Studies of the Kinetics and Mechanism of Stereochemical Rearrangement Processes for Tris(β-diketonato)-π-cyclopentadienylzirconium Complexes

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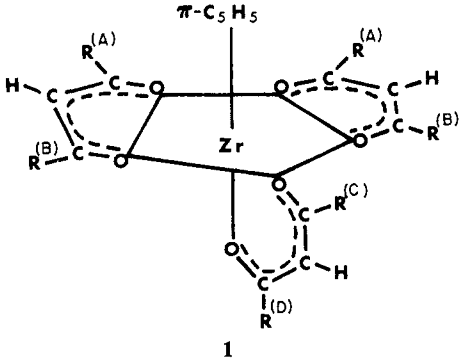
Abstract: Tris(β-diketonato)-π-cyclopentadienylzirconium complexes, which possess a stereochemistry based on a pentagonal bipyramid in which the center of the cyclopentadienyl ring occupies an axial vertex, undergo two distinct types of stereochemical rearrangement processes. The faster process (process 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. The kinetics of process I has been determined for the hexafluoroacetylacetone derivative, $(\pi\text{-}C_5H_5)Zr(hfac)_3$, in diisopropyl ether and for the dipivaloylmethanate, $(\pi\text{-}C_5H_5)Zr(dpm)_3$, in *o*-xylene by nmr line-broadening methods. For both compounds the process is first order and an intramolecular mechanism operates. The activation energies and the activation entropies at 25° are, respectively, 15.7 ± 0.5 kcal/mol and 5.1 ± 1.7 eu for $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and 21.3 ± 1.9 kcal/mol and 3.8 ± 5.5 eu for $(\pi\text{-}C_5H_5)Zr(dpm)_3$. Process II for $(\pi\text{-}C_5H_5)Zr(hfac)_3$ is first order, and the activation parameters are $E_a = 26.4 \pm 1.9$ kcal/mol and $\Delta S^{\ddagger}_{25°} = 17.2 \pm 5.2$ eu. Since in the presence of added free ligand the exchange of coordinated ligand with free ligand accompanies process II, an intermolecular mechanism involving complete dissociation of a diketonate ligand in the rate-limiting step cannot yet be ruled out. Studies of the trifluoroacetylacetone analog, in which the ligands are asymmetric, indicate that the most probable pathway for process I is either a bond-rupture or digonal-twisting mechanism involving the equatorial ligands.

Mixed β-diketonatocyclopentadienylzirconium complexes of the type $(\pi\text{-}C_5H_5)Zr(dik)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(dik)_3$ have been the subject of several recent stereochemical investigations.[1–6] In the case of tris(hexafluoroacetylacetonato)cyclopentadienylzirconium, $(\pi\text{-}C_5H_5)Zr(hfac)_3$, a single-crystal X-ray structure determination[4] has shown that the stereochemistry is describable in terms of either an icosahedral coordination polyhedron in which one vertex is suppressed or, more simply, a pentagonal bipyramid (**1**) in which the center of the C_5H_5 ring is positioned at an axial vertex and the donor oxygen atoms of the diketonate ligands occupy the remaining coordination positions. In solution the molecule has been shown to undergo two distinct types of rapid stereochemical rearrangement processes.[2] The faster process (process I) results in the interconversion of nonequivalent environments for the CF_3 terminal groups ($R^{(A)}$ and $R^{(B)}$) 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. In the present study the kinetics of the rearrangement processes have been determined by nmr line-broadening methods. In addition, the dipivaloylmethanate and trifluoroacetylacetonate analogs have been investigated, and possible mechanisms for process I have been evaluated.



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Experimental Section

General Synthetic Techniques. The compounds used in this study are sensitive to atmospheric moisture, especially when they are dissolved in solution. Therefore, all preparative reactions and manipulations of the products were conducted under a dry-argon atmosphere. All glassware was dried at 175°, cooled in a calcium sulfate desiccator, and flushed with argon before use. Tetrahydrofuran, diethyl ether, benzene, dibutyl ether, and hexane were dried by refluxing over lithium aluminum hydride. Dichloromethane was dried over calcium hydride, and acetone was dried by treatment with calcium sulfate. Hexafluoroacetylacetone and dipivaloylmethane were prepared by modification of previously described procedures.[7,8] Trifluoroacetone was purchased from Columbia Organic Chemicals Co., Inc. (bp 107°), and was fractionally distilled before use. The absence of organic impurities in the β-diketones was confirmed by nmr spectroscopy. Zirconocene dichloride was used as purchased from Aldrich Chemical Co., Inc. Tetracyclopentadienylzirconium was prepared according to the method described by Brainina and coworkers.[9,10] Since this latter

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compound does not melt sharply, its purity was checked by chemical analysis, a molecular weight determination, and nmr spectroscopy.

Anal. Calcd for $(C_5H_5)_4Zr$: 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.[10] δ 5.75).

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 × 10^{-3} *M* solution in $C_6H_5NO_2$ at 25°), 0.014 ohm^{-1} cm^2 mol^{-1}.

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 × 10^{-3} *M* solution in $C_6H_5NO_2$ at 25°), 0.028 ohm^{-1} cm^2 mol^{-1}.

Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)cyclopentadienylzirconium. 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 ~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 × 10^{-3} *M* solution in $C_6H_5NO_2$ at 25°), 0.059 ohm^{-1} cm^2 mol^{-1}.

Melting Point, Molecular Weight, and Molar Conductivity Measurements. Melting points were determined in sealed capillaries with a Thomas-Hoover capillary melting point apparatus. Molecular weights in benzene were determined by the freezing-point-depression method. A Wayne Kerr Model B221 universal bridge was used to measure molar conductivities. The conductivity cell was equipped with bright platinum electrodes and was calibrated with a standard KCl solution.

Nuclear Magnetic Resonance Spectra. Nuclear magnetic resonance spectra were recorded on a Varian A56/60D analytical spectrometer operated at 60.0 (^1H spectra) or 56.4 MHz (^{19}F spectra). The probe temperature was controlled to within ±0.5° by a Varian V-6040 variable-temperature controller. The methanol and ethylene glycol nmr thermometers described by Van Geet[11] 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 radiofrequency field strengths in order to avoid saturation effects.

Solvents and Preparation of Solutions. All solutions used in the nmr studies were prepared under a dry-nitrogen atmosphere. Diisopropyl ether, *o*-xylene, and toluene were dried over lithium aluminum hydride, and dichloromethane was dried over calcium hydride. 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 *tert*-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.

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, as expanded by Rogers and Woodbrey,[12] was used to calculate the theoretical spectra. Each calculated spectrum consisted of 100–250 coordinate pairs spaced at maximum intervals of 0.15 Hz. The calculations were carried out on either a CDC 3600 or an IBM 1136 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.

Results and Discussion

Preparative Reactions. The hexafluoroacetylacetonate- and trifluoroacetylacetonate–cyclopentadienylzirconium complexes $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and $(\pi\text{-}C_5H_5)Zr(tfac)_3$ were prepared by reaction of zirconocene dichloride and the neat β-diketone under anhydrous conditions. Earlier work has shown that reactions of

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

zirconocene dichloride and nonfluorinated diketones under similar conditions yield products of the type $(\pi\text{-}C_5H_5)Zr(dik)_2Cl$.[13] Apparently, the substitution of the second chlorine atom by a nonfluorinated diketone is slow. 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[14] or trifluoroacetylacetone,[15] for example, readily affords the tetrakis(β-diketonato)zirconium complex, whereas the reaction with acetylacetone[16,17] and certain other nonfluorinated diketones[16,18] gives mainly the chlorotris(diketonato) complex. Although replacement of chlorine in $Zr(acac)_3Cl$ by acetylacetonate can be achieved in the presence of water,[19] the hydrolyses of $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ and analogous β-diketonates afford stable dizirconoxanes of the type $[(\pi\text{-}C_5H_5)Zr(dik)_2]_2O$.[20-22]

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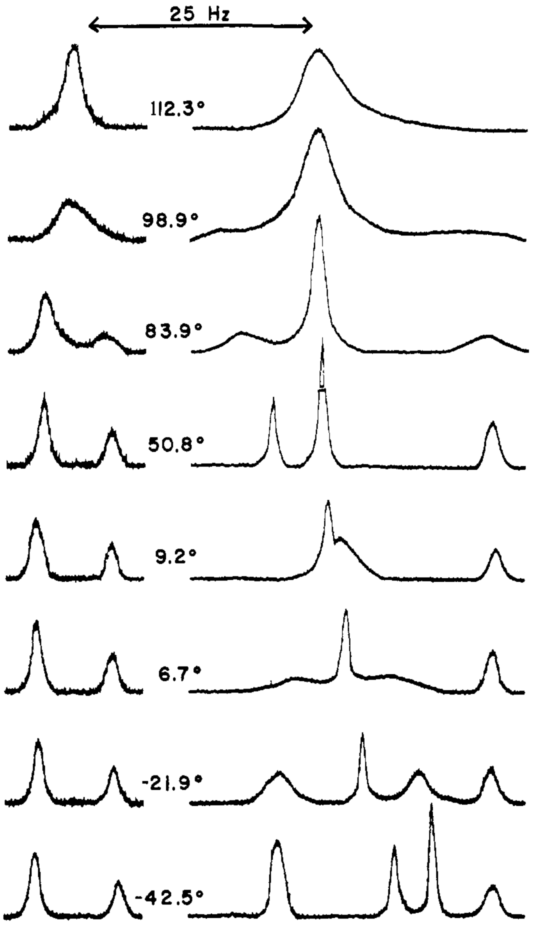

Figure 1. Temperature dependence of the ^{19}F and -CH= proton nmr lines for $(\pi\text{-}C_5H_5)Zr(hfac)_3$ in diisopropyl ether solution; concentration is 0.12 *M*.

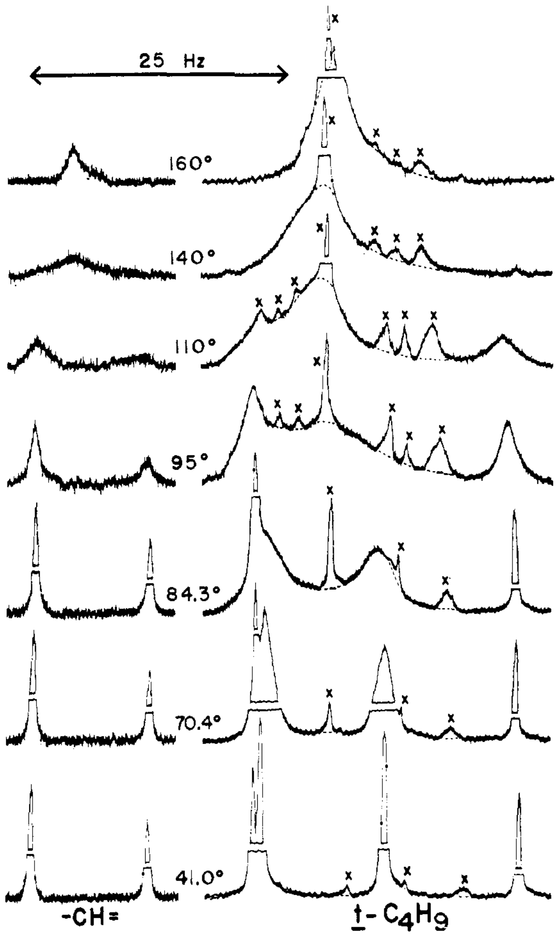

Figure 2. Temperature dependence of the *tert*-C_4H_9 and -CH= proton nmr lines for $(\pi\text{-}C_5H_5)Zr(dpm)_3$ in *o*-xylene; concentration is 0.21 *M*. The lines marked × in the *tert*-C_4H_9 region are due to unidentified thermal decomposition products.

The only known preparative pathway 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.[22] In the present study an analogous reaction with dipivaloylmethane gave $(\pi\text{-}C_5H_5)Zr(dpm)_3$ in moderate yield.

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

All of the $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes studied here are monomeric and very weak electrolytes in solution, as indicated by the molecular weight and conductivity data presented in the Experimental Section.

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 1 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. 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 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.[2] 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 **1**) 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 $(\pi\text{-}C_5H_5)Zr(dpm)_3$ in *o*-xylene solution. The temperature dependences of the *tert*-C_4H_9 and -CH= resonance lines shown in Figure 2 are qualitatively similar to those described for the CF_3 and -CH= resonances of $(\pi\text{-}C_5H_5)Zr(hfac)_3$. 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

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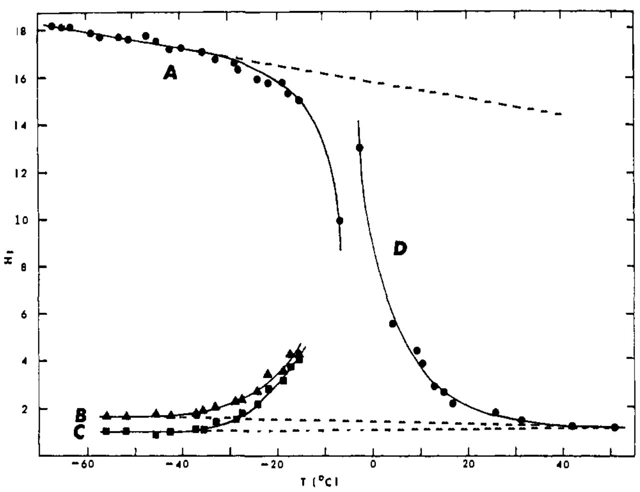

Figure 3. Temperature dependence of ^{19}F nmr line-shape parameters for the terminal CF_3 groups on the equatorial ligands of $(\pi\text{-}C_5H_5)Zr(hfac)_3$ in diisopropyl ether: curve A, frequency separation between the resonance components below coalescence; curves B and C, widths at half-maximum 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.

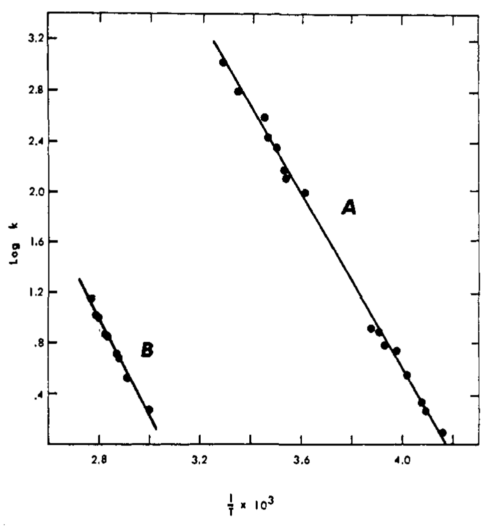

Figure 4. Arrhenius plots for the exchange of nonequivalent terminal groups on the equatorial ligands of $(\pi\text{-}C_5H_5)Zr(hfac)_3$ in diisopropyl ether (line A) and $(\pi\text{-}C_5H_5)Zr(dpm)_3$ in *o*-xylene (line B).

thermally stable, as evidenced by the appearance of several unidentified impurity lines in the *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 rates of process I.

Process I. Mean lifetimes τ_A and τ_B for the nonequivalent terminal groups on the equatorial ligands of $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and $(\pi\text{-}C_5H_5)Zr(dpm)_3$ were determined by comparing the experimental CF_3 and *tert*-C_4H_9 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 $(\pi\text{-}C_5H_5)Zr(hfac)_3$ 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 3 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 3 that the widths of the two CF_3 lines 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. The activation parameters for the exchange process (see below) are not appreciably dependent on the estimated temperature dependence for the relaxation times. For example, even if no temperature dependence is assumed for the relaxation times, the activation parameters obtained are nearly equal within the 95% confidence level estimates of error to those obtained by the above procedure. The frequency separation and widths for the *tert*-C_4H_9 proton resonance components of $(\pi\text{-}C_5H_5)Zr(dpm)_3$ are temperature dependent, but the widths of the lines are equal in the region of slow 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 solution and $(\pi\text{-}C_5H_5)Zr(dpm)_3$ in *o*-xylene are given in Tables I and II, respectively. Also shown in the tables are the Arrhenius activation energy, E_a, the frequency factor, A, the activation entropy at 25°, $\Delta S^{\ddagger}_{25°}$, and the extrapolated value of the first-order rate constant at 25°, $k_{25°}$. Values of E_a and A were determined from the slope and intercepts of log k *vs.* $1/T$ plots, where $k = (2\tau)^{-1}$. These plots are shown in Figure 4. A comparison of the activation parameters for $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and $(\pi\text{-}C_5H_5)Zr(dpm)_3$ shows that the greater stereochemical rigidity of the latter molecule is due primarily to a 5.6 ± 2.0 kcal/mol larger activation energy. 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, $A = \exp(14.68 \pm 0.68)$ in diisopropyl ether; $E_a = 22.5 \pm 1.3$ kcal/mol, $A = \exp(14.86 \pm 0.81)$ in toluene.

The mean lifetimes of the terminal groups on the equatorial ligands of both $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and $(\pi\text{-}C_5H_5)Zr(dpm)_3$ are independent of concentration over the range 0.12–0.21 *M* and, also, are not affected by the presence of equal molar amounts of free ligand.

Table I. ^{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	5.50	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
		E_a = 15.7 ± 0.5[f] kcal/mol	A = exp(14.38 ± 0.38)		
		$\Delta S^{\ddagger}_{25°}$ = 5.1 ± 1.7 eu	$k_{25°}$ = 646 sec^{-1}		

[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. [f] All errors are estimated at the 95% confidence level.

Table II. ^{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
E_a = 21.3 ± 1.9[f] kcal/mol			A = exp(14.05 ± 1.19)	
$\Delta S^{\ddagger}_{25°}$ = 3.8 ± 5.5 eu			$k_{25°}$ = 0.0284 sec^{-1}	

[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. [f] All errors are estimated at the 95% confidence level.

Therefore, the rearrangement processes are indeed first order, and an intramolecular mechanism operates. Figure 5 shows four simple intramolecular mechanisms which would lead to the interchange of nonequivalent environments for the terminal groups on the equatorial ligands of a $(\pi\text{-}C_5H_5)M(dik)_3$ 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 $(\pi\text{-}C_5H_5)Zr(hfac)_3$ or $(\pi\text{-}C_5H_5)Zr(dpm)_3$ does not accompany the collapse of the lines for the terminal groups on the equatorial ligands, mechanism A can be eliminated. The relative merit of the remaining three mechanisms can be evaluated, in part, by investigation of the trifluoroacetylacetonate derivative, $(\pi\text{-}C_5H_5)Zr(tfac)_3$.

Because of the asymmetry of the trifluoroacetylacetonate ligand, $(\pi\text{-}C_5H_5)Zr(tfac)_3$ may give rise to the six geometric isomers shown in Figure 6. In the absence of any exchange processes, an equilibrium mixture of all six isomers should give 6 C_5H_5, 14 $-CH=$, and 14 CH_3 proton nmr lines. The ^{19}F nmr spectrum should contain 14 CF_3 lines. The proton nmr spectrum of the compound at room temperature consists of two sets of 1:2 methyl doublets, four $-CH=$ lines, and two C_5H_5 resonances. The spectrum has been interpreted previously[2] 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 group is equatorial (IV ↔ V ↔ VI). However, the existence of all six isomers in solution has not yet been demonstrated. Elder[4] 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 isomers 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). 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 inter-

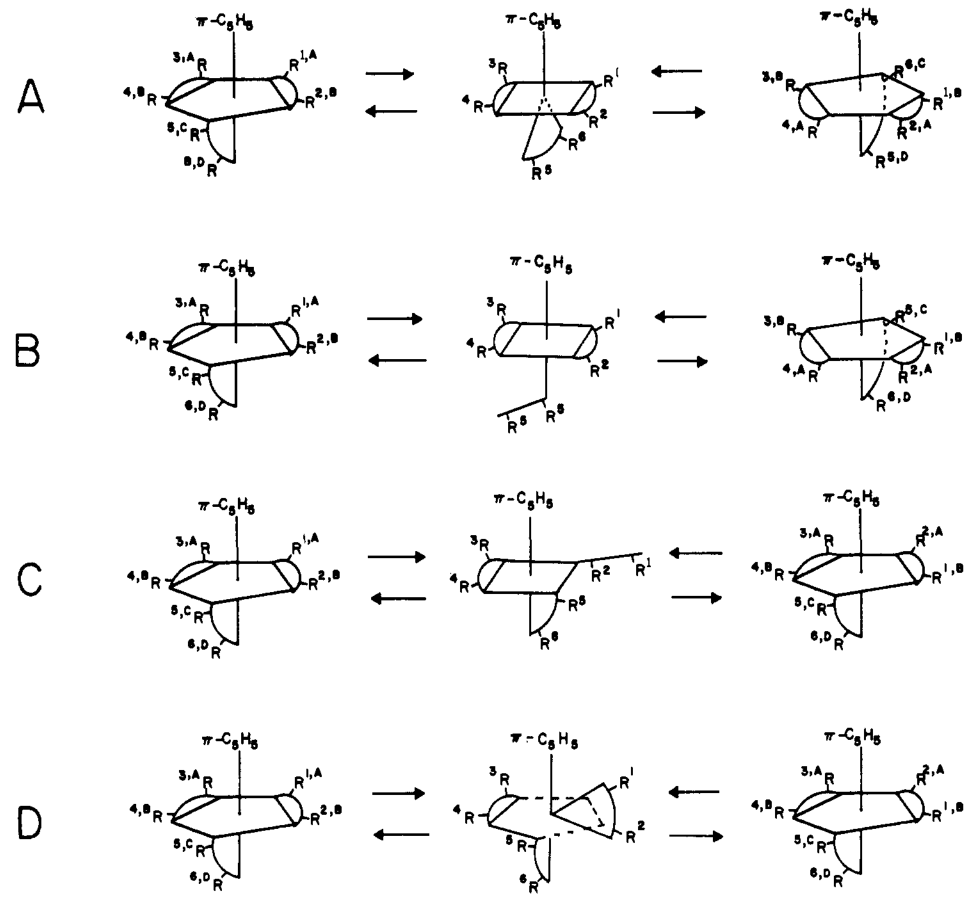

Figure 5. Possible intramolecular mechanisms for the interconversion of nonequivalent environments for the terminal group on the equatorial ligands of a (π-C_5H_5)M(dik)$_3$ complex. The superscripts label and identify the environments of each R group. Mechanisms C and D are degenerate in energy with analogous processes for the equatorial ligand containing terminal groups R^3 and R^4.

change 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.

We have investigated the ^1H and ^{19}F nmr spectra of (π-C_5H_5)Zr(tfac)$_3$ in dichloromethane in the temperature range −90 to −75°, where the exchange process is slow. In contrast to the room-temperature spectrum described above, the proton spectrum in the range −90 to −75° 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. We must assume that more than three isomers, probably all six isomers, are indeed present, and that the ^1H and ^{19}F chemical shifts for many of the isomers are nearly coincident. This assumption is also supported, in part, by the broadness of the CH_3 and -CH= lines. Thus the nmr data for (π-C_5H_5)Zr(tfac)$_3$ 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,[23] but in rearrangements of higher coordination number metal complexes, such twists could be favored and cannot be ruled out.

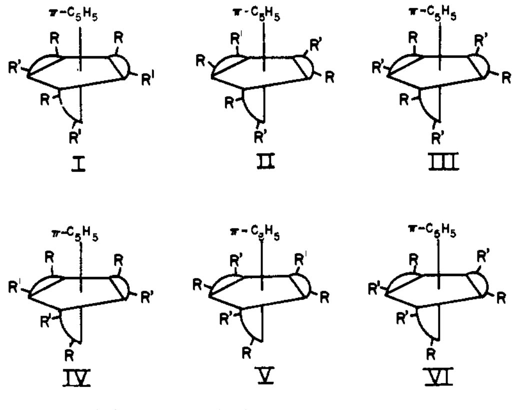

Figure 6. Possible geometric isomers for (π-C_5H_5)Zr(tfac)$_3$. R and R′ represent the distinguishable CH_3 and CF_3 terminal groups on the asymmetric diketonate ligand.

It may be argued that since the terminal *tert*-C_4H_9 groups in (π-C_5H_5)Zr(dpm)$_3$ are bulkier than the terminal CF_3 groups in (π-C_5H_5)Zr(hfac)$_3$, the larger activation energy for the former complex would be more consistent with a twisting mechanism than a bond-rupture mechanism. However, the mean thermochemical zirconium–oxygen bond energy should also be larger for the dipivaloylmethane analog. Therefore, the difference in the steric requirements of the terminal groups in these two derivatives does not provide a meaningful mechanistic criterion. Further

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[23] M. Gielen, *Bull. Soc. Chim. Belg.*, 78, 351 (1969).

Table III. ^{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_{2B},[b] sec	T_{2A},[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
		E_a = 26.4 ± 1.9[g] kcal/mol		$A = \exp(16.97 \pm 1.06)$		
		$\Delta S^{\ddagger}_{25°}$ = 17.2 ± 5.2 eu		$k_{A\,25°} = 4.51 \times 10^{-3}$ sec^{-1}		

[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. [g] All errors are estimated at the 95% confidence level.

information regarding the exchange mechanism must await the study of additional derivatives.

Process II. The exchange of the unique β-diketonate ligand with the two equivalent equatorial ligands on $(\pi\text{-}C_5H_5)Zr(hfac)_3$ was examined in diisopropyl ether solution 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°. Also, 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 methods similar to those described above for the equatorial CF_3 fluorine resonances of process I. The nmr line-shape parameters and values of τ are given in Table III. 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 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 III were determined from a plot of log k_A *vs.* $1/T$, where $k_A = 2(3\tau)^{-1}$ (see Figure 7).

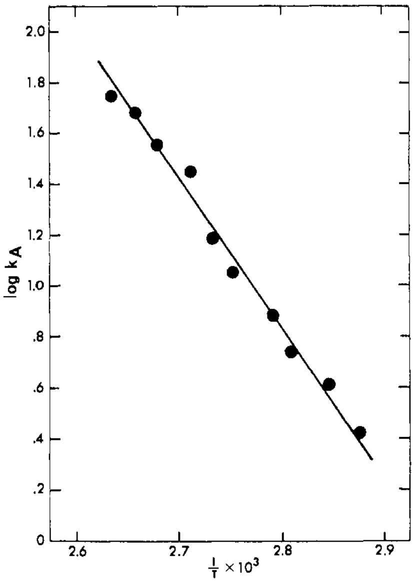

Figure 7. Arrhenius plot for the interchange of the unique diketonate ligand and the equatorial diketonate ligands on $(\pi\text{-}C_5H_5)Zr(hfac)_3$ in diisopropyl ether solution.

The activation energy for the interchange of the unique and equatorial ligands on $(\pi\text{-}C_5H_5)Zr(hfac)_3$ is 10.7 ± 2.0 kcal/mol larger than the activation energy for the exchange of nonequivalent environments for the terminal groups on the equatorial ligands. The activation entropy for process II is 12.1 ± 5.5 eu larger than that for process I. Since the mean lifetimes of the unique and equatorial ligands are independent of concentration over the range 0.13–0.26 *M*, process II is also first order. However, it is not yet possible to decide whether an intra- or intermolecular mechanism operates, because in the presence of added free ligand, the exchange of coordinated and free ligand accompanies the stereochemical rearrangement process. For example, at 98° in a solution containing a 1:3 molar ratio of $(\pi\text{-}C_5H_5)Zr(hfac)_3$ 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. Previous studies have shown that ligand exchange between zirconium β-diketonates and free diketones can occur *via* first-order as well as second-order paths.[24] In the case of $(\pi\text{-}C_5H_5)Zr(hfac)_3$, the formation of a square-pyramidal $(\pi\text{-}C_5H_5)Zr(hfac)_2^+$ intermediate in the rate-limiting step could 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. Although we tentatively favor an intramolecular mechanism for process II rather than a complete ligand-dissociation mechanism based on the magnitude of the activation energy, detailed kinetic studies of ligand exchange between $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and free diketone are planned in order to further test the possibility of a $(\pi\text{-}C_5H_5)Zr(hfac)_2^+$ intermediate.

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[24] A. C. Adams and E. M. Larsen, *Inorg. Chem.*, 5, 814 (1966).