

Figure 2. Iodine pentafluoride molecule. The dimensions are a weighted average over all three crystallographic types present in unit cell.

tween the ligands of neighboring molecules and the I atom of a given molecule. Such polar contacts do indeed exist in the IF_5 structure and the pertinent distances and angles are summarized in Table II. If it is assumed that the I-lone pair axis is directed in the opposite direction to the I-apex axis, then the angle between an attracted F atom and the lone pair axis is given by the supplement of the angle between the attracted F atom and the I-apex axis.

The polar contacts fall into two groups. The first which we call primary polar contacts have a weighted-average distance of 3.01 (6) Å and make a weighted-average angle of 36.4 (3.5)° with the I-lone pair axis. The secondary contacts have a weighted average distance of 3.25 (2) Å and a weighted-average angle of 42.6 (7.8)° with the I-lone pair axis. Given the shape of the molecules and their relative orientations in space the secondary contacts would appear to be merely a geometrical consequence of the formation of the primary contacts.

The environment around each crystallographic type of

molecule is quite distinct. The I1 molecule makes primary contacts with four I3 molecules and secondary contacts with two I2 molecules. The I2 molecule makes primary contacts with two I3 molecules and secondary contacts with one I1, one I2, and one I3 molecule. The I3 molecule makes primary contacts with two I1 and two I2 molecules and secondary contacts with one I2 and two I3 molecules. The total pattern of primary contacts is sufficient to define the crystal structure as a single array extended throughout three-dimensional space.

Referring again to Figure 1, the extended array may be regarded as based on a distortion of face-centered cubic packing. If, for the moment, each molecule is regarded as a simple sphere, the (204) and (402) planes are the most densely occupied planes in projection and indeed these planes give rise to the largest structure factors among the diffraction measurements. Each iodine atom has twelve iodine neighbors arranged approximately on a face-centered sublattice. The packing is quite compact as indicated by the intermolecular, nonpolar fluorine to fluorine distances in Table II.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or a microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1071.

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Metal-Centered Rearrangements of Zirconium β -Diketonates. Evidence for Twisting Modes of Activation

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Some key derivatives in a series of zirconium β -diketonates of the types $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dik})_2\text{Cl}$ and $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dik})_3$, along with an example of a new cationic species $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dik})_2^+$, have been prepared, and their rates of metal-centered rearrangement have been determined by nmr methods. The labilities of the molecular compounds have been compared with those of related derivatives in which the pentahapto C_5H_5 group has been replaced by a halogen. Significant relationships between structure and lability exist which provide a basis for favoring twisting over bond-rupture modes of activation. The methyl proton line-broadening patterns associated with ligand interchange in $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dpm})_2\text{Cl}$ and $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{acac})_2\text{Cl}$ ($\text{dpm} = (t\text{-C}_4\text{H}_9)\text{COCHCO}(t\text{-C}_4\text{H}_9)$ and $\text{acac} = \text{CH}_3\text{COCHCOCH}_3$) were analyzed in terms of specific twist mechanisms. Although the process is nonrandom, no simple, single-step facial twist mechanism operates. A reasonable combination of facial and digonal twists, however, is consistent with the observed line shapes.

It is generally recognized that metal chelates may undergo intramolecular rearrangements either by bond rupture processes in which one metal-chelate bond breaks to give an activated complex of reduced coordination number or by twisting processes in which the bonds rotate but do not open. Distinguishing between these two modes of activation is a challenging problem, as evidenced by the relatively few examples for which a mechanistic assignment has been possible.¹⁻³ Recently, dynamic nmr studies of the inversion of certain "fast" trigonal-antiprismatic

tropolonates^{4,5} and dithiocarbamates^{6,7} have led to an incisive

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identification of mechanism (twist). A similar approach to the rearrangements of fast β -diketonates of aluminum and gallium resulted in the exclusion of certain pathways but did not permit an unequivocal distinction between twisting and bond rupture.⁸ The only β -diketonates for which the rearrangement mechanism is known with reasonable certainty are those of Co(III) (bond rupture).^{9,10}

No attempt has yet been made to distinguish between twisting and bond rupture modes of activation for a series of fast metal chelates based on a knowledge of the structural factors which influence their relative labilities, perhaps, because of the lack of suitably related derivatives. Zirconium β -diketonates of the type $Zr(dik)_2X_2$, $Zr(dik)_3X$, $(h^5-C_5H_5)Zr(dik)_2X$ ($X = Cl, Br$), and $(h^5-C_5H_5)Zr(dik)_3$ seem to be uniquely suited for this purpose. The present work reports an nmr kinetic study of some key *pentahaptocyclopentadienyl*-zirconium diketonates and a new cationic species of the type $(h^5-C_5H_5)Zr(dik)_2^+$. Several relationships between structure and lability are described which provide a basis for favoring twisting over bond rupture processes.

Structures and Rearrangement Processes. $(h^5-C_5H_5)Zr(dik)_2X$. Nmr studies¹¹⁻¹⁴ of several $(h^5-C_5H_5)Zr(dik)_2X$ complexes and two independent X-ray structure determinations^{15,16} of a representative derivative, $(h^5-C_5H_5)Zr(acac)_2Cl$,¹⁷ have shown that the stereochemistry of the compounds is most simply described in terms of an octahedral coordination polyhedron in which the center of the C_5H_5 ring and the halogen atom occupy cis vertices^{18,19} (see Figure 1a). The complexes all undergo a first-order rearrangement process which interchanges the diketonate rings and leads to concomitant collapse of their $-CH=$ and R group nmr signals. The temperature dependence of the $-CH=$ and $t-C_4H_9$ proton resonances for $(h^5-C_5H_5)Zr(dpm)_2Cl$ in benzene is shown in Figure 2.

It has been shown that the rearrangement of $(h^5-C_5H_5)Zr(acac)_2Cl$ does not involve complete dissociation of an acac ligand.¹³ Also, it has been argued that the process does not involve halide dissociation, because the bromide derivative exhibited an identical set of activation parameters.

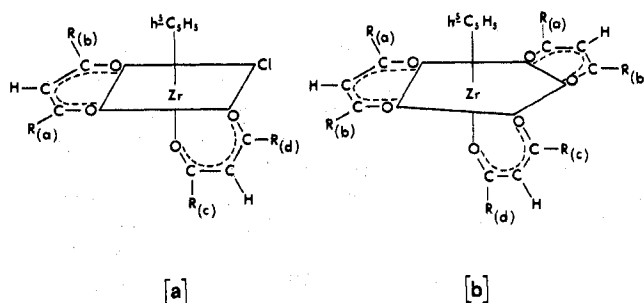


Figure 1. (a) Octahedral and (b) pentagonal-bipyramidal representations of the structures of $(h^5-C_5H_5)Zr(dik)_2X$ and $(h^5-C_5H_5)Zr(dik)_3$ complexes, respectively. Superscripts on R groups identify non-equivalent magnetic environments.

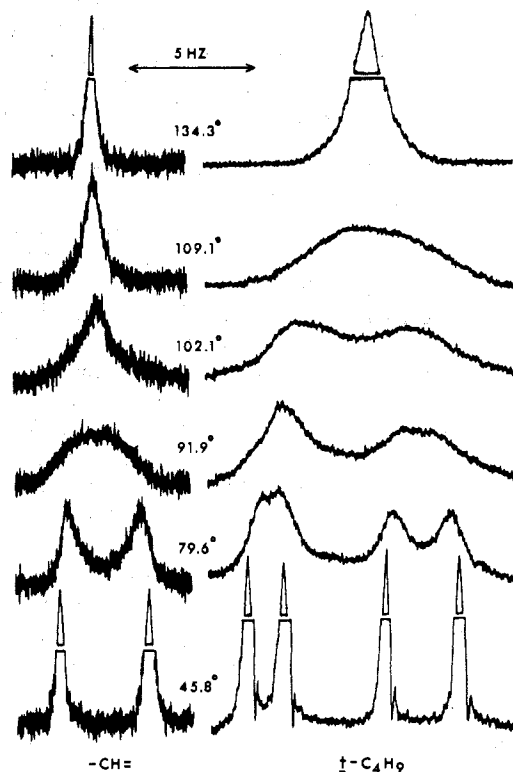


Figure 2. Temperature dependence of the $-CH=$ and $t-C_4H_9$ proton resonance lines of $(h^5-C_5H_5)Zr(dpm)_2Cl$ in benzene. Concentration is 11.0 g/100 ml of solvent.

To ensure that halide exchange is much slower than ligand interchange, the nmr spectrum of an equimolar mixture of the chloride and bromide complexes was observed in benzene at 80° where the rearrangements are sufficiently fast to broaden markedly their $-CH=$ and CH_3 resonances. The C_5H_5 resonances, however, remain sharp under these conditions. Based on the chemical shift difference for the C_5H_5 resonances, the rate of halide exchange was estimated to be at least 20 times lower than the rates of rearrangement. Therefore, the rearrangements are indeed intramolecular.

$(h^5-C_5H_5)Zr(dik)_3$. The stereochemistry of $(h^5-C_5H_5)Zr(dik)_3$ complexes¹⁹⁻²¹ is based on a pentagonal bipyramid in which the center of the C_5H_5 ring occupies an axial vertex (*cf.* Figure 1b). In solution, they undergo two types of first order rearrangements: a low-temperature process (LTP) that interchanges the R groups on the ligands spanning the equatorial edges and a higher temperature process (HTP)

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(17) Ligand abbreviations used in this work are defined as follows: acac, acetylacetonate; dpm, dipivaloylmethanate; hfac, hexafluoroacetylacetonate; bzac, benzoylacetonate.

(18) An alternative stereochemical description has been proposed^{11,13,15} in which the C_5H_5 ring is regarded as occupying a face of a D_{2d} dodecahedron. The dodecahedral formalism would appear to have special merit in describing the structure of a related titanium complex, $(h^5-C_5H_5)Ti(hfac)_2Cl$, which exhibits two isomers of C_1 symmetry.¹⁹ Since the $(h^5-C_5H_5)Zr(dik)_2Cl$ complexes of interest in the present work exhibit only one C_1 isomer, the octahedral formalism is adequate.

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in which the unique ligand spanning an axial-equatorial edge and the two equatorial ligands are interchanged. As can be seen from the temperature dependence of the $-\text{CH}=\text{}$ and CH_3 lines of $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{acac})_3$ in Figure 3, the fast-exchange region of the LTP is reached well below the temperature for the onset of the HTP. The thermal decomposition products which appear in the spectrum recorded at 127.6° persist when the solution is returned to room temperature. Varying the concentration of the impurities by altering the heating time at 127.6° caused no change in the line shapes for the LTP or HTP, indicating that they do not catalyze the rearrangement processes.

The line shapes for the LTP of $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{acac})_3$ are unaffected by a twofold increase in the concentration of the complex or the addition of an equimolar amount of free diketonate ligand. Therefore, the process is first order and an intramolecular mechanism operates. Analogous results have been obtained for the corresponding dpm and hfac derivatives.²¹ The HTP is also first order for all three derivatives, but for each complex some exchange of coordinated and free diketone accompanies the rearrangement in the fast-exchange limit. Attempts to determine rates of ligand exchange between $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{hfac})_3$ and $\text{H}(\text{hfac})$ at a temperature 35° above the coalescence temperature of the HTP were unsuccessful, because the exchange is catalyzed by thermal degradation products. It could be concluded, however, that the rate of exchange between equimolar amounts of free diketone and complex in a freshly prepared solution is initially about 10 times lower than the rate of rearrangement. Therefore, at least 90% of the HTP must occur *via* an intramolecular process.

$(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dik})_2^+$. The reaction of $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dpm})_2\text{Cl}$ and SbCl_5 in CH_3CN at 0° readily affords the crystalline solvate $[(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dpm})_2][\text{SbCl}_6]\cdot 2.5\text{CH}_3\text{CN}$. The ionic formulation of the compound is based in part on the presence of an ir absorption (345 cm^{-1}) in the region expected for SbCl_6^- ²² and a high molar conductivity value in nitrobenzene ($\Lambda_{25^\circ} = 20.8\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$, $c\ 2.51 \times 10^{-3}\text{ M}$) typical of a 1:1 electrolyte.²³ In CH_2Cl_2 solution at -55° , the compound exhibits two $-\text{CH}=\text{}$ resonances of equal intensity, three $t\text{-C}_4\text{H}_9$ resonances of relative intensity 1:2:1, and single C_5H_5 and CH_3CN lines. As the temperature is increased, the $-\text{CH}=\text{}$ and $t\text{-C}_4\text{H}_9$ lines broaden and merge into separate singlets, as illustrated in Figure 4. The C_5H_5 , $-\text{CH}=\text{}$, and $t\text{-C}_4\text{H}_9$ resonances are shifted substantially downfield relative to those for the molecular parent complex $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dpm})_2\text{Cl}$ by 0.16, 0.20, and 0.04 ppm, respectively. The $-\text{CH}=\text{}$ and $t\text{-C}_4\text{H}_9$ shifts are in accord with those previously observed for several related cationic diketonate complexes.²⁴

The nmr spectrum at -55° indicates that the simplest possible stereochemistry for $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dpm})_2^+$ is based on a trigonal bipyramid in which the center of C_5H_5 occupies an axial vertex. Some association of the cation and CH_3CN in CH_2Cl_2 solution is indicated by the fact that the CH_3CN resonance appears 0.09 ppm downfield from the position expected for free CH_3CN . However, the residence time of a CH_3CN molecule in the first coordination sphere of the cation must be much shorter than the preexchange lifetime of the nonequivalent diketonate ligands. The CH_3CN resonance remains sharp even at

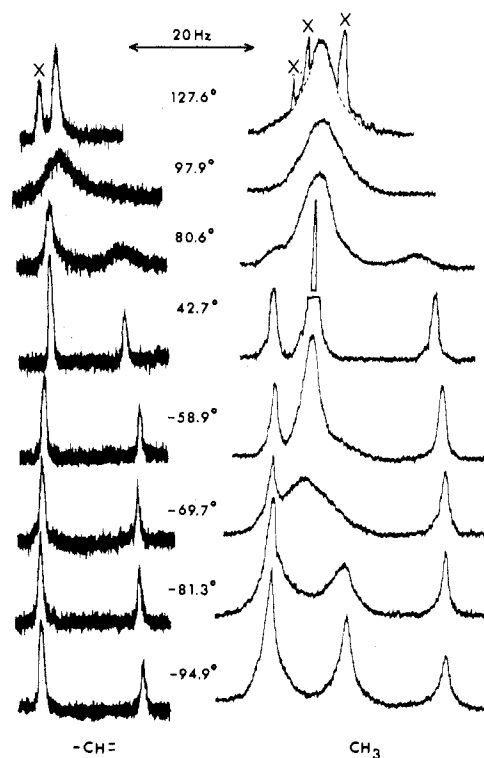


Figure 3. Temperature dependence of the $-\text{CH}=\text{}$ and CH_3 proton nmr lines for $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{acac})_3$. The low-temperature spectra (-58.9 to -94.9°) are in carbon disulfide solution; concentration is 0.22 M . At 42.7° and higher, the spectra are for a tetrachloroethylene solution; concentration, 0.32 M . The lines marked "X" are due to unidentified thermal decomposition products.

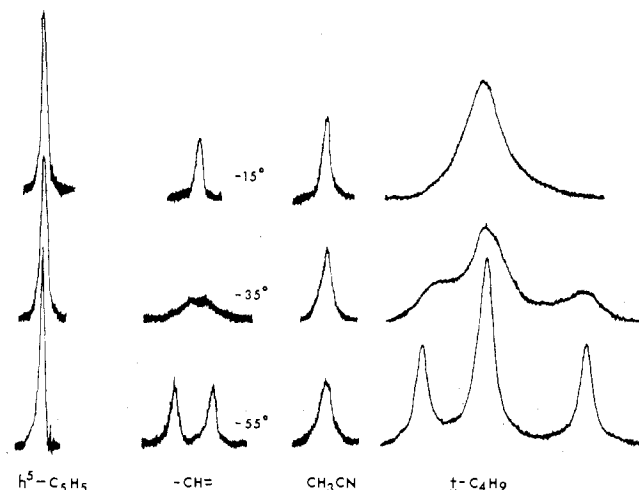


Figure 4. Proton nmr spectra for $[(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dpm})_2][\text{SbCl}_6]\cdot 2.5\text{CH}_3\text{CN}$ in dichloromethane.

-75° , and the addition of CH_3CN to the solution simply increases the intensity of the line and shifts it to higher field. Also, increasing the concentration of CH_3CN causes no change in the $-\text{CH}=\text{}$ and $t\text{-C}_4\text{H}_9$ line shapes in the region of exchange. Thus, even if one allows for the possibility of the cation being solvated by one CH_3CN molecule and possessing a structure in which chloride in $(h^5\text{-C}_5\text{H}_5)\text{Zr}(\text{dpm})_2\text{Cl}$ is replaced by CH_3CN , the nmr data would require that rapid intermolecular exchange of CH_3CN leads to environmental averaging of the $t\text{-C}_4\text{H}_9$ groups on the equatorial ligand but that the interchange of the two diketone rings occurs by a separate, higher energy, first-order process.

Kinetics. The first-order rate constant for interchange

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Table I. Activation Parameters for Metal-Centered Rearrangements of $(h^5-C_5H_5)Zr(dik)_2X$ and $(h^5-C_5H_5)Zr(dik)_3$ Complexes

Complex	Solvent	k_{25° , sec ⁻¹	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	E_a , kcal/mol	log A
Type of Rearrangement Process: Diketonate Ligand Interchange						
$(h^5-C_5H_5)Zr(dpm)_2Cl$	C_6H_6	2.0×10^{-2} ^a	18.8 ± 0.6 ^b	-3.3 ± 1.7	19.5 ± 0.6	12.60 ± 0.37
$(h^5-C_5H_5)Zr(acac)_2Cl^c$	C_6H_6	6.8×10^{-3}	22.5 ± 1.8	6.9 ± 5.0	23.1 ± 2.0	14.77 ± 1.18
$(h^5-C_5H_5)Zr(acac)_2Br^c$	C_6H_6	6.1×10^{-3}	21.7 ± 1.6	4.3 ± 4.2	22.8 ± 1.8	14.47 ± 1.05
$(h^5-C_5H_5)Zr(acac)_3$	C_2Cl_4	2.4×10^{-2}	20.4 ± 1.2	2.4 ± 3.0	21.1 ± 1.2	13.84 ± 0.74
$(h^5-C_5H_5)Zr(hfac)_3^c$	$[(CH_3)_2CH]_2O$	4.5×10^{-3}	25.5 ± 3.6	16.3 ± 9.6	26.4 ± 1.9	16.97 ± 1.06
Type of Rearrangement Process: Equatorial R Group Interchange						
$(h^5-C_5H_5)Zr(acac)_3$	CS_2	4.4×10^4	8.8 ± 0.4	-7.7 ± 2.0	9.2 ± 0.5	11.37 ± 0.50
$(h^5-C_5H_5)Zr(hfac)_3^c$	$[(CH_3)_2CH]_2O$	6.5×10^2	15.2 ± 0.5	5.2 ± 1.8	15.7 ± 0.5	14.38 ± 0.38
$(h^5-C_5H_5)Zr(dpm)_3^c$	$o-C_6H_4(CH_3)_2$	2.8×10^{-2}	20.7 ± 1.7	3.7 ± 4.9	21.3 ± 1.9	14.05 ± 1.19

^a All values of k are extrapolated values at 25°. ^b All errors are estimated at the 95% confidence level. ^c The activation parameters for these compounds are from data presented in ref 13 and 21.

of diketonate ligands in $(h^5-C_5H_5)Zr(dpm)_2^+$ was estimated from the Gutowsky-Holm equation to be 7.56 sec^{-1} at the coalescence temperature of the $-CH=$ resonances in CH_2Cl_2 (-35°). A more complete kinetic analysis was carried out for ligand interchange in $(h^5-C_5H_5)Zr(dpm)_2Cl$ based on the observed line shapes of the $-CH=$ resonances in the region of exchange. Values of the preexchange lifetime, τ , for the LTP and HTP of $(h^5-C_5H_5)Zr(acac)_3$ were determined from the shapes of the equatorial $-CH_3$ and $-CH=$ resonances, respectively. For the HTP the τ values are related to the first-order rate constant for the interchange equatorial \rightarrow unique ligand by $k = (3\tau)^{-1}$. For the reverse process of the unique \rightarrow equatorial ligands, $k = 2(3\tau)^{-1}$.

Activation parameters and extrapolated values of k at 25° for the rearrangements of $(h^5-C_5H_5)Zr(dpm)_2Cl$ and $(h^5-C_5H_5)Zr(acac)_3$ are compared in Table I with those previously reported for analogous derivatives. Considering first the rearrangements which lead to diketonate ligand interchange, one finds that for all of the $(h^5-C_5H_5)Zr(dik)_2X$ and $(h^5-C_5H_5)Zr(dik)_3$ complexes the values of k fall in the range 2.4×10^{-2} to $4.5 \times 10^{-3} \text{ sec}^{-1}$. Although the enthalpies differ by as much as $6.7 \pm 3.6 \text{ kcal/mol}$, the similarities in reactivity indicate that ligand interchange occurs by a common type of mechanism. Activation parameters are not available for ligand interchange in $(h^5-C_5H_5)Zr(dpm)_3$, but the first-order rate constant for this compound at its coalescence temperature (*ca.* 130°) is only 20 times slower than that for the hfac derivative at the same temperature. Thus, increasing the size of the terminal groups in the $(h^5-C_5H_5)Zr(dik)_3$ complexes may decrease the rate, but the effect is small. Increasing the steric requirement of terminal groups in the $(h^5-C_5H_5)Zr(dik)_2X$ complexes does not decrease the rate; in fact, the dpm complex is somewhat more labile than the acac derivative. Perhaps the most significant feature of the kinetic data for ligand interchange, however, is that all of the neutral $(h^5-C_5H_5)Zr(dik)_2X$ and $(h^5-C_5H_5)Zr(dik)_3$ complexes are more rigid than the cationic species $(h^5-C_5H_5)Zr(dpm)_2^+$. At -35° , the extrapolated value of k for $(h^5-C_5H_5)Zr(dpm)_2Cl$ is 10^6 times smaller than that for the cation.

In marked contrast to the ligand-interchange rearrangements of the $(h^5-C_5H_5)Zr(dik)_3$ complexes, the more facile process of interchanging the equatorial terminal groups in these compounds is highly dependent on the bulk of the groups. On passing from the acac to hfac and dpm derivatives the rate decreases by a factor of 10^4 and 10^6 , respectively. The differences in lability are due to enthalpy effects, $\Delta(\Delta H^\ddagger)$, being $11.9 \pm 1.8 \text{ kcal/mol}$ for the dpm and acac analogs. Solvation effects cannot be responsible for the enthalpy differences. It was previously shown²¹ that the

activation parameters for the LTP of $(h^5-C_5H_5)Zr(dpm)_3$ in toluene, *o*-xylene, and diisopropyl ether are equal within experimental error.

Mechanisms. Considerable insight into the mode of activation of zirconium β -diketonates is provided by a comparison of the relative labilities of the $h^5-C_5H_5$ derivatives and discrete six- and seven-coordinate analogs of the types $Zr(dik)_2Cl_2$ and $Zr(dik)_3Cl$. The $Zr(dik)_2Cl_2$ complexes have been assigned cis octahedral structures on the basis of their vibrational spectra,²⁵ and $Zr(acac)_3Cl$ has been recently shown to possess a distorted pentagonal-bipyramidal structure with Cl at an axial vertex.²⁶ Thus these compounds are "isostructural" with $(h^5-C_5H_5)Zr(dik)_2X$ and $(h^5-C_5H_5)Zr(dik)_3$ complexes insofar as C_5H_5 has been replaced by a chlorine atom. The replacement of C_5H_5 by chlorine, however, leads to a dramatic decrease in the rigidity of the first coordination sphere of the metal ion. $Zr(acac)_2Cl_2$ and $Zr(acac)_3Cl$, for example, exhibit time-averaged spectra even at -130° , where k for ligand interchange is $>10 \text{ sec}^{-1}$.²⁷ In comparison, ligand interchange for $(h^5-C_5H_5)Zr(acac)_2Cl$ and $(h^5-C_5H_5)Zr(acac)_3$ at -130° is slower by at least 18–19 orders of magnitude. These differences in lability exist despite the fact that the average Zr–O bond distances are slightly longer, and presumably weaker, in the C_5H_5 derivatives: $Zr(acac)_3Cl$, 2.13 Å,²⁶ $(h^5-C_5H_5)Zr(acac)_2Cl$, 2.15 Å;¹⁵ $(h^5-C_5H_5)Zr(hfac)_3$, 2.22 Å.²⁰ Metal–oxygen stretching frequencies also indicate that replacement of Cl by C_5H_5 decreases the average Zr–O bond strength.¹⁴

Clearly, the above differences in the rates of ligand interchange cannot be accommodated by a mode of activation in which the maximum in the free energy profile is attained upon opening of a Zr–O bond. Also, the greater lability of $(h^5-C_5H_5)Zr(dpm)_2^+$ relative to the neutral $(h^5-C_5H_5)Zr(dik)_2X$ and $(h^5-C_5H_5)Zr(dik)_3$ complexes is inconsistent with this type of mechanism. If a Zr–O bond opened in the rearrangement of $(h^5-C_5H_5)Zr(dpm)_2^+$, the same process should be more facile in the higher coordination number neutral complexes where the bonds should be weaker and the charge separation in the transition state smaller.

A mechanism in which the maximum in the free energy surface is reached subsequent to Zr–O bond rupture may also be excluded. In this type of mechanism, the 18 or more orders of magnitude decrease in rate which accompanies the replacement of Cl by C_5H_5 would have to be attributed to increased steric repulsions between the dangling diketonate

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ligand and the C_5H_5 group. A steric effect of this magnitude is untenable in view of the relative stereochemical labilities of *cis*-Ti(dik) $_2$ Cl $_2$ complexes, which may well rearrange by a bond-rupture mode of activation,^{28,29} and structurally related (h^5 -C $_5$ H $_5$)Ti(dik) $_2$ Cl complexes. Based on the reported nmr line broadening patterns of Ti(bzac) $_2$ Cl $_2$ ²⁹ and (h^5 -C $_5$ H $_5$)Ti(bzac) $_2$ Cl,¹⁴ for example, it is estimated that the rates of ligand interchange differ by less than a factor of 10^2 at 0°.

In the case of zirconium, therefore, the dramatic increase in rigidity that occurs with C $_5$ H $_5$ must be due to an electronic effect which increases the activation energy necessary to achieve the transition state *via* twisting processes. The most obvious electronic difference between a halo ligand and a pentahapto C $_5$ H $_5$ group is that the latter most likely uses three valence orbitals on the metal, whereas the former uses only one. Thus it is reasonable that the C $_5$ H $_5$ group should restrict the availability of empty valence orbitals for rehybridization on the metal and increase the energy required to achieve ligand interchange by facial and/or digonal (edge) twists.

The more facile process of equatorial terminal group interchange in the (h^5 -C $_5$ H $_5$)Zr(dik) $_3$ complexes has been previously shown *not* to occur by opening of the equatorial Zr-O bond to the unique ligand.²¹ This bond is the longest, and presumably the weakest, bond in the hfac derivative.²⁰ It is now apparent that the LTP must occur by a digonal twist of the equatorial ligands. The intermediate in such a process would resemble a capped octahedron or a pentagonal bipyramid with the C $_5$ H $_5$ group in an equatorial position. Indeed, it is significant that in Zr(acac) $_3$ Cl a distortion toward a capped octahedron is already achieved in the solid state by a 28° rotation of one equatorial ligand out of the equatorial plane. In comparison, the pentagonal girdle in the more rigid (h^5 -C $_5$ H $_5$)Zr(hfac) $_3$ complex is almost perfectly planar.

In order to obtain more direct evidence in support of twisting processes for ligand interchange, the methyl proton line broadening patterns of (h^5 -C $_5$ H $_5$)Zr(acac) $_2$ Cl and (h^5 -C $_5$ H $_5$)Zr(dpm) $_2$ Cl were compared with those calculated for various different facial twists using the preexchange lifetimes determined from the -CH= line broadening. Poor agreement was obtained for the dpm derivative assuming a cdCl facial twist to give a trans intermediate which subsequently decays to a rearranged ground state. A similar poor fit was obtained for the acac complex. Therefore, this process, which is kinetically equivalent to a random interchange of terminal groups on the diketone ligands, can be eliminated as the sole reaction pathway. Also, a cbCl facial twist can be ruled out by inspection, as this process would lead to a methyl group doublet in the region of fast exchange.

Attempts were made to fit the methyl patterns to abc and acd face twists. In these cases, unlike the random case, the kinetic exchange matrix needed in the calculation of the line shapes is dependent on the line assignments. Since there is no reliable basis for assigning a particular methyl group in the molecule to a specific line in the spectrum, all 24 possible line assignments were tested for each twist. Neither twist gave acceptable fits for either complex. Therefore, it may be concluded that although ligand interchange is nonrandom, no single-step facial twist mechanism operates.

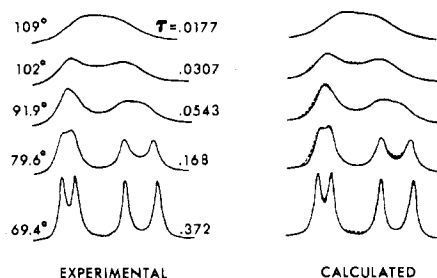


Figure 5. Comparison of experimental and calculated t -C $_5$ H $_5$ resonances of (h^5 -C $_5$ H $_5$)Zr(dpm) $_2$ Cl assuming abc and acd face twists and digonal twists of relative probability 0.5:0.5:0.1. The experimental line shapes are reproduced as dashed lines on the calculated spectra for ease of comparison. τ values (sec $^{-1}$) are based on the mean lifetimes for ligand interchange which were independently determined from -CH= line broadening patterns.

Several combinations of twists, including rotations of equal probability about all four types of faces, failed to give exact fits. The best agreement was obtained for a combination of abc and acd face rotations of equal probability. The experimental spectra coalesced somewhat more rapidly than the calculated spectra, suggesting that some terminal group interchange may be occurring without ligand interchange. Accordingly, the inclusion of a 10% probability that the diketone ligands undergo a digonal twist resulted in nearly perfect agreement between calculated and observed spectra. The agreement between calculated and observed spectra is illustrated in Figure 5. Comparable agreement was obtained for the methyl resonances of the acac derivative. These latter results, of course, do not constitute an unequivocal "proof" of mechanism, but they do illustrate for at least one class of compounds that a reasonable intimate mechanism can be envisioned which is in accord with the conclusion deduced from the relationships between structure and lability, namely, that twisting modes of activation operate in the intramolecular rearrangements of zirconium β -diketonates.

Experimental Section

Reagents and General Techniques. Reagent grade zirconocene dichloride was purchased and used without further purification. Acetylacetone was fractionally distilled before use (bp 136–140°). Dipivaloylmethane was prepared and purified by using previously described procedures.³⁰ Antimony pentachloride was distilled under argon at a pressure of 30 Torr through a 30-cm column packed with glass helices, the fraction boiling between 90 and 91° being collected.

All organic solvents used in the syntheses and physical measurements were dried over suitable desiccants. Benzene was distilled from lithium aluminum hydride. Dichloromethane, acetonitrile, and tetrachloroethylene were distilled from calcium hydride. Carbon disulfide and triethylamine were dried over phosphorus pentoxide and anhydrous magnesium sulfate, respectively.

Since the compounds used in this study are sensitive to atmospheric moisture, all preparative reactions and manipulations of the product were conducted under a dry argon atmosphere. As an extra precaution against hydrolysis in the preparation and manipulation of (h^5 -C $_5$ H $_5$)Zr(acac) $_3$ the solvent was deaerated by dispersing argon through the liquid for several minutes. All glassware was dried at 175°, cooled in a calcium sulfate desiccator whenever possible, and flushed with argon before use.

(h^5 -C $_5$ H $_5$)Zr(dpm) $_2$ Cl. A mixture of dipivaloylmethane (4.97 g, 27.0 mmol) and triethylamine (1.88 ml, 13.4 mmol) in 90 ml acetonitrile was added dropwise to a suspension of (h^5 -C $_5$ H $_5$) $_2$ ZrCl $_2$ (3.92 g, 13.4 mmol) in 100 ml of acetonitrile. The mixture was stirred at ambient temperature for 39 hr. The white insoluble solid, identified as (h^5 -C $_5$ H $_5$)Zr(dpm) $_3$ by its nmr spectrum, was separated by filtration and washed with four 30-ml portions of

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acetonitrile. The acetonitrile washings were combined with the original mother liquor, and the solvent was removed under vacuum. The resultant white solid was suspended in 100 ml of benzene, and the insoluble portion, identified as $(C_2H_5)_3N \cdot HCl$ by its ir spectrum, was removed by filtration. The product was isolated from the filtrate by vacuum distillation of the benzene at room temperature. The white compound was recrystallized from 200 ml of acetonitrile at -78° and was dried *in vacuo* at room temperature; mp $175-177^\circ$. The yield was 5.76 g (76.8%).

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

$(h^5-C_5H_5)Zr(acac)_3$. A suspension of $(h^5-C_5H_5)_2ZrCl_2$ (5.00 g, 17.2 mmol) and acetylacetone (5.25 ml, 51.3 mmol) in 50 ml of triethylamine was stirred at room temperature for 6 hr. The white precipitate of $(C_2H_5)_3N \cdot HCl$ was separated from the solution by filtration, and the filtrate was cooled at -25° overnight. The resultant white, crystalline solid was collected by filtration and dried *in vacuo* at room temperature for several hours; mp $135-137^\circ$. The yield was 4.65 g (59.7%). Cooling the mother liquor in a Dry Ice-acetone bath resulted in no further crystallization.

Anal. Calcd for $(C_5H_5)Zr(C_8H_7O_2)_3$: C, 52.96; H, 5.78; Zr, 20.11; mol wt 454. Found: C, 53.11; H, 5.80; Zr, 20.44; mol wt (C_6H_6) 448; $\Lambda(2.65 \times 10^{-3} M$ solution in $C_6H_5NO_2$ at 25°) $<0.029 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

$[(h^5-C_5H_5)Zr(dpm)_2][SbCl_6] \cdot 2.5CH_3CN$. A solution of $SbCl_5$ (1.34 g, 4.48 mmol) in 20 ml of acetonitrile was added dropwise to a suspension of $(h^5-C_5H_5)Zr(dpm)_2Cl$ (2.50 g, 4.48 mmol) in 30 ml of acetonitrile at 0° , and the mixture was stirred at 0° for 0.75 hr. The volume of the solution was reduced to ca. 20 ml by vacuum distillation at 0° , and the solution was cooled to -25° for 12 hr. The resultant yellow crystalline solid was separated from the cold solution by filtration and dried *in vacuo* for 8 hr at Dry Ice temperature. The crystals slowly decompose at room temperature to give a black oil. The product is insoluble in benzene but is readily soluble in polar solvents such as acetonitrile, acetone, dichloromethane, and nitrobenzene. The presence of 2.5 mol of CH_3CN per mole of complex was indicated by planimetric integration of CH_3CN and *trans*- C_4H_6 resonance lines in CH_2Cl_2 solution.

Anal. Calcd for $(C_5H_5)Zr(C_{11}H_{19}O_2)_2SbCl_6 \cdot 2.5CH_3CN$: C, 40.04; H, 5.30; Cl, 22.16. Found: C, 40.77; H, 5.48; Cl, 21.49; $\Lambda(2.51 \times 10^{-3} M$ in $C_6H_5NO_2$ at 25°) $= 20.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; ir (mull): 3180, 1129 ($h^5-C_5H_5$), 1606-1552 (C=O), 431-400 (Zr-O), 345 cm^{-1} ($SbCl_6^-$).

Conductometric titration of $(h^5-C_5H_5)Zr(dpm)_2Cl$ with $SbCl_5$ in CH_2Cl_2 indicated that a similar reaction occurs in absence of CH_3CN , but it was not possible to isolate a crystalline product from the solution.

Physical Measurements. Melting point, molecular weight, and conductance measurements were performed as previously described.^{13,21} The infrared spectrum of $(h^5-C_5H_5)Zr(dpm)_2 \cdot SbCl_6 \cdot 2.5CH_3CN$ was obtained as Nujol and Fluorolube mulls between CsI plates using a Perkin-Elmer 457 grating infrared spectro-

photometer. The 2851-, 1603-, and 907- cm^{-1} bands of polystyrene were used as reference frequencies. Variable-temperature proton magnetic resonance spectra were recorded on a Varian A56/60D analytical spectrometer operated at 60.00 MHz. All solutions used in the nmr studies were prepared in an argon atmosphere.

Kinetic Studies. Mean lifetimes for ligand interchange in $(h^5-C_5H_5)Zr(dpm)_2Cl$ and for the LTP and HTP of $(h^5-C_5H_5)Zr(acac)_3$ were determined from their -CH= or terminal methyl group line shapes using the Gutowsky-Holm equation and experimental methods previously described in detail for the kinetic treatment of related derivatives.^{13,21} The frequency separation between resonance components ($\delta\nu$) in the region of exchange was determined by linear least-squares extrapolation of the temperature dependence of $\delta\nu$ in the region of slow exchange. Similar extrapolation methods were used to obtain values of the transverse relaxation times (T_{2A} and T_{2B}) for the interchanging protons. For the LTP of $(h^5-C_5H_5)Zr(acac)_3$, it was not possible to determine accurately the T_2 value of the equatorial methyl group appearing at lowest field due to its overlap with a methyl line of the unique ligand. It was assumed, therefore, that the T_2 values of the equatorial methyl protons were equal.

Activation enthalpies and entropies were determined by linear least-squares fits of the kinetic data to the Eyring equation. Arrhenius activation parameters were determined from the least-squares slope and intercept of $\log k$ vs. $1/T$ plots. In all cases, the uncertainties in the activation parameters at the 95% confidence level were larger than the errors which would be generated due to reasonable systematic uncertainties in $\delta\nu$, T_{2A} , and T_{2B} .

Computer-Simulated Spectra. The methyl proton line broadening patterns for ligand interchange in $(h^5-C_5H_5)Zr(dpm)_2Cl$ and $(h^5-C_5H_5)Zr(acac)_2Cl$ assuming various twist mechanisms were calculated using a computer program similar in function to the Whitesides-Lisle program.^{23,31} Since the off-diagonal elements of the exchange matrices depend on the chemical shift assignments of the four nonequivalent methyl groups, each twisting process was tested for all 24 possible line assignments. Only the cdCl face twist that is kinetically equivalent to a random process gave a unique matrix. The abc and acd face twists each gave six matrices, and a 50:50 mixture of abc and acd twists gave three matrices. Rate constants for methyl group interchange for each mechanism were expressed in terms of the independently determined rate constants for ligand interchange.

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Registry No. $(h^5-C_5H_5)Zr(dpm)_2Cl$, 50803-57-1; $(h^5-C_5H_5)Zr(acac)_3$, 50803-55-9; $[(h^5-C_5H_5)Zr(dpm)_2][SbCl_6]$, 50803-58-2; $(h^5-C_5H_5)_2ZrCl_2$, 1291-32-3.

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