5$ stretching mode in these compounds. Such assignments might be possible if the h^5-C_5D_5 analogues were also investigated.

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APPENDIX

APPENDIX

A. Least-Squares Analysis, Computer Program

To determine kinetic data from a log k vs 1/T plot it is necessary to know the equation for the straight line that best fits the experimental points. This is conveniently done with the following least-squares Fortran computer program, written by Charles Sokol, which gives the slope and intercept along with their standard deviations. The data cards are prepared as explained by comment cards in the program itself.

```
      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=V/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
   20 FORMAT(* *,*SUMX=*,F15.6,5X,*SUMY=*,F15.6,5X,*SUMXSQ=*,F15.6,5X,*SUOPTIONAL
     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
'LOAD
'RUN,0.45,1000

CARD COUNT =  57                          NO LITTERING

02 PAGES                                  OR LOITERING
```

B. Line Shape Analysis, Computer Program

This program was written by John M. Sebeson, II. It is designed to calculate nmr line shapes by use of the Gutowski-Holm equation.[29] The output consists of nmr spectra which appear as coordinate pairs (OMEGA, AMPLITUDE) where OMEGA is the chemical shift in radians per second relative to a central reference line, and AMPLITUDE is the height of the spectrum at point OMEGA.

The program requires two data cards for each temperature or for each set of T_2 values for which theoretical spectra are desired. Any number of τ values may be used for calculating spectra at a given temperature or set of T_2 values. Also, any number of data card pairs may be used. The data should be entered as follows:

Data Card # 1

Columns 1-10	Value of peak separation at the slow exchange limit (radians per second) divided by 2.
Columns 11-20	T_{2A} (= 2/half width in radians per second)
Columns 21-30	T_{2B}
Columns 31-40	Proton fraction for site A
Columns 41-50	Proton fraction for site B.

Data Card # 2

Columns 1-10	The number of τ values for which spectra are to be calculated
Columns 11-20	The number of coordinate pairs desired in the output for each spectrum calculated

Columns 21-30	The amount by which τ should be incremented for each spectrum calculated
Columns 31-40	The incrementation constant for OMEGA values in radians per second
Columns 41-50	The lower limit of τ (the value of τ for the first spectrum calculated)
Columns 51-60	The lower limit of OMEGA in radians per second (this will be a negative number if the entire spectrum is to be included in the output or 0.0 if only the high field half of the spectrum is desired)

All data points must include a decimal point except the first two data points on Card #2 which must not contain a decimal point. The very last card after all the data card pairs must be exactly like the first card except that $T_{2A} = 0$. This is the only way to terminate the program.

```
      PROGRAM SHAPE
      REAL NUA,TAU,T2A,T2B,PA,PB,OMEGA,AMP,P,Q,R,K1,K2,LL
      COMMON N2,AMP(600),OMEGA(600)
      DIMENSION HERTZ(600),P(600),R(600),Q(600)
      NMRD=60
      NMWR=61
      TWOPI=2.0*3.14159237
      WRITE (NMWR,12)
   12 FORMAT (1H1)
      WRITE (NMWR,9)
    9 FORMAT(80HTHEORETICAL ANALYSIS OF THE DEPENDENCE OF NUCLEAR MAGNE
     1TIC RESONANCE LINE SHAPE)
      WRITE (NMWR,10)
   10 FORMAT(55H ON THE MEAN RESIDENCE TIME AT TWO NON-EQUIVALENT SITES)
  200 READ(NMRD,204) NUA,T2A,T2B,PA,PB
  204 FORMAT(5E10.5)
      IF(T2A) 202,202,206
  206 READ(NMRD,205) N1,N2,K1,K2,TLL,LL
  205 FORMAT(2I10,4E10.5)
  201 WRITE (NMWR,13) NUA,T2A,T2B,PA,PB
   13 FORMAT (6HONUA =,E10.3,10X,5HT2A =,E10.4,10X,5HT2B =,E10.3,10X,4HP
     1A =,F7.5,10X,4HPB =,F7.5)
      WRITE(NMWR,14) N1,K1,TLL
   14 FORMAT(19H0THIS RUN GENERATES,2X,I3,2X,13HTAU VALUES IN,3X,E7.4,3X
     1,32HINCREMENTS WITH A LOWER LIMIT OF,3X,E7.4)
      WRITE (NMWR,15) N2,K2,LL
   15 FORMAT(19H0THIS RUN GENERATES,2X,I3,2X,15HOMEGA VALUES IN,3X,E7.4,
     13X,32HINCREMENTS WITH A LOWER LIMIT OF,3X,E7.4)
      TAU=TLL-K1
      DO 3 L=1,N1
      TAU=TAU+K1
      WRITE(NMWR,4) TAU
    4 FORMAT (6H0TAU =,E10.6)
      OMEGAX=LL-K2
      DO 3 M=1,N2
      OMEGAX=OMEGAX+K2
      OMEGA(M)=OMEGAX
      P(M)=TAU*((1./(T2A*T2B))-OMEGA(M)**2+NUA**2)+PA/T2A+PB/T2B
      Q(M)=TAU*(OMEGA(M)-NUA*(PA-PB))
      R(M)=OMEGA(M)*(1.+TAU/T2A+TAU/T2B)+NUA*(PA-PB)
      AMP(M)=(P(M)*((PA/T2A+PA/T2B)*TAU+1.)+Q(M)*(NUA*TAU*(1./T2A-1./T2B
     1))+Q(M)*R(M)) /(P(M)**2+R(M)**2+(NUA*TAU*(1./T2A-1./T2B))**2+2.*R*
     2(NUA*TAU*(1./T2A-1./T2B)))
    3 CONTINUE
      DO 20 JJ=1,N2
```

```
      20 HERTZ(JJ)=OMEGA(JJ)/TWOPI
         XM=0.
         DO 902 I=1,N2
         IF(AMP(I).GT.XM) XM=AMP(I)
     902 CONTINUE
         AMPMIN=0.
         DO 903 I=1,N2
         IF(OMEGA(I).EQ.0.) AMPMIN=AMP(I)
     903 CONTINUE
         IF(AMPMIN.EQ.0.) GO TO 904
         PR=XM/AMPMIN
         WRITE (NMWR,905) PR
     905 FORMAT(48HORATIO OF PEAK MAXIMUM TO PETWEEN-PEAK MINIMUM =,F10.3)
         IF(.NOT.(AMPMIN.EQ.0.)) GO TO 906
     904 WRITE (NMWR,907)
     907 FORMAT(60H0ALL OMEGA VALUES NON-ZERO. RATIO CALCULATION NOT ATTEMP
        1TED.)
     906 XHM=XM/2.
         WRITE(NMWR,908) XM,XHM
     908 FORMAT(15H0PEAK MAXIMUM =,F10.5,3X,24HHALF-MAXIMUM AMPLITUDE =,F10
        1.5)
         WRITE (NMWR,6)
       6 FORMAT (1H0,10X,5HOMEGA, 8X,9HAMPLITUDE, 8X,5HHERTZ)
         DO 8 M=1,N2
         WRITE(NMWR,7) OMEGA(M),AMP(M),HERTZ(M)
       7 FORMAT (1H ,10X,3F15.5)
       8 CONTINUE
       2 CONTINUE
         GO TO 200
     202 WRITE (NMWR,203)
     203 FORMAT (19H0FUNCTION COMPLETED)
         END
```

CARD COUNT = 7