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Dynamic Stereochemical Properties of Some Halobis(β-diketonato)-π-cyclopentadienylzirconium and -hafnium Complexes

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The eight-coordinate acetylacetonatocyclopentadienyl complexes $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$, $(\pi\text{-}C_5H_5)Hf(acac)_2Cl$, and $(\pi\text{-}C_5H_5)Zr(acac)_2Br$ exist in solution as single stereoisomers with C_1 symmetry and undergo kinetically first-order stereochemical rearrangement processes which interchange the two nonequivalent acetylacetonate ligands. Rates of ligand interchange in benzene were determined from the temperature dependence of the acetylacetonate ring proton nmr lines. The activation energies (kcal/mol) and entropies at 25° (eu), respectively, are as follows: 23.1 ± 2.0 and 7.1 ± 5.4 for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$; 24.2 ± 2.2 and 7.5 ± 6.0 for $(\pi\text{-}C_5H_5)Hf(acac)_2Cl$; 22.8 ± 1.8 and 5.7 ± 3.8 for $(\pi\text{-}C_5H_5)Zr(acac)_2Br$. The benzoylacetonate derivative $(\pi\text{-}C_5H_5)Zr(bzac)_2Cl$ gives rise to four geometric isomers in solution, and the interconversion of all four geometric isomers accompanies the interchange of the two nonequivalent β-diketonate ligands in each isomer. Intermolecular mechanisms involving complete dissociation of either a diketonate or halogen ligand are unlikely. A plausible intramolecular mechanism involving formation of an eight-coordinate symmetric intermediate, in which the halogen atom is positioned trans to the center of the C_5H_5 ring, is briefly described.

Introduction

Zirconium(IV) forms a variety of β-diketonate complexes with diverse stereochemistries. With few exceptions the known molecular complexes are of the following general types: $Zr(dik)_2X_2$, $Zr(dik)_3X$, $Zr(dik)_4$, $(\pi\text{-}C_5H_5)Zr(dik)_2X$, and $(\pi\text{-}C_5H_5)Zr(dik)_3$, where dik is any diketonate ligand and X is a monodentate ligand such as a halogen. A characteristic feature of all the complexes is their ability to undergo rapid stereochemical rearrangement processes in solution which lead to environmental interchange for the terminal groups (*e.g.*, CH_3 or CF_3) on the diketonate ligands. The six-coordinate $Zr(dik)_2X_2$, seven-coordinate $Zr(dik)_3X$, and eight-coordinate $Zr(dik)_4$ complexes are so labile on the nmr time scale that the environmentally nonequivalent β-diketonate terminal groups present exhibit only sharp time-averaged resonance lines even at low temperatures.[1-4] The stereochemical rearrangement processes for the cyclopentadienylzirconium β-diketonates, however, are sufficiently slow at accessible temperatures to allow detection of nonequivalent terminal group environments by nmr spectroscopy.[5-7] Recently, nmr line-broadening methods have been employed to obtain quantitative kinetic data and mechanistic information on the rearrangement processes for some nine-coordinate[8] $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes.[9] In the present study similar nmr methods are used to describe the dynamic stereochemical properties of the eight-coordinate cyclopentadienylzirconium acetylacetonates $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(acac)_2Br$, along with $(\pi\text{-}C_5H_5)Hf(acac)_2Cl$. Also, the benzoylacetonate complex $(\pi\text{-}C_5H_5)Zr(bzac)_2Cl$ has been investigated.

Experimental Section

Syntheses.—All solvents used in the preparative reactions were reagent grade and were vigorously dried over a suitable drying agent. Benzene, hexane, diethyl ether, toluene, and tetrahydrofuran were dried by refluxing over lithium aluminum hydride. Acetonitrile and dichloromethane were dried over calcium hydride, and triethylamine was dried over barium oxide. Acetylacetone was freshly distilled before use, the fraction boiling at 136–138° being collected. Hafnium tetrachloride (spectroscopic grade) was purchased from Wah Chang Corp., Albany, Ore. Dicyclopentadienylzirconium dichloride (zirconocene dichloride) was obtained from Aldrich Chemical Co., Milwaukee, Wis.

Hafnocene dichloride was prepared by reaction of stoichiometric amounts of sodium cyclopentadienide and hafnium tetrachloride in tetrahydrofuran according to the general procedure described by Wilkinson and Birmingham.[10] Zirconocene dibromide was obtained by the metathesis reaction[11] of zirconocene dichloride and boron tribromide. The absence of impurities in the products was ensured by nmr spectroscopy and by checking their melting points against literature values.[11-13]

Unless otherwise noted, all of the operations involved in the synthesis, purification, and subsequent handling of the acetylacetonate complexes were conducted under an atmosphere of dry nitrogen, because they are readily hydrolyzed, especially when dissolved in solution. All glassware was dried at 180° and cooled, when possible, in a calcium sulfate desiccator.

Chlorobis(2,4-pentanedionato)-π-cyclopentadienylzirconium.—This compound was prepared by employing a modification of the method described by Freidlina, Brainina, and Nesmeyanov.[14] Zirconocene dichloride (5.00 g, 17.1 mmol) was placed in a 250-ml side-arm erlenmeyer flask equipped with a graduated dropping funnel containing acetylacetone. The flask was evacuated and placed in an oil bath at 80°. The stopcock on the dropping funnel was carefully opened to admit *ca.* 50 ml of acetylacetone into the flask. Every 2 min the flask was opened to a vacuum pump for a few seconds to remove volatile products (HCl and C_5H_6). After 15 min heating time, the excess acetylacetone was removed under vacuum to give a white crystalline residue. The residue was recrystallized from benzene, and the 6.30 g (94%) of product was dried *in vacuo* at room temperature; mp 189–190°; lit.[14] mp 188–190°. *Anal.* Calcd for $(\pi\text{-}C_5H_5)Zr(C_5H_7O_2)_2Cl$: C, 46.20; H, 4.91; mol wt 390. Found: C, 46.01; H, 5.00; mol wt ($C_6H_5NO_2$) 407; $\Lambda(7.3 \times 10^{-3}\ M$ in $C_6H_5NO_2$ soln at 25°) $< 0.014\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

Bromobis(2,4-pentanedionato)-π-cyclopentadienylzirconium.—To a stirred solution of zirconocene dibromide (5.72 g, 15.0 mmol)

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[1] A. C. Adams and E. M. Larson, *Inorg. Chem.*, **5**, 228 (1966).

[2] T. J. Pinnavaia and R. C. Fay, *ibid.*, **5**, 233 (1966).

[3] T. J. Pinnavaia and R. C. Fay, *ibid.*, **7**, 502 (1968).

[4] S. C. Chattoraj, C. T. Lynch, and K. S. Mazdiyasni, *ibid.*, **7**, 2501 (1968).

[5] T. J. Pinnavaia, J. J. Howe, and E. D. Butler, *J. Amer. Chem. Soc.*, **90**, 5288 (1968).

[6] M. Elder, J. G. Evans, and W. A. G. Graham, *ibid.*, **91**, 1245 (1969).

[7] M. Kh. Minacheva, E. M. Brainina, and L. A. Dederov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1007 (1969); *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1104 (1969).

[8] The cyclopentadienyl group is regarded herein as a tridentate ligand.

[9] J. J. Howe and T. J. Pinnavaia, *J. Amer. Chem. Soc.*, **92**, 7342 (1970).

[10] G. Wilkinson and J. M. Birmingham, *ibid.*, **76**, 4281 (1954).

[11] P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spaulding, and R. C. Srivastava, *J. Chem. Soc. A*, 2106 (1969).

[12] E. M. Brainina and R. Kh. Freidlina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 756 (1963); *Izv. Akad. Nauk SSSR, Ser. Khim.*, 835 (1963).

[13] E. M. Brainina and R. Kh. Freidlina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1331 (1964); *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1421 (1964).

[14] R. Kh. Freidlina, E. M. Brainina, and A. N. Nesmeyanov, *Dokl. Chem.*, **138**, 628 (1961); *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **138**, 1369 (1961).

in 200 ml of acetonitrile was added dropwise a second solution containing acetylacetone (2.94 ml, 29.4 mmol) and triethylamine (2.10 ml, 29.4 mmol) in 120 ml of acetonitrile. The reaction mixture was stirred for 3 hr at room temperature, and then the solvent was removed under vacuum at 50–60°. The residue was treated with 200 ml of benzene, and the slurry was filtered to remove the insoluble triethylamine hydrochloride. A white crystalline product was recovered from the filtrate by reducing its volume to *ca.* 100 ml, adding 200 ml of hot hexane, and cooling to room temperature. One recrystallization from benzene afforded 4.38 g (67%) of pure product, which was dried *in vacuo* at room temperature; mp 202–204°; lit.[13] mp 203.5–205°. *Anal.* Calcd for $(\pi\text{-}C_5H_5)Zr(C_5H_7O_2)_2Br$: C, 41.46; H, 4.38; mol wt 434. Found: C, 41.45; H, 4.65; mol wt (C_6H_6) 429; $\Lambda(1.0 \times 10^{-2}\ M$ in $C_6H_5NO_2$ soln at 25°) = 0.12 $ohm^{-1}\,cm^2\,mol^{-1}$.

Chlorobis(1-phenyl-1,3-butanedionato)-π-cyclopentadienylzirconium.—Zirconocene dichloride (1.00 g, 3.42 mmol) and benzoylacetone (1.10 g, 6.78 mmol) were placed in a 500-ml sidearm erlenmeyer flask equipped with a graduated dropping funnel containing benzene. The flask was evacuated, and 50 ml of benzene was carefully admitted through the dropping funnel. The reaction mixture was stirred at 70° for 12 hr. During the first few hours, the flask was periodically opened to a vacuum pump to reduce the concentration of volatile products. The solvent was removed under vacuum, leaving a foamlike solid residue. Recrystallization of the solid from benzene–hexane gave 1.52 g (86%) of yellow crystals, which were dried *in vacuo* at room temperature; mp 186.5–188.5°; lit.[14] mp 184–185.5°. *Anal.* Calcd for $(\pi\text{-}C_5H_5)Zr(C_{10}H_9O_2)_2Cl$: C, 58.40; H, 4.51; mol wt 477. Found: C, 58.47; H, 4.60; mol wt (C_6H_6) 454.

Chlorobis(2,4-pentanedionato)-π-cyclopentadienylhafnium.—The compound was prepared in 92% yield by reaction of hafnocene dichloride and acetylacetone. All operations were identical with those described above for the zirconium analog, except that the reaction time was 30 min. The product was recrystallized from benzene–hexane and dried *in vacuo* at room temperature; mp 181–182°; lit.[15] mp 176–179°. *Anal.* Calcd for $(\pi\text{-}C_5H_5)Hf(C_5H_7O_2)_2Cl$: C, 37.75; H, 3.98; mol wt 514. Found: C, 37.94; H, 4.03; mol wt (C_6H_6) 517; $\Lambda(1.0 \times 10^{-2}\ M$ in $C_6H_5NO_2$ soln at 25°) < 0.008 $ohm^{-1}\,cm^2\,mol^{-1}$.

Physical Measurements.—Molecular weights were determined cryoscopically by using benzil as a calibrant. Conductivity measurements were made with a Beckman Model RC 16B2 conductivity bridge. The conductivity cell was equipped with bright platinum electrodes and was calibrated with a standard aqueous potassium chloride solution. The nitrobenzene used in the conductivity measurements was purified and dried as described previously.[16] Variable-temperature proton nmr spectra were recorded on a Varian A56/60D analytical spectrometer equipped with a Varian V-6040 variable-temperature controller. Methods used for determining the probe temperature and for calibrating the magnetic field sweep have been described elsewhere.[9] All solutions used in the nmr studies were prepared under anhydrous conditions in benzene dried over lithium aluminum hydride. X-Ray powder diffraction patterns were obtained with a Guinier camera with a radius of 39.94 mm and Cu Kα radiation (λ 1.54051 Å). Platinum (a = 3.924 Å) was used as an internal reference in order to correct for film shrinkage. Interplanar spacings for the acetylacetonate complexes are given in Table I.

Determination of Mean Lifetimes.—Mean lifetimes for the two nonequivalent –CH= groups on the acetylacetonate ligands in the complexes were determined by comparing observed nmr line shape parameters with those obtained from spectra calculated for various trial values of mean lifetimes. Above the coalescence temperature the full line widths at half-maximum amplitude were compared. Below coalescence the ratios of the maximum to central minimum amplitudes and the frequency separation between the resonance components were used in comparing the observed and calculated spectra. At each temperature at least four, and normally five, spectral copies were recorded, and the line shape parameters were averaged. The methods used to obtain the calculated nmr spectra have been described in detail in a previous study of related $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes.[9]

TABLE I

X-RAY POWDER DIFFRACTION DATA[a]

$(\pi\text{-}C_5H_5)Zr(acac)_2Cl$		$(\pi\text{-}C_5H_5)Hf(acac)_2Cl$		$(\pi\text{-}C_5H_5)Zr(acac)_2Br$	
9.89 s	3.77 w	9.88 s	3.77 w	9.93 s	3.76 w
7.84 s	3.71 vw	7.82 s	3.72 vw	7.81 s	...
7.45 m	3.63 vw	7.47 m	3.68 vw	7.62 m	...
7.05 s	3.56 m	7.08 s	3.57 m	7.30 s	3.63 m
6.66 s	3.52 vw	6.66 s	3.51 vw	6.68 s	...
6.41 vs	3.28 m	6.43 vs	3.28 m	6.42 vs	3.30 m
5.88 s	3.17 w	5.89 s	3.18 w	5.94 s	3.21 w
5.74 w	3.09 w	5.74 w	3.10 w	...	3.12 w
5.23 w	2.93 vw	5.24 w	...	5.33 w	...
4.81 m	2.85 vw	4.83 m	2.87 vw	4.83 m	2.82 vw
4.44 w	2.79 w	4.43 w	2.79 w	4.46 w	2.79 w
4.26 w	...	4.26 w	2.77 vw	4.33 w	...
4.07 m	2.76 vw	4.09 m	2.75 vw	4.17 w	...
4.02 w	2.70 w	4.02 w	2.71 w	4.11 w	2.70 w
...	2.64 w	3.98 vw	2.65 w	4.02 w	2.64 w
				3.88 w	

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

All of the complexes exhibited an appreciable linear temperature dependence for $\delta\nu$, the frequency separation between the resonance components in absence of exchange. Therefore, values of $\delta\nu$ at temperatures in the region of exchange were obtained by linear least-squares extrapolation of the temperature dependence in the region of slow exchange. Also, the complexes each exhibited unequal –CH= line widths in the region of slow exchange. For $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ in benzene in the slow exchange region, the observed widths (Hz) of the low- and high-field –CH= lines, respectively, were as follows: 0.52, 0.38 (19.8°); 0.49, 0.41 (29.8°); 0.50, 0.30 (35.8°); 0.50, 0.30 (41.5°); 0.54, 0.36 (52.0°), where each width quoted is an average of three spectral measurements. Thus the observed relaxation times for the two –CH= protons in the two nonequivalent environments are unequal. The larger width for the low-field –CH= resonance may be due to some spin–spin coupling with the methyl protons on the acetylacetonate ligand. We were unable to determine if any differences in the CH_3 line widths due to coupling occur in the region of slow exchange, because of the extensive overlapping of two of the four CH_3 lines. The widths of the two resolvable CH_3 lines, however, were equal. In the region of intermediate exchange below the coalescence temperature of $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$, the two –CH= resonances coalesced almost symmetrically, indicating that the relaxation times became nearly equivalent or that any coupling has been collapsed. In the limit of very fast exchange (111–117°) the width of the time-averaged –CH= line was 0.45 ± 0.05 Hz, which is in agreement with the average width of the two –CH= lines in the region of slow exchange. Therefore, the relaxation time corresponding to the line width of 0.45 Hz (T_2 = 0.71 sec) was used in the calculation of spectra for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ in the region of intermediate exchange. Results analogous to those described for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ were obtained for the –CH= resonances of $(\pi\text{-}C_5H_5)Hf(acac)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(acac)_2Br$ in the regions of slow, intermediate, and fast exchange, except that for the latter compound the width of the time-averaged –CH= line in the very fast-exchange limit was 0.50 ± 0.05 Hz (T_2 = 0.64 sec).

Results and Discussion

In the solid state $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ possesses a stereochemistry based on a D_{2d} dodecahedral coordination polyhedron in which the $\pi\text{-}C_5H_5$ ring effectively occupies a triangular face, chlorine is positioned at a vertex adjacent to the ring, and the two diketonate ligands span equivalent polyhedral edges (1).[17] A more readily visualized but less accurate approximation of the stereochemistry can be based on an octahedron in which the center of the $\pi\text{-}C_5H_5$ ring is placed at one vertex with the chlorine atom positioned cis to the ring

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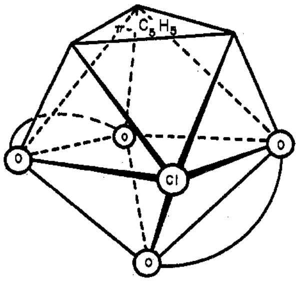
[15] M. Kh. Minacheva, E. M. Brainina, and R. Kh. Friedlina, *Dokl. Chem.*, **173**, 282 (1966); *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **173**, 581 (1966).

[16] T. J. Pinnavaia, L. J. Matienzo, and Y. A. Peters, *Inorg. Chem.*, **9**, 993 (1970).

[17] J. J. Stezowski and H. A. Eick, *J. Amer. Chem. Soc.*, **91**, 2890 (1969). The crystallographic and molecular parameters have been confirmed by V. S. Sudarikov, N. G. Bokii, V. I. Kulishov, and U. T. Struchkov, *Zh. Strukt. Khim.*, 941 (1969).

and the donor oxygens of the diketonate ligands at the remaining coordination positions (2). In solution the compound is a monomer and a very weak electrolyte. The proton nmr spectrum of the complex in benzene has been shown[5] to be consistent with the stereochemistry found in the solid state. At room temperature four equally intense acetylacetonate methyl proton resonances and two –CH= resonances of equal integral intensity are observed. The π-C_5H_5 ring, which presumably undergoes rapid rotation about the metal–ring axis, gives rise to a single, sharp resonance line. (π-C_5H_5)Hf(acac)$_2$Cl and (π-C_5H_5)Zr(acac)$_2$Br are also monomers and weak electrolytes in solution and give nmr spectra which are qualitatively similar to the spectrum of (π-C_5H_5)Zr(acac)$_2$Cl. The proton chemical shifts for all three compounds in benzene are given in Table II.



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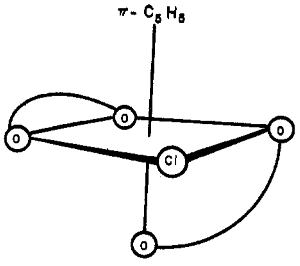

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TABLE II
PROTON CHEMICAL SHIFTS FOR (π-C_5H_5)M(acac)$_2$X COMPLEXES[a]

Compd	CH_3	-CH=	C_5H_5
(π-C_5H_5)Zr(acac)$_2$Cl	8.45[b]	4.82	3.50
	8.38	4.75	
	8.37		
	8.31		
(π-C_5H_5)Hf(acac)$_2$Cl	8.44	4.83	3.56
	8.39	4.79	
	8.37		
	8.30		
(π-C_5H_5)Zr(acac)$_2$Br	8.47	4.83	3.45
	8.39	4.73	
	8.37		
	8.33		

[a] In benzene at ambient temperature (36–40°); concentration is 7.5 g/100 ml of solvent. [b] All shifts are expressed as τ values with 1% TMS as an internal reference.

The nmr results suggest that each compound exists in solution as a single stereoisomer with C_1 symmetry. Although X-ray powder diffraction patterns (*cf.* Table I) indicate that (π-C_5H_5)Zr(acac)$_2$Cl is isomorphous with (π-C_5H_5)Hf(acac)$_2$Cl and probably isomorphous with (π-C_5H_5)Zr(acac)$_2$Br, the three compounds need not be isostructural in solution. It has been previously pointed out[5] that a dodecahedral or a square-antiprismatic coordination polyhedron can give rise to a variety of stereoisomers with C_1 symmetry, depending on which set of polyhedral edges are occupied by the diketonate ligands and, in the case of the dodecahedron, which one of the two types of triangular faces is effectively occupied by the π-C_5H_5 group. Since it is not possible to determine which C_1 stereoisomers are present for the complexes of interest here, it would appear that the cis octahedral formalism suggested by 2 adequately describes their gross stereochemical features. However, it must be emphasized such a formalism cannot be expected to apply to related systems. For example, (π-C_5H_5)Ti(hfac)$_2$Cl, where hfac is hexafluoroacetylacetonate, has been reported[6] to exist in solution as *two* C_1 stereoisomers; the octahedral formalism predicts only one C_1 isomer.

As the temperature of a benzene solution of (π-C_5H_5)Zr(acac)$_2$Cl is increased above *ca.* 70°, the four methyl lines broaden and coalesce into one symmetrical broad line, which then sharpens as the temperature is increased further. Simultaneously, the two –CH= lines broaden and coalesce, but the C_5H_5 resonance remains sharp. The temperature dependence of the CH_3 and –CH= lines in the range 40–105° is illustrated in Figure 1. A similar line-broadening behavior is observed for the acetylacetonate methyl and –CH= resonance lines of (π-C_5H_5)Hf(acac)$_2$Cl and (π-C_5H_5)Zr(acac)$_2$Br. In each case the line broadening results from a stereochemical rearrangement process which interconverts the two nonequivalent acetylacetonate ligands present in the molecule. Mean lifetimes for the nonequivalent acetylacetonate ligands were determined from the temperature dependence of the –CH= resonance lines (*cf.* Experimental Section). Nmr line shape parameters for the –CH= resonances of (π-C_5H_5)Zr(acac)$_2$Cl in benzene are presented in Table III along with the determined values of the quantity τ, where τ is related to the mean lifetimes τ_A and τ_B of the nonequivalent –CH= groups by $\tau = \tau_A/2 = \tau_B/2$. Similar data for ($\pi$-$C_5H_5$)Hf(acac)$_2$Cl and ($\pi$-$C_5H_5$)Zr(acac)$_2$Br are summarized in Tables IV and V, respectively.

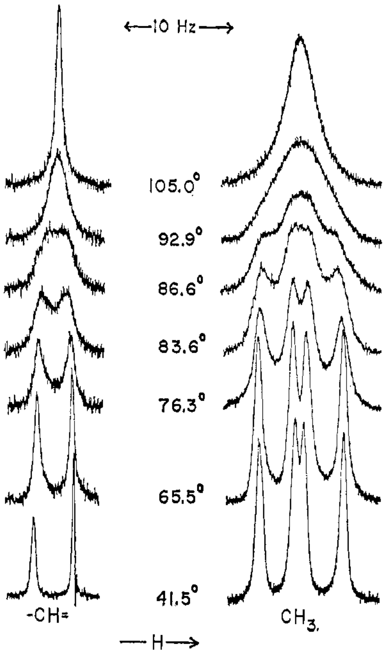

Figure 1.—Temperature dependence of the acetylacetonate methyl and –CH= proton resonance lines (60 MHz) for (π-C_5H_5)Zr(acac)$_2$Cl in benzene. Concentration is 7.5 g/100 ml of solvent.

No change was observed in the mean lifetimes of the –CH= groups of (π-C_5H_5)Zr(acac)$_2$Cl at 83.6 and 85.8° upon decreasing the concentration of the complex by a factor of 2, indicating that the rate of exchange is first order in complex. At temperatures near 110°, where

TABLE III

PROTON NMR LINE SHAPE PARAMETERS AND VALUES OF τ FOR THE NONEQUIVALENT –CH= GROUPS IN $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$[a]

Temp, °C	$\delta\nu$,[b] Hz	$\delta\nu_0$,[c] Hz	r[d]	W^*,[e] Hz	τ, sec
76.3	3.01[f]	2.92	3.00	. . .	0.261[g]
76.8	3.00	2.80	2.20	. . .	0.202
79.6	2.94	2.50	1.55	. . .	0.151
81.1	2.91	2.30	1.41	. . .	0.140
83.0	2.87	1.90	1.20	. . .	0.121
83.6	2.86	2.23	1.36	. . .	0.138
84.9	2.84	1.70	1.06	. . .	0.103
85.8	2.82	. . .	~1.00	3.60	0.104
89.4	2.75	. . .	. . .	2.88	0.0800
92.7	2.68	. . .	. . .	1.74	0.0493
92.9	2.68	. . .	. . .	1.96	0.0560
96.0	2.61	. . .	. . .	1.41	0.0400
99.3	2.55	. . .	. . .	1.08	0.0290
100.5	2.52	. . .	. . .	0.98	0.0255

[a] In benzene; concentration is 7.5 g/100 ml of solvent. [b] Frequency separation between the resonance components in absence of exchange. [c] Observed frequency separation. [d] Ratio of the maximum to central minimum signal intensities below coalescence. [e] Full line width at half-maximum amplitude for the time-averaged resonance above coalescence. [f] All values of $\delta\nu$ were obtained by linear least-squares extrapolation of the temperature dependence of $\delta\nu$ in the region of slow exchange (19.8–67.8°). [g] All values of τ were computed by taking $T_2 = 0.710$ sec.

TABLE IV

PROTON NMR LINE SHAPE PARAMETERS[a] AND VALUES OF τ FOR THE NONEQUIVALENT –CH= GROUPS IN $(\pi\text{-}C_5H_5)Hf(acac)_2Cl$[b]

Temp, °C	$\delta\nu$, Hz	$\delta\nu_0$, Hz	r	W^*, Hz	τ, sec
84.8	2.58[c]	1.95	2.87	. . .	0.385[d]
87.1	2.52	1.90	2.67	. . .	0.358
90.5	2.45	1.50	1.85	. . .	0.251
93.2	2.39	1.35	1.33	. . .	0.177
97.0	2.30	. . .	1.00	2.48	0.136
101.8	2.19	. . .	. . .	2.11	0.0805
107.1	2.07	. . .	. . .	1.83	0.0685
111.1	1.98	. . .	. . .	1.45	0.0515
116.5	1.86	. . .	. . .	0.95	0.0270
121.2	1.75	. . .	. . .	0.70	0.0148

[a] Definitions of all parameters are the same as those given in Table III. [b] In benzene, concentration is 7.5 g/100 ml of solvent. [c] All values of $\delta\nu$ were obtained by linear least-squares extrapolation of the temperature dependence of $\delta\nu$ in the region of slow exchange (41.7–76.9°). [d] All values of τ were computed by taking $T_2 = 0.710$ sec.

TABLE V

PROTON NMR LINE SHAPE PARAMETERS[a] AND VALUES OF τ FOR THE NONEQUIVALENT –CH= GROUPS IN $(\pi\text{-}C_5H_5)Zr(acac)_2Br$[b]

Temp, °C	$\delta\nu$, Hz	$\delta\nu_0$, Hz	r	W^*, Hz	τ, sec
86.3	4.45[c]	3.75	1.85	. . .	0.106[d]
88.2	4.39	3.40	1.67	. . .	0.100
88.5	4.38	3.33	1.49	. . .	0.0914
92.1	4.26	2.80	1.26	. . .	0.0764
93.7	4.20	. . .	1.05	. . .	0.0700
94.6	4.17	. . .	1.08	. . .	0.0700
95.9	4.13	. . .	1.00	4.45	0.0531
96.1	4.12	. . .	. . .	4.16	0.0547
99.4	4.01	. . .	. . .	3.14	0.0418
99.7	4.00	. . .	. . .	3.13	0.0418
103.7	3.86	. . .	. . .	2.16	0.0309
103.9	3.85	. . .	. . .	2.15	0.0308
104.7	3.82	. . .	. . .	1.67	0.0232
107.6	3.72	. . .	. . .	1.55	0.0224
109.7	3.66	. . .	. . .	1.29	0.0179
111.2	3.61	. . .	. . .	1.18	0.0159
113.7	3.52	. . .	. . .	1.00	0.0124
115.1	3.47	. . .	. . .	0.97	0.0121
116.1	3.44	. . .	. . .	0.85	0.00900

[a] Definition of all parameters are the same as those given in Table III. [b] In benzene; concentration is 7.5 g/100 ml of solvent. [c] All values of $\delta\nu$ were obtained by linear least-squares extrapolation of the temperature dependence of $\delta\nu$ in the region of slow exchange (38.1–66.0°). [d] All values of τ were computed by taking $T_2 = 0.640$.

the stereochemical rearrangement process is fast, a benzene solution containing equimolar amounts of $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ and free acetylacetone showed no broadening of the –CH= resonance of either the complex or the free ligand. This latter result indicates that exchange between coordinated ligand and added free ligand does not accompany the rearrangement process. It must be noted, however, that after the solution of complex and free ligand had aged several minutes at 110°, broadening of the –CH= resonance of the free ligand did occur, but the –CH= resonance of the complex remained sharp. The broadening of the free ligand line may have resulted from the formation of trace amounts of $(\pi\text{-}C_5H_5)Zr(acac)_3$[18] and subsequent ligand exchange between this latter complex and free ligand. Rapid intermolecular ligand exchange is known to occur between $(\pi\text{-}C_5H_5)Zr(hfac)_3$ and free hexafluoroacetylacetone at temperatures above 100°.[9]

Arrhenius activation parameters for the exchange processes were determined in the usual way from the slopes and intercepts of log k *vs.* $1/T$ plots, where k, the first-order rate constant, is equal to $(2\tau)^{-1}$. These activation parameters are summarized in Table VI along with extrapolated values of k and calculated values of $\Delta S^{\ddagger}$ at 25°. The activation parameters for $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ and the corresponding bromine analog are rather insensitive to uncertainties in the relaxation time (T_2) used in the calculation of mean lifetimes. In the case of $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$, a reasonable uncertainty of 0.07 sec in T_2 propagates systematic errors in E_a and $\Delta S^{\ddagger}_{25°}$ of only 1.3 kcal/mol and 3.5 eu, respectively; still smaller systematic errors are generated for the bromine derivative. Because of the small frequency separation between the resonance components in absence of exchange for $(\pi\text{-}C_5H_5)Hf(acac)_2Cl$, an uncertainty of 0.07 sec in T_2 generates a 4.2 kcal/mol error in E_a and a 11.3 eu error in $\Delta S^{\ddagger}_{25°}$ for this latter complex. Thus the errors in the activation parameters for $(\pi\text{-}C_5H_5)Hf(acac)_2Cl$ should probably be regarded as being appreciably larger than the estimates of random error quoted in Table VI.

TABLE VI

KINETIC PARAMETERS FOR EXCHANGE OF NONEQUIVALENT –CH= GROUPS IN $(\pi\text{-}C_5H_5)M(acac)_2X$ COMPLEXES IN BENZENE

Complex	$k_{25°}$, sec^{-1}	E_a, kcal/mol	Log A	$\Delta S^{\ddagger}_{25°}$, eu
$(\pi\text{-}C_5H_5)Zr(acac)_2Cl$	6.8×10^{-3}[a]	23.1 ± 2.0[b]	14.77 ± 1.18	7.1 ± 5.4
$(\pi\text{-}C_5H_5)Hf(acac)_2Cl$	1.3×10^{-3}	24.2 ± 2.2	14.88 ± 1.26	7.5 ± 6.0
$(\pi\text{-}C_5H_5)Zr(acac)_2Br$	6.1×10^{-3}	22.8 ± 1.8	14.47 ± 1.05	5.7 ± 4.8

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

It is also of interest in this study to investigate the proton nmr spectrum of the benzoylacetonate derivative $(\pi\text{-}C_5H_5)Zr(bzac)_2Cl$. Because of the asymmetry of the diketonate ligand, this complex should give rise to four geometric isomers in which the chlorine atom is positioned cis to the C_5H_5. The existence of all four isomers in benzene was confirmed by the presence of four sets of two equally intense methyl proton nmr

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(18) This complex has been isolated from benzene as an oil with the composition $(\pi\text{-}C_5H_5)Zr(acac)_3 \cdot C_6H_6$: E. M. Brainina, E. I. Mortikova, L. A. Petrashkevich, and R. Kh. Freidlina, *Dokl. Chem.*, **169**, 681 (1966); *Dokl. Akad. Nauk SSSR, Ser. Khim.*, **169**, 335 (1966).

lines at room temperature. At *ca.* 70° the eight methyl resonances begin to broaden and, as the temperature is increased further, the lines merge into a single sharp line. This latter result indicates that the interconversion of the four geometric isomers accompanies the interchange of the two nonequivalent β-diketonate ligands in each isomer.

A mechanism for the stereochemical rearrangement processes of the above complexes cannot be established unequivocally based on the present data. However, important mechanistic conclusions are possible. Since in the case of $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ the exchange of coordinated acetylacetonate and an added amount of free acetylacetone does not accompany the rearrangement process in the region of fast exchange, a mechanism involving complete dissociation of a diketonate ligand can be eliminated. Also, it is unlikely that a bis(β-diketonato)cyclopentadienylmetal cation is formed as an intermediate in the stereochemical rearrangement processes. The difference in the activation energies for dissociation of halogen from $(\pi\text{-}C_5H_5)Zr(acac)_2Cl$ and $(\pi\text{-}C_5H_5)Zr(acac)_2Br$ should be larger than the observed difference of 0.3 ± 2.7 kcal/mol. For the anhydrous zirconium tetrahalides, for example, the difference in mean thermochemical Zr–Cl and Zr–Br bond energies is 15.5 kcal/mol.[19] Furthermore, the activation energies for the $(\pi\text{-}C_5H_5)Zr(acac)_2X$ complexes are comparable in magnitude to those for the intramolecular interchange of nonequivalent terminal groups on the equatorial ligands of certain "pentagonal-bipyramidal" $(\pi\text{-}C_5H_5)Zr(dik)_3$ complexes in which no halogen ligands are present.[9] Thus, an intramolecular mechanism involving either a twisting process or rupture of one diketonate oxygen–metal bond must operate.

One plausible intramolecular bond rupture mechanism, for example, involves the formation of a symmetric eight-coordinate intermediate as shown in Figure 2. The intermediate is readily envisioned in terms of the octahedral formalism by placing the halogen atom trans to the center of the $\pi\text{-}C_5H_5$ ring. In the case of the acetylacetonate complexes, the formation of such an intermediate would account for the fact that all four nonequivalent terminal methyl group environments are averaged upon ligand interchange, because rupture of any one of the four metal–oxygen bonds in the intermediate can occur with equal probability when it returns to the ground state. Formation of similar trans intermediates for $(\pi\text{-}C_5H_5)Zr(bzac)_2Cl$ would also account for the random interchange of all nonequivalent methyl group environments among the four geometric isomers of the complex if it is assumed that ruptures of bonds to the benzoyl and acetyl oxygen atoms on the diketonate ligand occur with nearly equal probability.

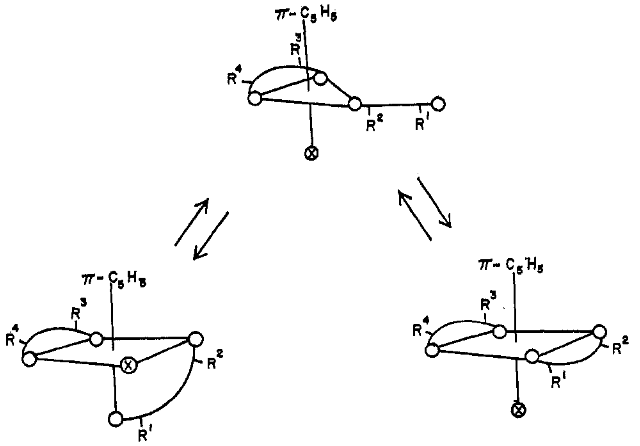

Figure 2.—Formation of a symmetric eight-coordinate $(\pi\text{-}C_5H_5)M(dik)_2X$ intermediate *via* rupture of one coordinate metal–oxygen bond. The octahedral formalism is used for convenience to represent the gross stereochemical features of the ground state and the intermediate. Superscripts label the terminal groups on the diketonate ligands.

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[19] Calculated from the enthalpy data in "JANAF Thermochemical Tables," compiled by the Dow Chemical Co., Midland, Mich., 1960.