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Stereochemistry and Stereochemical Rearrangements of Eight-Coordinate Tetrakis Chelates. 1. Group 4B β-Diketonates[1]

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Abstract: Until very recently, NMR studies of eight-coordinate tetrakis chelates have failed to provide stereochemical and kinetic information because these chelates undergo very rapid stereochemical rearrangements. Using the Freon solvent $CHClF_2$, the ^1H and ^{19}F NMR spectra of Zr(IV), Hf(IV), Ce(IV), and Th(IV) tetrakis(β-diketonates) have been investigated at considerably lower temperatures than employed in earlier work, and several complexes have been identified which become stereochemically rigid on the NMR time scale at temperatures in the range −115 to −170 °C. The spectra of $Zr(acac)_4$ and $Hf(acac)_4$ in the slow-exchange limit are most simply interpreted in terms of the presence of a single stereoisomer (*ssss*-D_2, *mmmm*-D_{2d}, *gggg*-D_2, or *gggg*-S_4); the square antiprismatic *ssss*-D_2 configuration is preferred on the basis of the solid-state structure of $Zr(acac)_4$. The alkyl resonances of $Zr(dmh)_4$ and $Zr(tfac)_4$ (dmh = t-$C_4H_9COCHCOCH_3^-$; tfac = CF_3CO-$CHCOCH_3^-$) do not probe the overall symmetry of these molecules, only the local site symmetry of the alkyl groups. However, the ^{19}F spectra of $Zr(tfac)_4$ show that more than one geometric isomer is present. The ^1H spectrum of $Zr(acac)_2(NO_3)_2$ is consistent with the *mmmm*-C_2 dodecahedral structure found in the solid state. No splitting of the time-averaged NMR resonances was found for the Ce and Th complexes. The kinetics of the intramolecular rearrangement processes which exchange acac methyl groups or dmh *tert*-butyl groups between the two inequivalent sites of $Zr(acac)_4$, $Zr(acac)_2(NO_3)_2$, and $Zr(dmh)_4$ have been studied by NMR line-shape analysis. Rate constants (s^{-1} at −125 °C), $\Delta H^{\ddagger}$ (kcal/mol), and $\Delta S^{\ddagger}$ (eu) are respectively as follows: 2.0×10^2, 4.1 ± 0.3, and −18.7 ± 2.5 for $Zr(acac)_4$; 2.9×10^2, 4.5 ± 0.3, and −15.2 ± 2.5 for $Zr(acac)_2(NO_3)_2$; 6.8, 5.5 ± 0.5, and −16.2 ± 2.9 for $Zr(dmh)_4$. Polytopal rearrangement, involving a series of Hoard-Silverton rearrangements, is the preferred path for these rearrangements; however, one-bond rupture mechanisms cannot be ruled out.

Introduction

Stereochemical nonrigidity is a characteristic property of eight-coordinate complexes, and until very recently no examples of "stereochemically rigid" tetrakis chelates had been identified. Low-temperature NMR studies of tetrakis β-diketonates,[2,3] tropolonates,[4] and *N,N*-dialkyldithiocarbamates[5-8] had afforded only time-averaged NMR spectra. The first examples of tetrakis chelates which become rigid on the NMR time scale have been reported within the past 3 years. The reported examples are (1) the tetrakis(*N,N*-dimethyldithiocarbamato)tantalum(V) cation, $[Ta(S_2CNMe_2)_4]^+$;[9] (2) the *N,N*-dimethylmonothiocarbamate complexes, $Ti(SOCNMe_2)_4$ and $Zr(SOCNMe_2)_4$;[10] and (3) the W(IV) mixed ligand complexes, $W(mpic)_3(dcq)$ and $W(mpic)_2(dcq)_2$[11] (mpic = 5-methylpicolinate and dcq = 5,7-dichloro-8-quinolinolate). $W(mpic)_2(dcq)_2$ can be separated into two geometric isomers which isomerize slowly on the laboratory time scale; $\Delta G^{\ddagger}$ = 24.1 kcal/mol at 25 °C.[11]

Using the Freon solvent $CHClF_2$, we have investigated the ^1H and ^{19}F NMR spectra of Zr(IV), Hf(IV), Ce(IV), and Th(IV) tetrakis(β-diketonates) at considerably lower temperatures than employed in earlier work,[2] and we have identified several complexes which become stereochemically rigid on the NMR time scale at temperatures in the range −115 to −170 °C. In this paper we describe the low-temperature spectra, consider the stereochemistry of these complexes in solution, and discuss the kinetics and mechanism of stereochemical rearrangements. A subsequent paper will deal with the paramagnetic uranium(IV) analogues.

Experimental Section

Reagents and General Techniques. Zirconium(IV) chloride (Chemical Procurement Laboratories), zirconium(IV) isopropoxide

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(Alfa), aluminum(III) isopropoxide (Eastman), acetylacetone (Fisher), and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (Htftb) (Eastman) were reagent grade and were used without further purification. Trifluoroacetylacetone (Htfac) (Chemical Procurement Laboratories) was refluxed over P_4O_{10} for 12 h, distilled, and stored in a refrigerator.

5,5-Dimethyl-2,4-hexanedione (Hdmh) was prepared in 75% yield according to the procedure of Adams and Hauser[12] by Claisen condensation of pinacolone (0.90 mol) and ethyl acetate (0.45 mol) in the presence of sodium amide (1.03 mol); the fraction boiling in the range 40–50 °C at 0.05 Torr was collected (lit. bp 70–71 °C at 20 Torr[12]). 2,6-Dimethyl-3,5-heptanedione (diisobutrylmethane, Hdibm) was prepared in a similar manner by condensation of 3-methyl-2-butanone and ethyl 2-methylpropanoate; the diketone was purified by conversion to the copper chelate, treatment of the chelate with 1 M HCl to regenerate the diketone, followed by vacuum distillation (bp 25–27 °C, 0.02 Torr), yield 30%. 2,2,6,6-Tetramethyl-3,5-heptanedione (dipivaloylmethane, Hdpm) was synthesized by the method of Man et al.[13]

1-Methylethyl 3-oxobutanoate (isopropyl acetoacetate, Hipa) was prepared by transesterification of methyl acetoacetate (21.5 g, 0.185 mol) with 2-propanol (100 mL, 1.31 mol) in the presence of concentrated sulfuric acid (6 mL). The reaction mixture was stirred for 1 h at room temperature, and then the methanol produced and the excess 2-propanol were removed by rotary evaporation. Another 100 mL of 2-propanol was added and, after ~12 h, the alcohols were again removed by rotary evaporation. After addition of 10 mL of water to the solution, the product was extracted with three 30-mL portions of diethyl ether and the organic phase was washed with two 50-mL portions of saturated sodium carbonate solution and two 50-mL portions of water. The ether layer was dried with anhydrous magnesium sulfate and filtered, and the solvent was removed by vacuum distillation at room temperature. The Hipa was purified by vacuum distillation (bp 40–44 °C, 0.02 Torr), yield 21 g (79%).

Bis(1-methylethyl) propanedioate (diisopropyl malonate, Hdipm) was prepared by esterification of malonic acid (100 g, 0.961 mol) with 2-propanol (225 mL, 2.94 mol) in the presence of concentrated sulfuric acid (37.5 mL). The reaction mixture was stirred at room temperature for 20 h. The Hdipm was isolated by extraction into diethyl ether and was purified by vacuum distillation (bp 75–79 °C, 0.02 Torr), yield 164 g (91%).

Solvents (acetonitrile, dichloromethane, benzene, and hexane) and triethylamine were dried by refluxing over calcium hydride for at least 24 h and were freshly distilled under an atmosphere of dry nitrogen or argon prior to use. Methanol and ethanol were dried by refluxing over sodium metal for 12 h.

Tetrakis(β-diketonato)zirconium(IV) complexes, $Zr(dik)_4$, derived from the more acidic β-diketones (e.g., Htftb), were readily prepared in aqueous solution. Synthesis of $Zr(dik)_4$ complexes derived from the less acidic β-diketones (e.g., Hdibm, Hdpm, Hdmh) required a nonaqueous chelation procedure. Because the latter complexes are moderately sensitive to moisture, they were prepared, purified, and subsequently handled under a dry nitrogen atmosphere. Low-temperature recrystallizations were carried out by preparing a saturated solution at room temperature and then cooling the solution to −28 or −78 °C. In cases where mixed solvents were used, a saturated solution in the better solvent was first prepared followed by addition of an equal volume of the poorer solvent.

Tetrakis(2,6-dimethyl-3,5-heptanedionato)zirconium(IV), Zr(dibm)$_4$. This compound was prepared by reaction of $ZrCl_4$ (1.22 g, 5.24 mmol), Hdibm (4.14 g, 26.5 mmol), and triethylamine (3.7 mL, 26 mmol) in 50 mL of freshly distilled dry acetonitrile. The mixture was refluxed with stirring under an atmosphere of dry nitrogen for 20 h. The triethylamine hydrochloride formed was removed by filtration, and the solvent was vacuum distilled at room temperature. The resulting oily residue was dissolved in dry benzene, the solution filtered, and the solvent removed under vacuum at room temperature. Heating the resulting yellow oil at 100 °C (0.02 Torr) for 4 h removed unreacted Hdibm and afforded an oily, yellow, crystalline solid (2.05 g, 55% theoretical). The compound was recrystallized three times from methanol at −78 °C until the crystals were colorless, mp >250 °C. Anal. Calcd for $Zr(C_9H_{15}O_2)_4$: C, 60.72; H, 8.49; Zr, 12.81. Found: C, 60.96; H, 8.60; Zr, 13.01.

Tetrakis(5,5-dimethyl-2,4-hexanedionato)zirconium(IV), Zr(dmh)$_4$. Using a similar procedure, this compound was prepared by reaction of $ZrCl_4$ (1.28 g, 5.49 mmol), Hdmh (3.42 mL, 22.0 mmol based on the measured density of 0.916 g/mL), and triethylamine (3.07 mL, 21.9 mmol) in 15 mL of acetonitrile. The viscous oil obtained after removing the solvent under vacuum was purified by vacuum distillation at 90 °C (0.02 Torr). An oily glass collected on the cold finger. The glass was transferred to a flask where it slowly crystallized on standing for 2 weeks in vacuo at room temperature, mp 93–94 °C dec. Anal. Calcd for $Zr(C_8H_{13}O_2)_4$: C, 58.59; H, 7.99; Zr, 13.91; mol wt, 656. Found: C, 58.32; H, 7.82; Zr, 13.98; mol wt, 664.

Attempts to recrystallize this compound from a variety of solvents at −28 and −78 °C were unsuccessful. The solvents tried included dichloromethane–hexane, benzene–hexane, hexane, pentane, ethanol, methanol, and diethyl ether.

Tetrakis(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)zirconium(IV), Zr(tftb)$_4$. This complex was prepared by reaction of $ZrCl_4$ (1.20 g, 5.15 mmol) and Htftb (3.65 mL, 20.5 mmol based on a measured density of 1.10 g/mL) in 20 mL of distilled water. A solution of potassium carbonate (1.42 g, 10.3 mmol) in 10 mL of distilled water was added dropwise with stirring. After stirring for 30 min at room temperature, the reaction mixture was filtered, and the solid was air dried overnight. Water of hydration was removed by pumping on the sample (0.02 Torr) for 3 h at room temperature. Recrystallization from boiling hexane afforded 4.13 g of product (92% theoretical), mp 188 °C. Anal. Calcd for $Zr(C_8H_{10}F_3O_2)_4$: C, 44.08; H, 4.62; F, 26.15; Zr, 10.46; mol wt, 872. Found: C, 44.08; H, 4.52; F, 26.12; Zr, 10.04; mol wt, 847.

Tetrakis(1-methylethyl 3-oxobutanoato)zirconium(IV), Zr(ipa)$_4$. This compound was prepared by ligand exchange between zirconium(IV) isopropoxide (2.10 g, 6.41 mmol) and isopropyl acetoacetate (3.68 g, 25.6 mmol). A mixture of the reagents was heated with stirring at 100 °C for 1 h under an atmosphere of dry nitrogen. The isopropyl alcohol formed was removed by vacuum distillation at 45 °C (0.02 Torr), and any unreacted isopropyl acetoacetate was removed by pumping at 65 °C for 24 h. Attempts to purify the resulting waxy, yellow solid by recrystallization at −78 °C from dichloromethane hexane, benzene–hexane, hexane, methanol, ethanol, and diethyl ether were unsuccessful because of the high solubility of $Zr(ipa)_4$. The compound decomposed on attempted sublimation. Because the ^1H NMR spectrum of the product was free of impurity resonances, the compound was used without further purification, yield 3.80 g (89%), mp 72 ° C dec. Anal. Calcd for $Zr(C_7H_{11}O_3)_4$: C, 50.66; H, 6.68; Zr, 13.74; mol wt, 664. Found: C, 49.99; H, 6.44; Zr, 14.11; mol wt, 610.

Other Group 4B β-Diketonates. The following compounds were prepared by standard methods, and the purity of these compounds was checked by their melting points and their ^1H NMR spectra: $Zr(acac)_4$,[14] $Zr(acac)_3(NO_3)$,[15] $Zr(acac)_2(NO_3)_2$,[16] $Zr(tfac)_4$,[17] $Hf(acac)_4$,[18] $Ce(acac)_4$,[19] $Ce(tfac)_4$,[19] $Th(acac)_4$,[20] and $Th(tfac)_4$.[2] $Zr(dpm)_4$[21] was prepared by ligand exchange between $Zr(tfac)_4$ and Hdpm, and was purified by recrystallization from hexane at −28 °C.

Tris(bis(1-methylethyl)propanedioato)aluminum(III), Al(dipm)$_3$. This complex was prepared by reaction of aluminum(III) isopropoxide (3.27 g, 16.0 mmol) and diisopropyl malonate (18.1 g, 96.2 mmol) in 50 mL of anhydrous benzene. The reaction mixture was refluxed with stirring for 48 h under an atmosphere of dry nitrogen. The solution was filtered and the isopropyl alcohol and benzene were pumped off at room temperature. Unreacted diisopropyl malonate was removed by vacuum distillation at 90 °C (0.02 Torr). Recrystallization from hexane at −28 °C afforded 7.60 g of product (81% theoretical), mp 143–144 °C. Anal. Calcd for $Al(C_9H_{15}O_4)_3$: C, 55.09; H, 7.71; Al, 4.58. Found: C, 55.19; H, 7.77; Al, 4.39.

Molecular Weights. Molecular weights were determined cryoscopically in benzene solution using the thermistor apparatus described by Knight et al.[22] The apparatus was calibrated with benzil, freshly recrystallized from anhydrous ethanol and dried in vacuo for 24 h.

Nuclear Magnetic Resonance Spectra. Low-temperature ^1H and ^{19}F NMR spectra of $CHClF_2$ (Freon 22) solutions of the metal β-diketonates were recorded in the temperature range −45 to −170 °C with a Bruker HX-90 spectrometer operating with 4.167-kHz audio frequency modulation in the continuous wave mode. The spectrometer was locked on the first upper sideband of one of the spin-coupled doublet ^{19}F resonances of the solvent, and the spectrum was recorded by sweeping the first upper sideband of the observing channel.

Solutions (5–20 mg/mL) were prepared under dry nitrogen by first loading the solid samples into 5-mm NMR tubes and then condensing the solvent (bp −41 °C) in the tubes at −78 °C. The tubes were

Table I. Names and Abbreviations for $[RCOCHCOR']^-$ Ligands

R	R′	trivial name	systematic name	abbreviation
CH_3	CH_3	acetylacetonate	2,4-pentanedionate	acac
t-C_4H_9	t-C_4H_9	dipivaloylmethanate	2,2,6,6-tetramethyl-3,5-heptanedionate	dpm
i-C_3H_7	i-C_3H_7	diisobutrylmethanate	2,6-dimethyl-3,5-heptanedionate	dibm
i-C_3H_7O	i-C_3H_7O	diisopropylmalonate	bis(1-methylethyl)propanedioate	dipm
CH_3	t-C_4H_9	pivaloylacetonate	5,5-dimethyl-2,4-hexanedionate	dmh
CF_3	CH_3	trifluoroacetylacetonate	1,1,1-trifluoro-2,4-pentanedionate	tfac
CF_3	t-C_4H_9	pivaloyltrifluoroacetonate	1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionate	tftb
i-C_3H_7O	CH_3	isopropylacetoacetate	1-methylethyl 3-oxobutanoate	ipa

capped with plastic caps which were wrapped with several layers of parafilm to protect the solutions from the atmosphere. The tubes were stored in a dry ice-methanol bath prior to use, and were transferred directly from the bath to the HX-90 probe precooled to −50 °C. The NMR tubes were not sealed with a flame in the conventional manner because a sealed tube might explode in the expensive probe insert if there was a temperature failure in the probe cooling system. Sample temperatures were measured with a copper-constantan thermocouple which was immersed directly in the sample or in pure solvent contained in a separate sample tube. It is estimated that reported temperatures are accurate to ±0.5 °C. Temperature fluctuations were minimized by reducing the flow rate of the cooling gas to a rate which would just actuate the temperature controller heater at a given temperature.

Rate constants k for exchange of acetylacetonate methyl groups (or dmh *tert*-butyl groups) between the two inequivalent environments of $Zr(acac)_4$, $Zr(acac)_2(NO_3)_2$, and $Zr(dmh)_4$ were determined by quantitative comparison of experimental spectra with theoretical spectra calculated using the Gutowsky-Holm total line-shape equation.[23] Spectra were compared with respect to the following characteristic line-shape parameters which were used to determine an average value of k at each temperature: line widths at one-fourth ($\Delta_{1/4}$), one-half ($\Delta_{1/2}$), and three-fourths ($\Delta_{3/4}$) maximum amplitude and, below coalescence, $\delta\nu_e$, the frequency separation between the two absorption maxima, and r, the ratio of the maximum amplitude to the amplitude at the central minimum. Because the transverse relaxation times T_2 were temperature dependent, theoretical line shapes were computed for a range of T_2's, and the experimental line shape at each temperature was compared with a theoretical line shape computed using a value of T_2 appropriate to that temperature. T_2 values were obtained by extrapolating plots of log $\Delta_{1/2}$ vs. $1/T$ from the fast- and slow-exchange regions into the coalescence region. The observed frequency separation $\delta\nu$ between the two resonances in the slow-exchange region was essentially independent of temperature.

Results and Discussion

NMR Spectra. ^1H and ^{19}F NMR spectra of several eight-coordinate tetrakis(β-diketonate) complexes of Zr(IV), Hf(IV), Ce(IV), and Th(IV) have been investigated at very low temperatures in an effort to slow the rate of stereochemical rearrangement and obtain information about the stereochemistry of tetrakis chelates in solution. The complexes were studied in the Freon solvent $CHClF_2$ in the temperature range −45 to −170 °C. Table I lists the ligands which were employed and the ligand abbreviations which are used in this paper. The unsymmetrical ligands were chosen in order to investigate the possibility of geometric isomerism. The ligands which contain the potentially diastereotopic isopropyl methyl groups were used in an effort to detect a chiral metal center. Some fluorinated ligands were included so that ^{19}F NMR spectra could be studied, and the β-keto ester, isopropyl acetoacetate, was employed because it was expected that the electron-releasing isopropoxy group would slow the rate of stereochemical rearrangement. This idea was tested by comparing the isopropyl methyl region of the ^1H NMR spectra of the β-diester complex tris(diisopropylmalonato)aluminum(III), Al (dipm)$_3$, and the corresponding β-diketonate complex tris(diisobutrylmethanato)aluminum(III), Al(dibm)$_3$.[24,25] At room temperature, Al(dipm)$_3$ and Al(dibm)$_3$ both exhibit two equal-intensity, spin-coupled doublets due to the two diastereotopic isopropyl methyl groups; at higher temperatures these doublets coalesce to a single doublet owing to rapid enantiomerization. As expected, the coalescence temperature is higher for Al(dipm)$_3$ (~135 °C) than for Al(dibm)$_3$ (120 °C[24]), but the difference is disappointingly small. Nevertheless, we did examine NMR spectra of the β-keto ester complex Zr(ipa)$_4$; unfortunately, attempts to prepare Zr(β-diester)$_4$ complexes were unsuccessful.

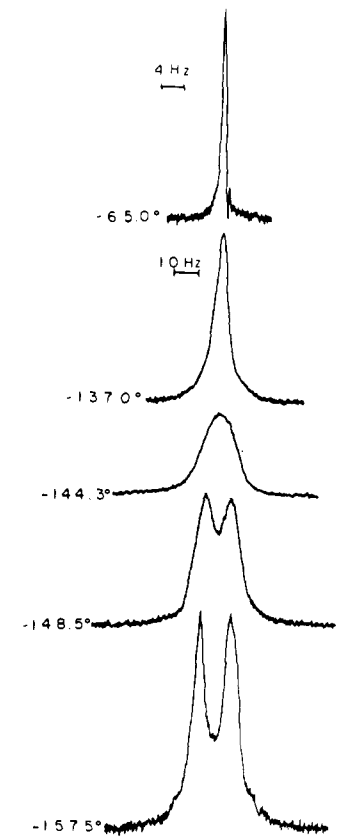

Figure 1. Methyl proton resonances for $Zr(acac)_2(NO_3)_2$ in $CHClF_2$ solution, 10 mg/mL, at 90 MHz.

Zr(IV) Complexes with Symmetrical Ligands. The following complexes of this type were studied: $Zr(acac)_4$, $Zr(acac)_3(NO_3)$, $Zr(acac)_2(NO_3)_2$, $Zr(dpm)_4$, and $Zr(dibm)_4$. $Zr(acac)_4$ and $Zr(acac)_2(NO_3)_2$ exhibit very similar spectra. The single, time-averaged methyl proton resonance characteristic of the higher temperatures splits into two lines of equal intensity below the coalescence temperatures of −145 and −144 °C, respectively. Typical spectra for $Zr(acac)_2(NO_3)_2$ are presented in Figure 1; typical spectra for $Zr(acac)_4$ are shown in Figure 1 of ref 1a. The frequency separation in the slow-exchange limit ($\delta\nu$) at 90 MHz is 11.1 Hz for $Zr(acac)_4$ and 13.5 Hz for $Zr(acac)_2(NO_3)_2$. No splitting was observed for the ring proton resonance. In both cases, the ring proton resonance simply broadens with decreasing temperature, from

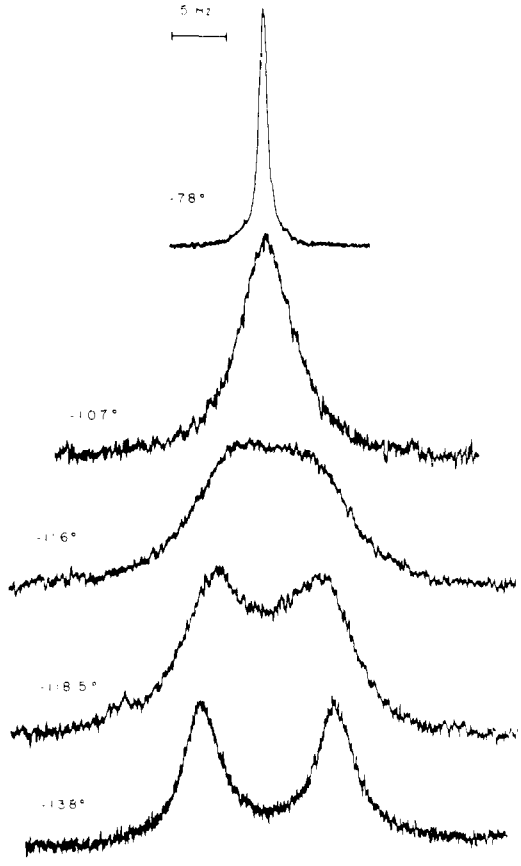

Figure 2. *tert*-Butyl proton resonances for $Zr(dmh)_4$ in $CHClF_2$ solution, 10 mg/mL, at 90 MHz.

~2 Hz at −55 °C to ~6 Hz at −160 °C, presumably owing to increasing solvent viscosity.

No splittings were observed for any of the proton resonances of $Zr(acac)_3(NO_3)$, $Zr(dpm)_4$, and $Zr(dibm)_4$. Line widths for the alkyl resonances (Table II) are very large at the lower temperatures, and it is possible that splitting of the alkyl resonances is obscured by T_2 broadening.

Zr(IV) Complexes with Unsymmetrical Ligands. The following complexes of this type were studied: $Zr(dmh)_4$, $Zr(tfac)_4$, $Zr(tftb)_4$, and $Zr(ipa)_4$. For $Zr(dmh)_4$, the single time-averaged methyl resonance and the single time-averaged *tert*-butyl resonance both split into two lines of equal intensity below the same coalescence temperature of −116 °C; typical spectra in the *tert*-butyl region are reproduced in Figure 2. The frequency separation in the slow-exchange limit at 90 MHz is 11.7 Hz for the methyl resonances and 12.5 Hz for the *tert*-butyl resonances. The line width of the single ring proton resonance increases from 1.6 Hz at −104 °C to 4.5 Hz at −134 °C, but no splitting is observed.

$Zr(tfac)_4$ exhibits a single methyl proton resonance which remains relatively sharp at low temperatures; line widths are 2.0, 3.4, and 6.1 Hz at −134, −155, and −170 °C, respectively. However, the single trifluoromethyl resonance in the ^{19}F spectrum splits into four lines below the coalescence temperature of −140 °C. The spectrum at −160 °C is depicted in Figure 3. The relative intensities of the four lines appear to be ~1:3:3:2, and the chemical shifts of the three higher field lines relative to the lowest field line are 0.31, 0.47, and 0.59 ppm. Because of the poor solubility of $Zr(tfac)_4$ in $CHClF_2$, the ring proton resonance was not observed.

No splittings were observed for any of the resonances of $Zr(tftb)_4$ (^1H and ^{19}F), nor for $Zr(ipa)_4$. Once again, the line widths become very broad at the lower temperatures (cf. Table II).

Table II. Line Widths for the Alkyl Resonances of Compounds Showing No Low-Temperature Splitting[a]

compd	R	line width[b] (temp, °C)
$Zr(acac)_3(NO_3)$	CH_3	1.3 (−104), 3.3 (−144), 17.5 (−168)
$Zr(dpm)_4$	*t*-C_4H_9	0.93 (−47), 1.6 (−67), 2.2 (−87), 3.4 (−108), 8.1 (−127), 12.0 (−137), 21.6 (−147), 35.0 (−167)
$Zr(dibm)_4$	CH_3(*i*-Pr)	2.0 (−54), 13.0 (−108), 19.6 (−155)
$Zr(tftb)_4$	*t*-C_4H_9	7.6 (−134), 18.8 (−155), 31.2 (−165), 82.0 (−168)
	CF_3	4.6 (−124), 15.0 (−134), 18.0 (−155), 48.0 (−165), 55.0 (−168)
$Zr(ipa)_4$	CH_3	1.2 (−54), 1.5 (−84), 2.5 (−114), 4.6 (−134), 5.4 (−144), 13.0 (−165)
	CH_3(*i*-Pr)	2.1 (−54), 3.8 (−84), 15.0 (−114), 21.4 (−134), 25.2 (−144)
$Ce(acac)_4$	CH_3	31.4 (−170)
$Ce(tfac)_4$	CH_3	20.0 (−167)
	CF_3	75.0 (−167)
$Th(acac)_4$	CH_3	1.6 (−104), 2.6 (−124), 4.0 (−144), 6.8 (−155), 8.3 (−169)
$Th(tfac)_4$	CH_3	6.0 (−170)
	CF_3	2.1 (−164)

[a] In $CHClF_2$; concn 20 mg/mL. [b] In Hz at 90 MHz. ^1H resonances for CH_3 and *t*-C_4H_9; ^{19}F resonance for CF_3.

Hf(IV), Ce(IV), and Th(IV) Complexes. Low-temperature ^1H NMR spectra of $Hf(acac)_4$ are very similar to spectra of $Zr(acac)_4$. The methyl resonance splits into two peaks of equal intensity below the coalescence temperature of −149 °C ($\delta\nu$ = 10.3 Hz), and the ring proton resonance remains a singlet.

No splitting was observed for the proton resonances of $Ce(acac)_4$ and $Th(acac)_4$, nor for the ^1H and ^{19}F resonances of $Ce(tfac)_4$ and $Th(tfac)_4$. Low-temperature line widths are included in Table II. The resonances of the Th complexes exhibit normal viscosity broadening and remain quite sharp, even at the lowest temperatures (e.g., the line width for the ^{19}F resonance of $Th(tfac)_4$ is only 2.1 Hz at −164 °C). In contrast, the resonances of the Ce complexes become unusually broad at low temperatures.

Stereochemistry in Solution. The NMR spectra of $Zr(acac)_4$ and $Hf(acac)_4$ in the slow-exchange limit are most simply interpreted in terms of the presence of a single stereoisomer which has two equally populated methyl environments and one ring proton environment. The most likely coordination polyhedra are the D_{4d} square antiprism (SAP) and the D_{2d} dodecahedron (DD)[26] (Figure 4). Of the nine possible SAP and DD stereoisomers (Table III), five may be ruled out on the basis of the number of the observed resonance lines. Consistent with two methyl resonances and a single ring proton resonance are the SAP stereoisomer *ssss*-D_2 and the three DD stereoisomers *mmmm*-D_{2d}, *gggg*-D_2, and *gggg*-S_4. In the solid state, $Zr(acac)_4$ adopts a structure which most closely approximates that of the idealized *ssss*-D_2 stereoisomer,[27-30] and, in the absence of information to the contrary, it seems reasonable to assume that this isomer persists in solution; note, however, that the *mmmm* and *gggg* DD stereoisomers cannot be ruled out on the basis of the NMR spectra. On the basis of crystallographic studies of $Zr(acac)_2(NO_3)_2$[16] and $Zr(acac)_3(NO_3)$,[15] an *mmmm* structure for $Zr(acac)_4$ is much less likely than *ssss* or *gggg*; the *mmmm* stereoisomer is destabilized by nonbonded

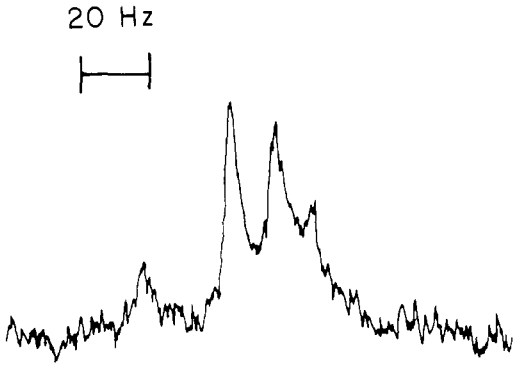

Figure 3. Trifluoromethyl ^{19}F resonances for $Zr(tfac)_4$ in $CHClF_2$ solution, 5 mg/mL, at 84.67 MHz and −160 °C.

Table III. Square Antiprismatic (SAP) and Dodecahedral (DD) Stereoisomers for $M(acac)_4$

polyhedron	ligand wrapping pattern	symmetry	no. of NMR lines CH_3	no. of NMR lines CH
SAP	*ssss*	D_2	2	1
DD	*mmmm*	D_{2d}	2	1
DD	*gggg*	D_2	2	1
DD	*gggg*	S_4	2	1
SAP	*llll*	D_4	1	1
SAP	*llss*	C_2	4	2
DD	*aabb*	D_2	2	2
DD	*mmgg*	C_2	4	2
DD	*abmg*	C_1	8	4

repulsions because the bite of the acetylacetonate ligand is too large for two acac ligands to be located on the *m* edges of the same trapezoid of an MO_8 dodecahedron when the metal atom is as small as Zr(IV).[15,16]

If the complexes which contain unsymmetrical ligands, e.g., $Zr(dmh)_4$, adopt the SAP *ssss* structure, seven geometric isomers are possible, depending on the relative orientation of the alkyl groups (Table IV). It is convenient to label the two inequivalent methyl sites in $Zr(acac)_4$ as "inner" and "outer" (cf. Figure 6); the inner sites lie directly above the nearest-neighbor chelate ring on the opposite square face, whereas the outer sites are further removed from this chelate ring. The seven $Zr(dmh)_4$ geometric isomers differ in the number and orientation of the alkyl groups of one type, say t-C_4H_9, in the inner and outer sites. There are no obvious steric or electronic reasons for ruling out any of these geometric isomers, and previous studies of octahedral complexes which contain unsymmetrical β-diketonate ligands indicate that all possible geometric isomers are present in solution in close to random statistical relative concentrations.[31] Therefore, we might have expected as many as 16 t-C_4H_9, 16 CH_3, and 16 CH resonances in low-temperature NMR spectra of $Zr(dmh)_4$ (cf. Table IV); the 16 resonances for each type of group would be of equal intensity for a statistical equilibrium mixture of the seven geometric isomers. Since only two t-C_4H_9, two CH_3, and one CH resonances are observed, it is evident that these groups are insensitive probes of the overall symmetry of the molecule. Evidently the resonance frequencies of the alkyl groups are determined by the local site symmetry. We suggest that one of the alkyl resonances arises from all of the alkyl groups in inner sites, and the other from all of the alkyl groups in outer sites.[32]

Since the low-temperature ^{19}F NMR spectrum of $Zr(tfac)_4$ exhibits four CF_3 resonances, the CF_3 groups are probes of more than local site symmetry (inner/outer), but they still do

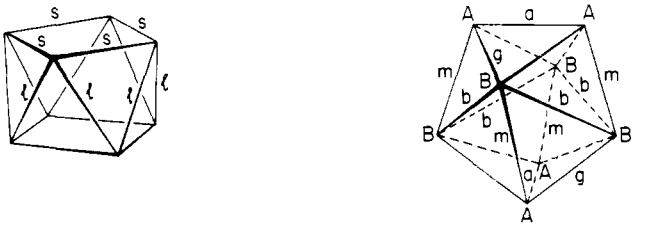

Figure 4. The D_{4d} square antiprism and the D_{2d} dodecahedron with vertices and edges labeled according to Hoard and Silverton.[26]

Table IV. Geometric Isomers for $Zr(dmh)_4$ Assuming an SAP Coordination Polyhedron and an *ssss* Ligand Wrapping Pattern

location of t-C_4H_9 in	location of t-C_4H_9 out	symmetry	no. of t-C_4H_9 resonances[a]
4[b]	0[b]	D_2	1
3	1	C_1	4
2	2	$C_2(x)$	2
2	2	$C_2(y)$	2
2	2	$C_2(z)$	2
1	3	C_1	4
0	4	D_2	1

[a] The number of CH_3 and CH resonances is, of course, the same. [b] These numbers are the number of t-C_4H_9 groups in "inner" and "outer" sites, respectively. See Figure 6 for a definition of the two kinds of sites.

not serve as probes of the overall symmetry of the molecule. Perhaps the CF_3 groups are able to sense whether a CF_3 or a CH_3 group is in an inner site in the nearest-neighbor chelate ring on the opposite square face, thus doubling the number of resonance lines from two to four. In any case, it is clear from Table IV and the fact that the four CF_3 resonances are of unequal intensity (~1:3:3:2) that solutions of $Zr(tfac)_4$ contain more than one geometric isomer.

In the solid state, $Zr(acac)_2(NO_3)_2$ exists as the dodecahedral *mmmm*-C_2 stereoisomer in which the *m* edges of each trapezoid contain one acac ligand and one NO_3^- ligand. The reasons for the stability of this particular stereoisomer have been discussed.[16] The NMR spectra of $Zr(acac)_2(NO_3)_2$ in the slow-exchange limit (two CH_3 resonances and one CH resonance) suggest that this complex exists in solution as a single stereoisomer having twofold symmetry. While these spectra do not define a unique structure, they are fully consistent with the *mmmm*-C_2 dodecahedral structure found in the solid state.

The reasons why some complexes exhibit low-temperature splitting of the NMR resonances, and others do not, are not fully understood. No doubt T_2 broadening varies considerably from one complex to another. In some cases, splitting may be obscured by the presence of many overlapping resonance lines; e.g., $Zr(acac)_3(NO_3)$ exists as the dodecahedral *abmg*-C_1 stereoisomer in the solid state[15] and may give rise to as many as six methyl resonances in solution. The isopropyl methyl resonances of $Zr(dibm)_4$ and $Zr(ipa)_4$ are broadened by spin coupling between the methyl protons and the methine proton, and these resonances may be further broadened by the fact that the isopropyl methyl groups are diastereotopic in the SAP *ssss* stereoisomer.

It is of course possible that the slow-exchange limit has not been reached in all cases. Indeed the relatively narrow resonance lines observed for the Th complexes (Table II) suggest that stereochemical rearrangement of the Th complexes is still fast on the NMR time scale at −160 to −170 °C. Since splitting of the resonance lines has been observed for several of the Zr complexes, it seems to us unlikely that any of the Zr com-

Table V. NMR Line-Shape Parameters and Rate Constants for Exchange of Methyl Groups in $Zr(acac)_4$[a]

temp, °C	$\delta\nu_e$,[b] Hz	line widths,[c] Hz $\Delta_{3/4}$	$\Delta_{1/2}$	$\Delta_{1/4}$	k, s^{-1}
−128.0		1.99	3.51	5.94	147
−137.0		3.70	6.21	10.27	52.0
−140.0		4.85	8.30	13.72	39.3
−143.0		6.62	10.74	16.84	28.4
−144.0		8.80	12.75	17.57	23.6
−145.0		10.20	14.63	20.52	19.7
−146.0	7.7				14.5
−150.0	9.35				10.0
−152.0	10.1				7.23
	$\delta\nu^d$ = 11.1 Hz; T_c^e = −145 °C				

[a] 10 mg/mL in $CHClF_2$. [b] Observed frequency separation at 90 MHz. [c] Full line width at designated fraction of maximum amplitude. [d] Frequency separation in the slow-exchange limit. [e] Coalescence temperature.

Table VI. NMR Line-Shape Parameters[a] and Rate Constants for Exchange of Methyl Groups in $Zr(acac)_2(NO_3)_2$[b]

temp, °C	$\delta\nu_e$, Hz	r[c]	line widths, Hz $\Delta_{3/4}$	$\Delta_{1/2}$	$\Delta_{1/4}$	k, s^{-1}
−132.2			2.77	4.90	7.12	120
−137.0			4.00	7.10	11.90	68.5
−140.1			6.65	11.00	16.80	42.8
−142.2			7.75	12.55	20.15	36.6
−143.3			8.70	13.60	20.95	33.3
−144.3			11.15	16.30	23.00	26.3
−145.4	6.58	1.04	14.55			21.3
−146.4	9.07	1.13				18.6
−148.5	11.7	1.36	7.00			12.2
−152.5	12.6	2.08	4.86	9.35		6.98
	$\delta\nu$ = 13.5 Hz; T_c = −144 °C					

[a] Symbols are defined in Table V. [b] 10 mg/mL in $CHClF_2$. [c] Ratio of the maximum amplitude to the amplitude at the central minimum.

Table VII. NMR Line-Shape Parameters[a] and Rate Constants for Exchange of *tert*-Butyl Groups in $Zr(dmh)_4$[b]

temp, °C	$\delta\nu_e$, Hz	r	line widths, Hz $\Delta_{3/4}$	$\Delta_{1/2}$	$\Delta_{1/4}$	k, s^{-1}
−107.0			3.64	6.08	9.97	60.5
−110.0			5.73	9.48	14.87	40.3
−111.0			6.68	10.95	15.97	35.3
−114.0			9.59	13.83	19.11	26.6
−116.0			11.81	15.44	20.43	22.4
−117.3	7.8	1.14	13.16	16.47		18.5
−118.5	9.7	1.35				15.1
−120.0	10.6	1.58	4.76			12.8
	$\delta\nu$ = 12.5 Hz; T_c = −116 °C					

[a] Symbols are defined in Tables V and VI. [b] 10 mg/mL in $CHClF_2$.

plexes are still nonrigid on the NMR time scale at −160 to −170 °C. We can draw no conclusions about the Ce complexes. Previous work on $M(dik)_2X_2$ complexes (M = Ti, Zr; X = Cl, Br)[33,34] suggests that rates of stereochemical rearrangement of $M(dik)_4$ complexes should increase with increasing size of the metal atom (Zr, Hf < Ce < Th).

Kinetics of Stereochemical Rearrangements. Rate constants k for exchange of acetylacetonate methyl groups (or dmh *tert*-butyl groups) between the two inequivalent sites of $Zr(acac)_4$, $Zr(acac)_2(NO_3)_2$, and $Zr(dmh)_4$ are listed in Tables V–VII along with NMR line-shape parameters. Arrhenius

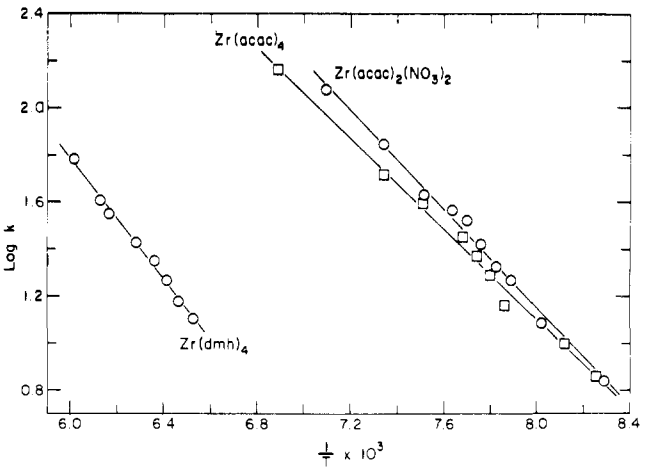

Figure 5. Arrhenius plots for exchange of acetylacetonate methyl groups in $Zr(acac)_4$ and $Zr(acac)_2(NO_3)_2$, and dmh *tert*-butyl groups in $Zr(dmh)_4$.

Table VIII. Kinetic Data for Methyl or *tert*-Butyl Group Exchange in Zr(IV) β-Diketonate Complexes[a]

	$Zr(acac)_4$[b]	$Zr(acac)_2(NO_3)_2$[b]	$Zr(dmh)_4$[c]
T_c, °C	−145	−144	−116
$k_{25°C}$, s^{-1}	4.7×10^5	1.4×10^6	1.7×10^5
$k_{-125°C}$, s^{-1}	2.0×10^2	2.9×10^2	6.8
$\Delta G^{\ddagger}$ (−125 °C), kcal/mol	6.90 ± 0.06	6.80 ± 0.05	7.90 ± 0.03
$\Delta H^{\ddagger}$, kcal/mol	4.1 ± 0.3	4.5 ± 0.3	5.5 ± 0.5
$\Delta S^{\ddagger}$, eu	−18.7 ± 2.5	−15.2 ± 2.5	−16.2 ± 2.9
E_a, kcal/mol	4.4 ± 0.3	4.8 ± 0.3	5.8 ± 0.5
log A	8.8 ± 0.6	9.5 ± 0.5	9.4 ± 0.6

[a] In $CHClF_2$ solution. All errors are random errors estimated at the 95% confidence level. [b] Methyl group exchange. [c] *tert*-Butyl group exchange.

and Eyring activation parameters were obtained in the usual way from the least-squares straight lines of log k vs. $1/T$ plots (Figure 5) and log (k/T) vs. $1/T$ plots, respectively. The activation parameters are presented in Table VIII along with coalescence temperatures, extrapolated values of k at 25 °C, and values of k and $\Delta G^{\ddagger}$ at a common temperature near the coalescence regions (−125 °C). The data for $Zr(dmh)_4$ were obtained from an analysis of the *tert*-butyl line shapes because of the greater signal to noise ratio for the *tert*-butyl resonances; however, the methyl line shapes were similar and the coalescence temperature was the same. A detailed line-shape analysis was not performed for $Hf(acac)_4$, but the methyl line shapes are similar to those for $Zr(acac)_4$ and the coalescence temperatures for the Zr and Hf compounds are almost identical (−145 and −149 °C, respectively).

As expected from the low coalescence temperatures, the rearrangement rates are fast (~10^5–10^6 s^{-1} at 25 °C) and the activation energy barriers are low (4–6 kcal/mol). Comparison of the data for $Zr(acac)_4$ and $Zr(dmh)_4$ indicates that substitution of an electron-releasing *tert*-butyl group for a methyl group decreases the rate by a factor of ~30 at −125 °C and increases the activation energy by 1.4 kcal/mol. The activation entropies are quite highly negative for all three complexes (−15 to −19 eu). Because errors in the determination of the temperature-dependent transverse relaxation times T_2 can have a significant effect on the activation parameters derived from NMR line-shape analysis, the line shapes for $Zr(acac)_4$ were reanalyzed using T_2 values which are appreciably smaller and appreciably larger than our best estimates of T_2 obtained by

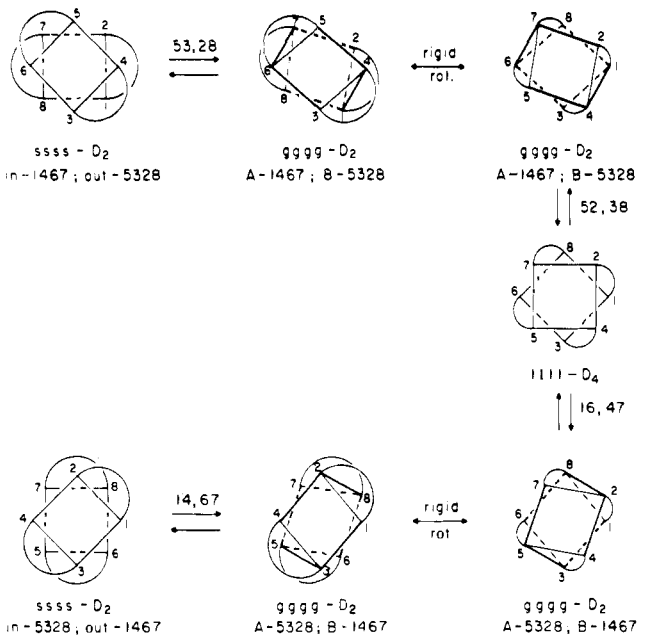

Figure 6. Exchange of β-diketonate alkyl groups between the inner and outer sites of the square antiprismatic *ssss*-D_2 stereoisomer by a series of Hoard-Silverton rearrangements. The DD stereoisomers are viewed along a twofold axis so as to emphasize the relation between the square faces of the SAP and the "diamond faces" of the DD. The BAAB trapezoids of the DD are outlined by thicker lines; the two thick lines which connect the two "diamond faces" represent the dodecahedral *a* edges. Numbers represent ligand donor atoms, and the numbers above the arrows specify which face diagonals are compressed on going from the SAP to the DD, or which *b* edges are elongated on going from the DD to the SAP.

extrapolating log $\Delta_{1/2}$ vs. $1/T$ plots into the coalescence region. Using the smaller T_2 values, derived from the broader methyl resonance of Th(acac)$_4$, increases E_a to 5.4 ± 0.5 kcal/mol and $\Delta S^{\ddagger}$ to −12.5 ± 4.0 eu. Using the larger T_2 values, derived from the sharper methyl resonance of Zr(tfac)$_4$, decreases E_a to 4.1 ± 0.4 kcal/mol and $\Delta S^{\ddagger}$ to −23.0 ± 3.0 eu. Thus, $\Delta S^{\ddagger}$ for Zr(acac)$_4$ remains quite highly negative even when unrealistically small T_2 values are used in the line-shape analysis.

Mechanism of Stereochemical Rearrangements. Three classes of mechanisms may be considered for the rearrangement of eight-coordinate tetrakis chelates: (1) intermolecular mechanisms involving complete dissociation of a bidentate ligand, catalysis by trace amounts of free ligand present as an impurity, or intermolecular ligand exchange between two molecules of complex; (2) one-bond rupture or "arm off" mechanisms involving formation of a seven-coordinate intermediate, followed by intramolecular rearrangement of the intermediate and subsequent ring closure to regenerate the tetrakis chelate; (3) polytopal rearrangement mechanisms, which effect rearrangement without rupture of any metal-ligand bonds.

Intermolecular mechanisms for rearrangement of the complexes studied in this work can be ruled out on the basis of the following experimental evidence: (1) NMR spectra of 1:4 molar mixtures of Zr(acac)$_4$ and Hacac, Zr(acac)$_2$(NO$_3$)$_2$ and Hacac, and Zr(dmh)$_4$ and Hdmh in CHClF$_2$ exhibit, in the coalescence region, a separate resonance for the complex and a separate, sharp resonance for the free diketone. (2) Previous studies of ligand exchange between M(dik)$_4$ complexes (M = Zr, Hf; dik = acac, tfac) and the free diketone indicate that temperatures in the neighborhood of room temperature or above are required before ligand exchange becomes fast on the NMR time scale.[35] (3) Intermolecular ligand exchange between M(acac)$_4$ and M(tfac)$_4$ (M = Zr, Hf) is still slow on the NMR time scale at 168 °C.[2]

Polytopal rearrangement mechanisms are attractive mechanisms for rearrangement of eight-coordinate complexes because the various idealized eight-coordination polyhedra are readily interconverted by relatively small displacements of the ligand donor atoms.[6,26,36-42] The two most common eight-coordination polyhedra, the D_{4d} square antiprism and the D_{2d} dodecahedron, are interconverted in one step by the Hoard-Silverton rearrangement[26] (Figure 6). The DD may be generated from the SAP by a motion that involves compression along one diagonal of each square face of the SAP (53 and 28 for the first rearrangement in Figure 6) and simultaneous elongation along the other diagonal of each square face (46 and 17). The effect of this motion is to convert the two square faces of the SAP into "diamond faces" of the DD. However, because the metal-ligand bond distances are fixed in the hard-sphere model, the compression and elongation of the square faces are subject to the constraint that the ligand donor atoms move on the surface of a sphere. Thus, the square faces must fold about the compressed diagonals (53 and 28), and these diagonals become two of the *b* edges (cf. Figure 4) of the product DD. Therefore each "diamond face" of the DD is really a pair of triangular faces which join along a *b* edge and which terminate at two of the A sites (Figure 4). Because the *b* edges of the DD are 25% longer than the *a*, *m*, and *g* edges, the elongation and compression of the square faces of the SAP must also be accompanied by a small amount of tetragonal twisting. For example, the bottom square face of the first SAP in Figure 6 (1278) is twisted clockwise with respect to the top square face (3456) so as to lengthen the *b* edges (52 and 38) of the product DD relative to the *a*, *m*, and *g* edges. The amount of twisting required is ~10° since the dihedral angle between the diagonals 53 and 28 in the SAP is 45.0° and the dihedral angle between the *b* edges 53 and 28 in the hard sphere DD is 55.3°.

The product DD can return to the starting SAP by elongation of the *b* edges 53 and 28, or it can rearrange to a new SAP by elongation of the other pair of *b* edges, 52 and 38. If the initial SAP complex is a tetrakis chelate having the *ssss*-D_2 wrapping pattern, the DD intermediate (or transition state) is the *gggg*-D_2 stereoisomer and the product SAP complex is the *llll*-D_4 stereoisomer. The *llll*-D_4 stereoisomer can then revert to the original *ssss*-D_2 isomer by the reverse path, or it can convert to a new *ssss*-D_2 stereoisomer by compression of the 16 and 47 face diagonals of the SAP followed by elongation of the 14 and 67 *b* edges of the intermediate DD. Note that this sequence of Hoard-Silverton rearrangements exchanges ligand donor atoms between the inner and outer sites of the *ssss*-D_2 stereoisomer, thus providing a mechanism for exchange of alkyl groups in Zr(acac)$_4$ and Zr(dmh)$_4$. This mechanism should have a relatively low activation energy since examples of the intermediate *gggg*-D_2 and *llll*-D_4 stereoisomers are known for tetrakis(β-diketonates); the *gggg*-D_2 configuration has been found for Pr(tta)$_4^-$ [43] and Y(hfac)$_4^-$ [44] (tta = thenoyltrifluoroacetonate; hfac = hexafluoroacetylacetonate), and the *llll*-D_4 structure is known for Nb(dpm)$_4$[45] and Th(tfac)$_4$.[46]

A graph which summarizes the effect of the Hoard-Silverton rearrangement on all nine SAP and DD stereoisomers is presented in Figure 7. This graph embodies the results of Porai-Koshits and Aslanov,[40] but takes account of the fact that seven of the stereoisomers are chiral. The graph displays a vertical mirror plane, with the two nonchiral DD stereoisomers (*mmmm*-D_{2d} and *gggg*-S_4) lying in the mirror plane and the enantiomers of the chiral stereoisomers being symmetrically disposed on opposite sides of the plane. Several interesting features of this graph are worthy of comment: (1) The connectivity at the vertices occupied by the DD stereoisomers having no ligands on *b* edges is two because there are two ways of elongating a pair of opposite *b* edges. (2) The graph terminates at vertices occupied by the *aabb*-D_2 and *abmg*-C_1 DD stereoisomers because there is only one way of elongating a pair

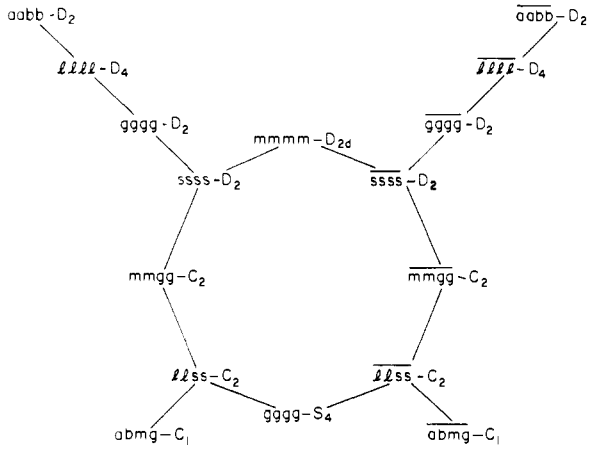

Figure 7. Interconversion of square antiprismatic and dodecahedral stereoisomers of a tetrakis(bidentate) chelate complex via the Hoard-Silverton rearrangement.

of opposite *b* edges when one or two of the four *b* edges are spanned by bidentate ligands. (3) The connectivity of the vertices occupied by SAP stereoisomers is two or three, depending on the symmetry of the stereoisomer. (4) Enantiomers can only be interconverted via the nonchiral DD stereoisomers *mmmm*-D_{2d} and *gggg*-S_4.

The reaction path depicted in Figure 6 corresponds to the *ssss*-$D_2 \rightleftarrows$ *gggg*-$D_2 \rightleftarrows$ *llll*-D_4 portion of the graph in Figure 7. An alternative path for exchange of alkyl groups between the inner and outer environments would involve the reaction sequence *ssss*-$D_2 \rightarrow$ *mmgg*-$C_2 \rightarrow$ *llss*-$C_2 \rightarrow$ *gggg*-$S_4 \rightarrow$ *llss*-$C_2 \rightarrow$ *mmgg*-$C_2 \rightarrow$ *ssss*-D_2. However, this path is considered less likely because the intermediate stereoisomers have not been observed for β-diketonate complexes. The reaction sequence *ssss*-$D_2 \rightarrow$ *mmmm*-$D_{2d} \rightarrow$ *ssss*-D_2 interconverts enantiomers but does not exchange alkyl groups between the inner and outer environments.

Rearrangement of the mixed ligand complex $Zr(acac)_2(NO_3)_2$ involves exchange of acetylacetonate methyl groups between the A and B sites of the DD *mmmm* stereoisomer. This can occur via the polytopal rearrangement: *mmmm* $\rightleftarrows$ *ssss* $\rightleftarrows$ *gggg* $\rightleftarrows$ *llll*.

Our experimental results provide no definitive basis for distinguishing between polytopal rearrangement and one-bond rupture mechanisms, although the highly negative activation entropies (Table VIII) tend to support polytopal rearrangement. Previous studies of octahedral β-diketonate complexes have yielded negative values of $\Delta S^{\ddagger}$ for complexes which are believed to rearrange by a twist mechanism (−6 to −14 eu for $Ti(dik)_2(OR)_2$[47]) and positive values of $\Delta S^{\ddagger}$ for complexes which rearrange by a one-bond rupture mechanism (+7 to +12 eu for $Co(dik)_3$[31c,d]). Furthermore, as has been pointed out by Muetterties,[6] polytopal rearrangement seems more likely on grounds of pure simplicity.

On the other hand, two lines of evidence can be cited in support of a bond rupture mechanism. First, rates and activation parameters for $Zr(acac)_4$ and $Zr(acac)_2(NO_3)_2$ (Table VIII) are closely similar. This similarity is easily understood if both complexes rearrange via opening of a metal–acetylacetonate ring, but it is somewhat surprising if the mechanism is polytopal rearrangement. $Zr(acac)_2(NO_3)_2$ might be expected to exhibit a higher activation energy for polytopal rearrangement because the bite of the nitrate ligand is too short to properly span the *s* and *l* edges of the SAP intermediates. Second, the Hoard-Silverton rearrangement does not account for coalescence of the four CF_3 resonances of $Zr(tfac)_4$. It is of course possible that $Zr(tfac)_4$ rearranges by a bond rupture mechanism while the other Zr complexes undergo polytopal rearrangements. The electron-withdrawing CF_3 group may weaken the nearest-neighbor Zr–O bond, thus facilitating Zr–O bond rupture. Indeed Pickering et al.[25] have suggested that Al(III) β-diketonates rearrange by a bond rupture mechanism when the diketonate ligands carry fluorocarbon substituents but they rearrange by a twist mechanism when the substituents are alkyl or aryl groups.

Acknowledgment. The support of this research by the National Science Foundation is gratefully acknowledged.

References and Notes

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