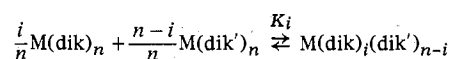


Redistribution Reactions of d<sup>0</sup> Metal Diketonates Containing MO<sub>6</sub> and MO<sub>8</sub> Cores

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Several ligand redistribution equilibria for six-coordinated aluminum and eight-coordinated zirconium diketonates in solvents of low donor ability have been studied by means of nmr spectroscopy in order to assess the factors influencing the stabilization of mixed-ligand d<sup>0</sup> metal complexes containing MO<sub>6</sub> and MO<sub>8</sub> cores. The equilibria are of the type

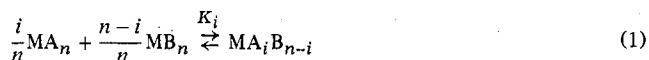


where dik and dik' are distinguishable diketonate ligands,  $n = 3$  when  $M = \text{Al(III)}$  or  $n = 4$  when  $M = \text{Zr(IV)}$ , and  $i = 1, 2, \dots, n - 1$ . The results, along with those reported previously for related systems, show that when dik and dik' both possess protonated terminal groups (type I exchange), the values of  $K_i$  are equal to or slightly smaller than the values expected for a random statistical distribution of ligands. However, when one diketonate is protonated and the other is fluorinated (type II exchange), the equilibrium constants are  $10^2$ – $10^5$  times larger than the statistical values. The impetus for type I reactions is due to entropy effects; enthalpy changes are zero or nearly zero within experimental error. Substantial exothermic enthalpy changes ( $-1.2$  to  $-5.5$  kcal/mol) and entropy changes which are somewhat larger ( $1.5$ – $4.8$  eu) than the values expected for random exchange are associated with type II reactions. The enthalpy changes are attributed mainly to differences in mean metal–oxygen bond energies between the mixed-ligand and parent complexes. No appreciable dependence on solvent polarity over the dielectric constant range 2.2–34.8 was observed for the enthalpy changes for acetylacetonate–hexafluoroacetylacetonate exchange on aluminum. Decreases in the repulsive energies between the donor oxygen atoms of the diketonate ligands probably play an important role in the stabilization of the mixed complexes formed in the type II reactions.

## Introduction

Redistribution reactions, first described more than 40 years ago by Calingaert and Beatty,<sup>1,2</sup> continue to be of interest<sup>3–10</sup> in part because of their importance in chemical syntheses<sup>6,7,9</sup> and utility as models in understanding the discriminating behavior of metal ions and ligands in biological systems.<sup>10</sup>

An important feature of a redistribution reaction between two binary parent complexes MA<sub>n</sub> and MB<sub>n</sub> to form the mixed-ligand complexes MA<sub>i</sub>B<sub>n-i</sub>, where  $i = 1, 2, \dots, n - 1$ , is the occurrence of  $n - 1$  independent equilibria



Depending on the nature of the metal ion and ligands, the values of  $K_i$  in some cases lie near those expected for a random statistical distribution of ligands, whereas in others the equilibria deviate markedly from statistical scrambling. The mixed complexes are often strongly favored when the ligands differ in charge or electronic structure, as in the reaction of As(NMe<sub>2</sub>)<sub>3</sub> and AsCl<sub>3</sub><sup>11</sup> or the exchange of 2,2'-bipyridyl with the pyrocatechol dianion on divalent metal ions.<sup>12,13</sup> However, large deviations from random scrambling can occur

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even when the parent and mixed complexes have the same inner coordination sphere of donor atoms. Ligand exchange between distinguishable nickel-bis(dithiolene) complexes containing NiS<sub>4</sub> cores, for example, strongly favors the mixed complexes.<sup>14</sup> In contrast, random scrambling has been observed for the exchange of N-substituted salicylaldiminate ligands on nickel.<sup>15</sup>

The reactions of d<sup>0</sup> metal-tris(β-diketonato) complexes provide an excellent example of the large substituent effects which can occur in the exchange equilibria between complexes containing MO<sub>6</sub> cores.<sup>16,17</sup> Although near-random scrambling is observed when the terminal groups of the distinguishable diketonates are both protonated, the mixed complexes are favored when one ligand possesses protonated terminal groups and the other possesses fluorinated groups. For the reaction of Ga(acac)<sub>3</sub><sup>18</sup> and Ga(bzbx)<sub>3</sub> in benzene, the values of  $K_i$  at 25° are only ca. 20% smaller than the values expected for random scrambling, whereas in the reaction of Ga(acac)<sub>3</sub> and Ga(hfac)<sub>3</sub> they are ca. 400 times larger than the statistical values.<sup>16</sup> The deviations from random scrambling in the latter system are due mainly to exothermic enthalpy changes, but the factors contributing to the enthalpy changes have not yet been ascertained. Several redistribution reactions have been reported for metal β-diketonates containing MO<sub>8</sub> cores (M = Zr(IV),<sup>19,20</sup> Hf(IV),<sup>19,20</sup> Ce(IV),<sup>20</sup> Th(IV),<sup>20</sup> U(IV),<sup>21</sup> or Y(III)<sup>22,23</sup>), but only relatively small deviations from ran-

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- (18) The following ligand abbreviations are used throughout: acac, acetylacetonate; bzbx, dibenzoylmethanate; dpm, dipivaloylmethanate; hfac, hexafluoroacetylacetonate; tfac, trifluoroacetylacetonate; β-T, β-isopropyltropolonate.
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dom scrambling have been observed for the ligand systems studied thus far.

We have undertaken a study of several redistribution reactions of aluminum and zirconium diketonates, with special emphasis being placed on ligand systems that lead to large deviations from random scrambling. The results, together with those previously reported for related systems, allow some conclusions to be reached on the behavior of  $d^0$  metal  $\beta$ -diketonate exchange equilibria in general.

### Experimental Section

**Syntheses.** Previously reported methods were used for the preparation and purification of  $\text{Al}(\text{acac})_3$ ,<sup>24</sup>  $\text{Al}(\text{hfac})_3$ ,<sup>25</sup> and  $\text{Zr}(\text{acac})_4$ .<sup>26</sup> The melting points of the compounds were in good agreement with the literature values, and their proton nmr spectra indicated the absence of organic impurities. Dipivaloylmethane was prepared according to the method described by Adams and Hauser.<sup>27</sup> Hexafluoroacetylacetone was prepared by the alkaline condensation of ethyl trifluoroacetate and 1,1,1-trifluoroacetone<sup>28-30</sup> to obtain the sodium salt of the diketone, conversion of the salt to hexafluoroacetylacetone dihydrate, and its subsequent dehydration with  $\text{P}_4\text{O}_{10}$ .<sup>31</sup>

**Tris(1,3-diphenyl-1,3-propanedionato)aluminum(III).** Reagent grade dioxane was further purified for use as a solvent allowing it to reflux over freshly cut sodium for 24 hr prior to distillation. To a mixture of dibenzoylmethane (2.82 g, 12.6 mmol) and sodium (0.29 g, 12.6 mg-atom) in 80 ml of purified dioxane at reflux temperature was added a solution of aluminum(III) chloride (0.56 g, 4.2 mmole) in 30 ml of dioxane. After a reaction time of 1 hr the hot solution was filtered through a sintered-glass disk, and the filtrate was concentrated by boiling off half of the solvent. Cooling the concentrated filtrate in an ice bath afforded a pale yellow crystalline product. The product was recrystallized from benzene-hexane and then dried *in vacuo* at 100° for 1 hr; mp 307-310°. The yield was 1.77 g (60%).

*Anal.* Calcd for  $\text{Al}(\text{C}_{15}\text{H}_{11}\text{O}_2)_3$ : C, 77.58; H, 4.77; Al, 3.87. Found: C, 77.80; H, 4.90; Al, 4.05.

**Tetrakis(1,1,1,5,5,5-hexafluoro-2,5-pentanedionato)zirconium(IV).** This compound was prepared by reaction of zirconium(IV) chloride and hexafluoroacetylacetone.<sup>32</sup> Since the reactants and product are hygroscopic, the reaction and subsequent manipulation of the product were carried out under a dry argon atmosphere. To a slurry of zirconium(IV) chloride (2.78 g, 11.9 mmol) in 50 ml of dry carbon tetrachloride was added dropwise hexafluoroacetylacetone (6.80 ml, 47.7 mmol). When the evolution of HCl subsided, the reaction mixture was heated at reflux temperature for 15 min. The solvent was then removed under vacuum at room temperature. The solid residue was slurried in 150 ml of dry hexane, and the small insoluble fraction was removed by filtration through a sintered-glass disk. The volume of the hexane solution was reduced to ca. 75 ml by vacuum distillation of solvent at room temperature. Cooling the solution in ice yielded white crystals, which were recrystallized from hexane and dried *in vacuo* at room temperature for 1 hr. The melting point of the product in a sealed capillary (48.5-49°) was not in good agreement with that reported<sup>32</sup> for the compound when purified by sublimation (39-42°). Therefore, the product was analyzed.

*Anal.* Calcd for  $\text{Zr}(\text{C}_5\text{HO}_2\text{F}_6)_4$ : C, 26.12; H, 0.44; F, 49.59; Zr, 9.92. Found: C, 25.89; H, 0.42; F, 48.66; Zr, 9.62.

**Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium(IV).** This compound was prepared by metathesis reaction of  $\text{Zr}(\text{acac})_4$  and dipivaloylmethane. A mixture of zirconium acetylacetonate (4.75 g, 9.89 mmol) and dipivaloylmethane (24.5 g, 133 mmol) was stirred in

a three-neck round-bottom flask equipped with a distilling head and an inlet tube for dry nitrogen. The flask was immersed in an oil bath at 140-145° until 7.0 ml of acetylacetone and dipivaloylmethane was distilled from the reaction mixture (ca. 24 hr). Cooling the mixture in an ice bath gave a crystalline product which was collected by filtration. The product was repeatedly recrystallized from benzene until the absence of a free dipivaloylmethane impurity was verified by proton nmr spectroscopy. The colorless crystals were dried *in vacuo* at 100° for 1 hr; mp 346-350°. The compound has been previously reported<sup>33</sup> to be an orange solid which, when purified by sublimation, melts in the range 330-332°. The discrepancies in the color and melting point necessitated elemental analyses.

*Anal.* Calcd for  $\text{Zr}(\text{C}_{11}\text{H}_{19}\text{O}_2)_4$ : C, 64.11; H, 9.29; Zr, 11.07. Found: C, 64.69; H, 9.45; Zr, 11.08.

**Tetrakis( $\beta$ -isopropyltropolonato)zirconium(IV).** This compound was prepared by using a method similar to that described previously for the analogous tropolonate derivative.<sup>34</sup> To a solution of  $\beta$ -isopropyltropolone (3.94 g, 24.0 mmole) in 40 ml of chloroform was added slowly a slurry of zirconium(IV) chloride (1.40 g, 6.00 mmol) in 80 ml of chloroform under an atmosphere of dry nitrogen. After a reaction time of 2 hr at room temperature the reaction mixture was filtered, yielding a clear yellow filtrate. The volume of the filtrate was reduced to ca. 50 ml by boiling off some solvent, and then an equal volume of hexane was added. A massive cream-colored precipitate formed. This was collected by filtration, washed with hexane, and recrystallized from benzene-hexane. The crystals were dried *in vacuo* at 100° for 20 hr; mp 173-174°.

*Anal.* Calcd for  $\text{Zr}(\text{C}_{16}\text{H}_{11}\text{O}_2)_4$ : C, 64.54; H, 5.92. Found: C, 64.60; H, 5.96.

### Preparation of Solutions and Equilibration of Reaction Mixtures.

All solvents were reagent grade. Dioxane was purified by heating at reflux temperature over freshly cut sodium for at least 1 hr prior to distillation in a dry nitrogen atmosphere. 1,2-Dichloroethane was washed with 5% potassium hydroxide, dried over  $\text{P}_4\text{O}_{10}$ , and freshly distilled before use. Nitrobenzene was washed successively with 1:1  $\text{H}_2\text{SO}_4$ , water, and 1 M NaOH, with the last washing repeated until a colorless wash solution was obtained. The nitrobenzene was then washed with water, allowed to stand over molecular sieves for 1 day, and vacuum distilled from over a fresh supply of molecular sieves. Benzene was dried over lithium aluminum hydride; chlorobenzene was dried over calcium hydride. For a given reaction system, the two parent complexes were weighed into tared screw-cap vials, and the desired volume of solvent was added in a dry nitrogen atmosphere to avoid possible hydrolysis in solution. All weighings of  $\text{Zr}(\text{hfac})_4$  were conducted under anhydrous conditions as this compound is hygroscopic in the solid state.

At the concentrations and ligand compositions employed (see below) the parent complexes for the zirconium diketonate exchange systems dissolved readily at room temperature. However, the aluminum complexes were very slow to dissolve at room temperature, the rate of dissolution being in part dependent on the rate of ligand exchange. Thus the dissolution of the aluminum complexes was hastened by heating to ca. 64° in a boiling methanol bath. Attempts to hasten the dissolution of  $\text{Al}(\text{acac})_3$ - $\text{Al}(\text{hfac})_3$  mixtures by heating them above the melting point of  $\text{Al}(\text{hfac})_3$  (73-74°) led to decomposition and irreproducible equilibrium quotients. Similar decomposition problems have been encountered previously in the dissolution of analogous gallium complexes.<sup>16</sup> It is to be emphasized, however, that when homogeneous solutions of  $\text{Al}(\text{acac})_3$  and  $\text{Al}(\text{hfac})_3$  were achieved, the solutions were stable to temperatures as high as 138° and the experimental equilibrium constants were reproducible. All solutions were transferred to nmr tubes, and the tubes were sealed with a flame.

Less than 10 min at temperatures above 12° was required for equilibration of zirconium diketonate exchange reactions. Thus these reaction systems were conveniently equilibrated in the probe of the nmr spectrometer. The aluminum systems were appreciably less labile. Equilibration at temperatures in the range 60-138° was achieved by suspending the nmr tubes in the vapors of a suitable refluxing liquid. The following times were found to be adequate for equilibration of both the  $\text{Al}(\text{acac})_3$ - $\text{Al}(\text{bzbz})_3$  and  $\text{Al}(\text{acac})_3$ - $\text{Al}(\text{hfac})_3$  exchange systems: 24 hr over refluxing chloroform ( $60.0 \pm 0.3^\circ$ ); 12 hr over benzene ( $79.4 \pm 0.4^\circ$ ); 1.5 hr over water ( $100.2 \pm 0.4^\circ$ ); 0.5 hr over 1-butanol ( $117.0 \pm 0.3^\circ$ ); 0.25 hr over *m*-xylene ( $138.2 \pm 0.4^\circ$ ). After the indicated equilibration times, the solutions were quenched in ice.

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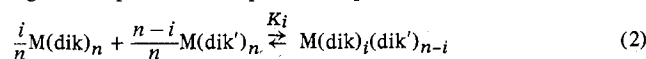
**Nmr Spectra and the Determination of Equilibrium Concentrations.** All equilibrium concentrations were determined by <sup>1</sup>H or <sup>19</sup>F nmr spectroscopy. Spectra were recorded on a Varian A56/60D analytical spectrometer operated at 60.0 (<sup>1</sup>H spectra) or 56.4 MHz (<sup>19</sup>F spectra). The probe temperature was controlled to within ±0.5° by a Varian V-6040 variable-temperature controller. The methanol and ethylene glycol nmr thermometers described by Van Geet<sup>35</sup> were used to determine probe temperatures. All spectra were recorded at sufficiently low radiofrequency field strengths to avoid saturation effects.

The equilibrium concentrations of the aluminum diketonate reaction mixtures were determined by recording their nmr spectra at 10–20° (Al(acac)<sub>3</sub>–Al(hfac)<sub>3</sub> system) or at 30° (Al(acac)<sub>3</sub>–Al(bz bz)<sub>3</sub> system) within 1 hr after quenching. Preliminary studies in each solvent indicated that detectable changes in the relative concentrations of the various species occurred only after the solutions age at least 1.5 hr at these temperatures. The concentrations of the acac-containing complexes in the Al(acac)<sub>3</sub>–Al(bz bz)<sub>3</sub> exchange reactions were determined from the heights of their acac ring proton resonances; the concentration of Al(bz bz)<sub>3</sub> was determined by difference. The necessary condition for obtaining quantitative data from peak heights, namely, that the transverse relaxation times of the nuclei be identical,<sup>36</sup> was verified by the identical half-widths for the resonance lines of each compound of different stoichiometry. The concentrations of complexes in the Al(acac)<sub>3</sub>–Al(hfac)<sub>3</sub> exchange reactions in chlorobenzene and nitrobenzene were determined by planimetric integration of the hfac fluorine resonance lines, whereas in dioxane and 1,2-dichloroethane the acac methyl proton signals were integrated. These were the best resolved sets of signals in the solvents indicated.

The redistribution reactions between Zr(acac)<sub>4</sub> and Zr(bz bz)<sub>4</sub>, Zr(β-T)<sub>4</sub>, and Zr(hfac)<sub>4</sub> were studied by integrating planimetrically the methyl proton resonances of each acac-containing species. In both the Zr(acac)<sub>4</sub>–Zr(bz bz)<sub>4</sub> and Zr(acac)<sub>4</sub>–Zr(β-T)<sub>4</sub> systems, where the resonance signals overlapped severely, the resolution of the signals facilitated by the use of a Du Pont 310 curve resolver. The Zr(dpm)<sub>4</sub>–Zr(hfac)<sub>4</sub> exchange reaction was studied by integration of *tert*-butyl proton resonance lines.

Examples of the various sets of resonance signals used in the determination of equilibrium concentrations in the aluminum and zirconium systems are shown in Figures 1–3. It is to be noted that Al(acac)<sub>2</sub>(hfac)<sub>2</sub> at 10° in nitrobenzene (*cf.* Figure 1) exhibits two fluorine resonance lines of equal intensity as expected for idealized C<sub>2</sub> symmetry, whereas Al(acac)<sub>2</sub>(hfac)<sub>2</sub> at 30° in 1,2-dichloroethane shows only a single methyl proton resonance. The existence of a single resonance line in the latter case is the result of an intramolecular rearrangement process which rapidly interchanges the nonequivalent methyl group environments on the nmr time scale. These intramolecular rearrangement processes for aluminum diketonates have been studied in considerable detail previously.<sup>17,37–41</sup> Similar rapid rearrangements are responsible for the presence of only one terminal group resonance for each zirconium diketonate complex of different stoichiometry.<sup>19,20</sup>

**Determination of Equilibrium Constants and Thermodynamic Data.** All of the equilibrium constants and thermodynamic data reported in this study correspond to the formation of 1 mol of mixed-ligand complex from the parent complex



where  $i = 1, 2, \dots, n-i$ . However, because the equilibrium concentration of one or both parent complexes is small at a given ligand composition, it was not possible to determine values of  $K_i$  directly by nmr spectroscopy. Therefore, the desired thermodynamic data for eq 2 were obtained by algebraic combination of enthalpies and entropies for an independent set of operational equilibrium constants which could be accurately determined experimentally. The set selected is defined by

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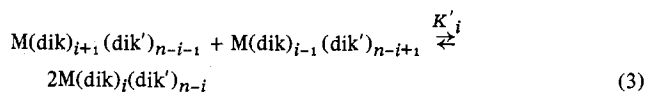
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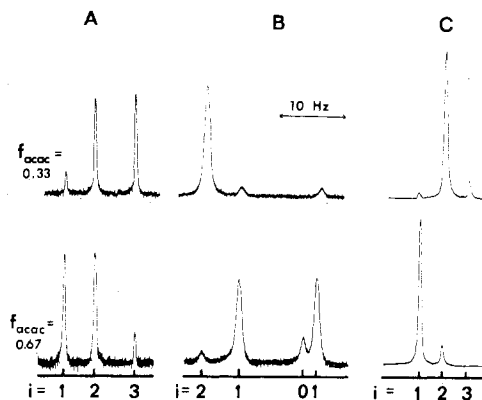
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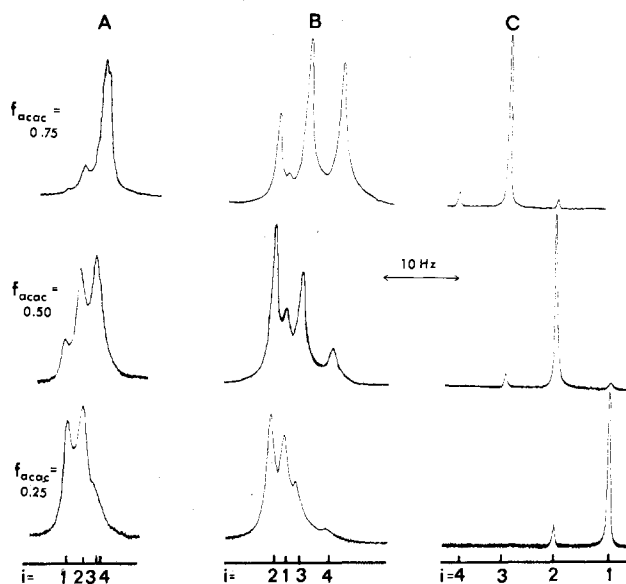
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The most accurate values of  $K_i$  were obtained at ligand compositions corresponding to the stoichiometry of each  $M(\text{dik})_i(\text{dik}')_{n-i}$  complex. Under such conditions the equilibrium concentration of the  $M(\text{dik})_i(\text{dik}')_{n-i}$  complex is optimum (*cf.* Figures 1–3). In the aluminum systems studied, where  $\text{dik} = \text{acac}$  and  $\text{dik}' = \text{bz bz}$  or  $\text{hfac}$ , the molar fraction of total ligand present as acac,  $f_{\text{acac}}$ , was 0.333 for the determination of  $K'_1$  and 0.667 for the determination of  $K'_2$ . Enthalpy and entropy changes were determined from the slopes and intercepts, respectively, of the best straight lines of  $\ln K'_i$  vs.  $1/T$  plots. At least five independent spectral determinations of  $K'_i$  at each temperature were included in the linear regression analyses. Extrapolated values of  $K'_i$  at 25° were calculated from the least squares lines. The temperature dependence of  $K'_i$  for the aluminum diketonate reactions was investigated at *ca.* 20° intervals over the range 60–138°. Values of  $K'_i$  for ligand redistribution between the eight coordinated zirconium diketonates were determined at ligand compositions of  $f_{\text{dik}} = 0.25, 0.50,$  and  $0.75$ . The temperature dependence of  $K_i$  for the



**Figure 1.** Nmr signals for equilibrium mixtures of aluminum diketonate complexes at 80° and two different values of ligand composition: A, acetylacetonate –CH= resonances of Al(acac)<sub>i</sub>(bz bz)<sub>3-i</sub> complexes in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>; B, <sup>19</sup>F resonance lines of Al(acac)<sub>i</sub>(hfac)<sub>3-i</sub> complexes in nitrobenzene; C, methyl proton resonances of Al(acac)<sub>i</sub>(hfac)<sub>3-i</sub> complexes in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>.  $f_{\text{acac}}$  defines the molar fraction of total ligand present as acetylacetonate. Spectral set A was recorded at 30°. Spectra B and C were recorded at 10°.



**Figure 2.** Acetylacetonate methyl proton resonances of equilibrium mixtures of zirconium diketonates at three different values of ligand composition: A, of Zr(acac)<sub>i</sub>(bz bz)<sub>4-i</sub> complexes in CH<sub>2</sub>Cl<sub>2</sub> at 40°; B, Zr(acac)<sub>i</sub>(β-T)<sub>4-i</sub> in 1:1 benzene–nitrobenzene at 35°; C, Zr(acac)<sub>i</sub>(hfac)<sub>4-i</sub> in benzene at 40°.  $f_{\text{acac}}$  is the molar fraction of total ligand present as acetylacetonate.

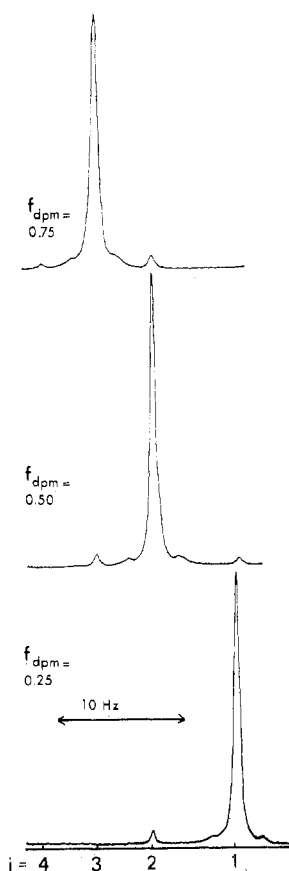


Figure 3.  $t\text{-C}_4\text{H}_9$  proton resonance lines of  $\text{Zr}(\text{dpm})_i(\text{hfac})_{4-i}$  equilibrium mixtures in benzene at  $40^\circ$ .  $f_{\text{dpm}}$  is the molar fraction of total ligand present as dipivaloylmethanate.

$\text{Zr}(\text{acac})_4\text{-Zr}(\text{hfac})_4$  system was studied at *ca.*  $12^\circ$  intervals over the range  $12\text{-}83^\circ$ .

## Results

**Aluminum Systems.** Equilibrium constants,  $K_i$  (eq 2), and thermodynamic data for the formation of several mixed aluminum(III)  $\beta$ -diketonates from their corresponding parent complexes are presented in Table I. Included in the table are the values of  $K_i$  for a random statistical distribution of ligands in which the driving force is determined only by the entropy of exchange. It is readily seen that the mixed acetylacetonate-dibenzoylmethanate complexes exhibit values of  $K_i$  which are nearly equal to that expected for random scrambling. As indicated by the experimental values of  $\Delta H$  and  $\Delta S$  in benzene and 1,2-dichloroethane solutions, the small deviations from statistical behavior can be attributed to small endothermic enthalpy effects and/or entropy changes which are somewhat smaller than the value expected for random exchange.

In marked contrast to the  $\text{Al}(\text{acac})_3\text{-Al}(\text{bzbz})_3$  system, the exchange of acetylacetonate and hexafluoroacetylacetonate strongly favors the mixed-ligand complexes. The extrapolated values of  $K_i$  at  $25^\circ$  in four different solvents over the dielectric constant range 2.2 (dioxane)-34.8 (nitrobenzene) are larger than the statistical value of 3.00 by a factor of about  $10^2$ . These deviations from random exchange are due to exothermic enthalpy changes in the range  $-1.22$  to  $-2.48$  kcal/mol and to entropy changes which are 1.5-4.0 eu larger than the statistical values. Within experimental error the values of  $\Delta H$  and  $\Delta S$  for both mixed acac-hfac complexes are independent of solvent polarity. The average values of  $\Delta H$  and  $\Delta S$  for the two complexes in the four solvents are, respectively,  $-1.71 \pm 0.26$  kcal/mol and  $5.38 \pm 0.67$  eu. Attempts to

observe the redistribution of acac and hfac in the donor solvents 2-propanol and hexamethylphosphoramide were complicated by the displacement of the coordinated diketonate ligands. Related ligand displacement reactions for  $\text{Al}(\text{acac})_3$  in dimethylformamide have been previously shown to afford cationic species of the type  $\text{Al}(\text{acac})(\text{DMF})_4^{2+}$  and  $\text{Al}(\text{acac})_2(\text{DMF})_2^{+}$ .

In an earlier study we reported equilibrium constants and thermodynamic data for the formation in benzene solution of the gallium(III) analogs of the aluminum complexes described above. The data for the formation of  $\text{Ga}(\text{acac})(\text{bzbz})_2$  and  $\text{Ga}(\text{acac})_2(\text{bzbz})$  are identical within experimental error with those presented in Table I for the aluminum derivatives. The earlier study, however, overestimated by *ca.* 20% the exothermic enthalpy changes and underestimated the entropy changes associated with the formation of  $\text{Ga}(\text{acac})(\text{hfac})_2$  and  $\text{Ga}(\text{acac})_2(\text{hfac})$ . Systematic errors were introduced by the use of erroneous nmr temperature calibration curves supplied by Varian Associates. These curves have since been corrected by Van Geet.<sup>35</sup> The redistribution reactions in the  $\text{Ga}(\text{acac})_3\text{-Ga}(\text{hfac})_3$  system have been reinvestigated in dichloromethane over the temperature range  $4.7\text{-}76.7^\circ$ . The values of  $\Delta H$  (kcal/mol) and  $\Delta S$  (eu) and the extrapolated values of  $K_i$ , respectively, are  $-2.40 \pm 0.57$ ,  $3.46 \pm 1.83$ , and  $3.29 \times 10^2$  for  $\text{Ga}(\text{acac})(\text{hfac})_2$  and  $-2.27 \pm 0.60$ ,  $3.95 \pm 1.96$ , and  $3.34 \times 10^2$  for  $\text{Ga}(\text{acac})_2(\text{hfac})$ . Thus the deviations from statistical scrambling are comparable to those observed in the analogous aluminum system.

Previous observations by Fortman and Sievers<sup>17</sup> of ligand redistribution reactions between aluminum diketonates in chlorobenzene are in qualitative agreement with the results of the present study. Slightly less than statistical scrambling was observed between the acetylacetonate and dipivaloylmethane complexes. Thus the  $\text{Al}(\text{acac})_3\text{-Al}(\text{dpm})_3$  and  $\text{Al}(\text{acac})_3\text{-Al}(\text{bzbz})_3$  systems, both of which involve exchange of ligands containing protonated terminal groups, exhibit similar equilibria. Fortman and Sievers also observed large deviations from random scrambling for the exchange of acac, as well as dpm, with hfac on aluminum, but no thermodynamic data were reported.<sup>43,44</sup>

**Zirconium Systems.** Equilibrium constants and thermodynamic data for the formation of some mixed eight-coordinated zirconium diketonates are set out in Table II. As in the case of six-coordinated aluminum, the exchange of acac and bzbz exhibits values of  $K_i$  which are only slightly less than those expected for random exchange. Similar results are observed for the exchange of acac and  $\beta$ -isopropyltropolonate on zirconium, despite the differences in chelate ring size and steric requirements of the ligands. Values of  $K_i$  up to 3.6 times larger than the statistical values have been observed for the exchange of 2-thenoyltrifluoroacetone and  $\beta$ -T on copper(II) and zinc(II) in  $\text{CCl}_4$  and  $\text{CHCl}_3$  solution,<sup>45</sup> but in these systems one of the diketonates is partially fluorinated.

In the exchange of acac and hfac on zirconium the mixed complexes are favored over the parent complexes to a much

(42) W. G. Movius and N. A. Matviyoff, *J. Amer. Chem. Soc.*, **90**, 5452 (1968).

(43) The equilibrium constants reported by Fortman and Sievers for the  $\text{Al}(\text{acac})_3\text{-Al}(\text{hfac})_3$  system are not in acceptable quantitative agreement with those reported in the present study. Since their solutions were prepared by heating the mixtures above the melting point of  $\text{Al}(\text{hfac})_3$ , some thermal decomposition of the complexes probably occurred (*cf.* Experimental Section). However, the constants estimated earlier by Linck and Sievers<sup>44</sup> in  $\text{C}_2\text{H}_6$  and  $\text{CCl}_4$  ( $K_i \approx 300$ ) are in good agreement with the results of the present study.

(44) R. G. Linck and R. E. Sievers, *Inorg. Chem.*, **5**, 806 (1966).

(45) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 2022 (1964).

**Table I.** Equilibrium Constants and Thermodynamic Data for the Formation of Some Mixed Six-Coordinated Aluminum(III) Diketonates<sup>a</sup>

Mixed complex	Solvent	$K_i$	$\Delta H$ , kcal/mol	$\Delta S$ , eu
Al(acac)(bzbz) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	2.3 <sup>b</sup>	0.03 ± 0.20	2.63 ± 0.51
	Dioxane	2.08 <sup>c</sup> ± 0.23 <sup>d</sup>		
Al(acac) <sub>2</sub> (bzbz)	1,2-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	2.9	-0.06 ± 0.05	1.89 ± 0.13
	C <sub>6</sub> H <sub>6</sub>	2.4	0.16 ± 0.14	2.30 ± 0.39
Al(acac)(hfac) <sub>2</sub>	Dioxane	2.50 <sup>c</sup> ± 0.36 <sup>d</sup>		
	1,2-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	3.0	-0.03 ± 0.05	2.04 ± 0.10
	Dioxane	2 × 10 <sup>2</sup>	-1.39 ± 0.22	6.03 ± 0.56
	C <sub>6</sub> H <sub>5</sub> Cl	3 × 10 <sup>2</sup>	-1.81 ± 0.22	5.42 ± 0.65
Al(acac) <sub>2</sub> (hfac)	1,2-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	2 × 10 <sup>2</sup>	-1.70 ± 0.21	4.88 ± 0.58
	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	3 × 10 <sup>2</sup>	-1.95 ± 0.30	5.08 ± 0.81
	Dioxane	3 × 10 <sup>2</sup>	-1.80 ± 0.20	5.20 ± 0.50
	C <sub>6</sub> H <sub>5</sub> Cl	3 × 10 <sup>2</sup>	-1.44 ± 0.22	6.52 ± 0.63
	1,2-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	2 × 10 <sup>2</sup>	-1.62 ± 0.17	5.01 ± 0.46
	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	3 × 10 <sup>2</sup>	-1.98 ± 0.50	4.89 ± 1.20
Values for a Random Distribution of Ligands				
Al(dik)(dik') <sub>2</sub>		3.00	0.00	2.18
Al(dik) <sub>2</sub> (dik')		3.00	0.00	2.18

<sup>a</sup> All data refer to the formation of 1 mol of mixed-ligand complex from the corresponding parent complexes as defined by eq 2. <sup>b</sup> All values of  $K_i$  are extrapolated values at 25° unless otherwise noted. <sup>c</sup> This value of  $K_i$  was determined at 60°. <sup>d</sup> Standard error for five independent spectral measurements.

**Table II.** Equilibrium Constants and Thermodynamic Data for the Formation of Some Mixed Eight-Coordinated Zirconium Diketonates<sup>a</sup>

Mixed complex	$K_i$	$\Delta H$ , kcal/mol	$\Delta S$ , eu
Solvent = CH <sub>2</sub> Cl <sub>2</sub>			
Zr(acac)(bzbz) <sub>3</sub>	1.3 <sup>b</sup> ± 1.0 <sup>c</sup>		
Zr(acac) <sub>2</sub> (bzbz) <sub>2</sub>	2.9 <sup>b</sup> ± 1.5 <sup>c</sup>		
Zr(acac) <sub>3</sub> (bzbz)	3.1 <sup>b</sup> ± 1.0 <sup>c</sup>		
Solvent = 1:1 (v/v) C <sub>6</sub> H <sub>6</sub> -C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>			
Zr(acac)(β-T) <sub>3</sub>	1.8 <sup>b</sup> ± 0.6 <sup>c</sup>		
Zr(acac) <sub>2</sub> (β-T) <sub>2</sub>	4.9 <sup>b</sup> ± 1.5 <sup>c</sup>		
Zr(acac) <sub>3</sub> (β-T)	3.3 <sup>b</sup> ± 1.1 <sup>c</sup>		
Solvent = C <sub>6</sub> H <sub>6</sub>			
Zr(acac)(hfac) <sub>3</sub>	4 × 10 <sup>3</sup> <sup>d</sup>	-3.48 ± 0.16	4.75 ± 0.50
Zr(acac) <sub>2</sub> (hfac) <sub>2</sub>	8 × 10 <sup>4</sup> <sup>d</sup>	-5.24 ± 0.23	4.79 ± 0.74
Zr(acac) <sub>3</sub> (hfac)	5 × 10 <sup>3</sup> <sup>d</sup>	-4.15 ± 0.16	2.93 ± 0.51
Zr(dpm)(hfac) <sub>3</sub>	2.3 ± 0.3 × 10 <sup>4</sup> <sup>e</sup>		
Zr(dpm) <sub>2</sub> (hfac) <sub>2</sub>	2.8 ± 0.7 × 10 <sup>5</sup> <sup>e</sup>		
Zr(dpm) <sub>3</sub> (hfac)	2.9 ± 0.2 × 10 <sup>4</sup> <sup>e</sup>		
Zr(acac)(tfac) <sub>3</sub> <sup>f</sup>	17.2	0.00 ± 0.25	5.5 ± 0.9
Zr(acac) <sub>2</sub> (tfac) <sub>2</sub> <sup>f</sup>	42.7	-0.02 ± 0.35	7.2 ± 1.2
Zr(acac) <sub>3</sub> (tfac) <sup>f</sup>	16.5	0.02 ± 0.42	5.3 ± 1.5
Values for a Random Distribution of Ligands			
M(dik)(dik') <sub>3</sub>	4.00	0.00	2.75
M(dik) <sub>2</sub> (dik') <sub>2</sub>	6.00	0.00	3.56
M(dik) <sub>3</sub> (dik')	4.00	0.00	2.75

<sup>a</sup> All data refer to the formation of 1 mol of mixed-ligand complex from the corresponding parent complexes as defined by eq 2. <sup>b</sup> Values determined at 35°. <sup>c</sup> Estimates of error are based on uncertainties in resolving overlapping nmr lines of equilibrium mixtures (cf. Figure 2). <sup>d</sup> Extrapolated values at 25°. <sup>e</sup> These values of  $K_i$  were determined at 35°; estimates of error are standard deviations for five independent spectral measurements. <sup>f</sup> All data for these compounds were computed from the results presented in ref 20.

greater extent than was observed for the exchange of these two ligands on aluminum. The extrapolated values of  $K_i$  at 25° are 3–4 orders of magnitude larger than the statistical values. Still larger values of  $K_i$  are observed for the mixed dpm-hfac complexes. The deviations from statistical scrambling in the Zr(acac)<sub>4</sub>-Zr(hfac)<sub>4</sub> system are due mainly to enthalpy changes in the range -3.32 to -5.45 kcal/mol.

Included in Table II are the results of a previous study<sup>20</sup> of ligand redistribution between the acetylacetonate and trifluoroacetylacetonate of zirconium. The extrapolated values of  $K_i$  at 25° are 4–6 times greater than the statistical values. The deviations from random scrambling are due to entropy effects; the enthalpy changes are zero or nearly zero within

experimental error. Deviations of comparable magnitude also occur for acac-tfac exchange on eight-coordinated Hf(IV),<sup>19,20</sup> Th(IV),<sup>20</sup> and Ce(IV)<sup>20</sup> and for hfac-tfac exchange on Y(III).<sup>23</sup> In the Y(hfac)<sub>4</sub><sup>-</sup>-Y(tfac)<sub>4</sub><sup>-</sup> system, however, the deviations from statistical scrambling are believed to be due to small enthalpy effects.<sup>23</sup>

## Discussion

The redistribution reactions which have been studied for d<sup>0</sup> metal diketonates containing MO<sub>6</sub> and MO<sub>8</sub> cores may be classified according to two general types: *type I exchange* in which the terminal groups on the two ligands are protonated (e.g., acac-bzbz, acac-dpm, or, in the case of MO<sub>8</sub>, acac-β-T) and *type II exchange* in which the terminal groups of one diketonate are protonated and those of the other are fluorinated (e.g., acac-hfac or dpm-hfac). A third type of redistribution system can be defined on the basis of results available for eight-coordinate complexes, viz., exchange involving a partially fluorinated diketonate (e.g., tfac) and either a protonated or fluorinated diketonate.

In solvents of low donor ability each type of redistribution exhibits a characteristic equilibrium behavior relative to the equilibria expected for a random statistical distribution of ligands. The type I reactions give values of  $K_i$  which are equal to or slightly less than the values expected for random scrambling, the deviations from randomness being ascribable to small enthalpy and/or entropy effects. The type II redistributions on the other hand strongly favor the mixed complexes at the expense of the parent complexes. The extrapolated values of  $K_i$  at 25° are ca. 10<sup>2</sup>-10<sup>5</sup> times larger than the statistical values. In those systems for which thermodynamic parameters have been determined, the deviations are due to substantial exothermic enthalpy changes (-1.2 to -5.5 kcal/mol) and to entropies which are somewhat larger (1.5-4.8 eu) than the values for random exchange. The type III reactions for the MO<sub>8</sub> complexes also favor the mixed complexes, but to a much lesser extent than is observed for the type II processes. In the two type III systems which have been studied in greatest detail, the deviations from randomness are due to entropy effects in one case (Zr(acac)<sub>4</sub>-Zr(tfac)<sub>4</sub> system<sup>20</sup>) and to enthalpy effects in the other (Y(hfac)<sub>4</sub><sup>-</sup>-Y(tfac)<sub>4</sub><sup>-</sup> system<sup>23</sup>).

Two factors of potential importance may be singled out for consideration in explaining the exothermic enthalpies associated with the type II reactions: (1) differences in solvation enthalpies between the mixed-ligand products and the

parent complexes and (2) differences in mean metal-oxygen bond energies for the mixed and parent complexes. Their relative importance can be assessed qualitatively based on the results obtained for the  $\text{Al}(\text{acac})_3\text{-Al}(\text{hfac})_3$  exchange reactions. In this system the mixed complexes both have calculated dipole moments of 3.15 D,<sup>46</sup> whereas the parent complexes, of course, are nonpolar. If the exchange enthalpies were due mainly to differences in solvation energies, one should expect the enthalpies to become more exothermic as the polarity of the solvent increased because of greater solvation of the mixed complexes. However, no appreciable solvent dependence was observed over the dielectric constant range 2.2-34.8. Solvation effects should be even less important for acac-hfac exchange between the more spherical, eight-coordinated zirconium complexes. Thus although solvation effects may contribute to the somewhat larger than statistical values of  $\Delta S$  for the type II reactions, nonadditive bond energies appear to play the dominant role in deciding the magnitudes of the enthalpy changes.

It has been pointed out previously<sup>16,47</sup> that because of the difference in inductive effects between the protonated and fluorinated terminal groups on the diketonate ligands of a type II reaction, the effective charge on the donor oxygen atoms of the ligands should differ. The difference in charge should contribute to the stabilization of the mixed complexes relative to the parents because of a decrease in ligand-ligand repulsive energy. The electrostatic effect would be less important in a type I reaction where the inductive effects of the terminal groups are more nearly equal. The role of electrostatic effects is further suggested by the differences in stabilization observed between the mixed acac-hfac and dpm-hfac complexes of zirconium. The formation constants of the latter complexes are larger (by a factor of *ca.* 10) than those of the former, which is consistent with the differences in inductive effects of the terminal groups in the two ligand systems.

The appraisal of electrostatic factors can be placed on a somewhat more quantitative basis by evaluating the enthalpies observed for acac-hfac exchange on aluminum and zirconium in terms of a point charge model. Such a model requires that the electrostatic stabilization energy for 1 mol of mixed complex relative to its parents be given by  $A(e - e')^2/r$ , where  $e - e'$  is the charge difference on the donor atoms of the exchanging ligands,  $r$  is the metal-ligand bond distance, and  $A$  is a constant which depends on stereochemistry. The value of  $A$  for the formation of an octahedral mixed diketonate of the type  $\text{M}(\text{dik})(\text{dik}')_2$  is 2.621. For the square-antiprismatic complexes  $\text{M}(\text{dik})(\text{dik}')_3$  and  $\text{M}(\text{dik})_2(\text{dik}')_2$ , in which the ligands span opposite edges of the square faces, the values of  $A$  are 4.109 and 5.807, respectively.<sup>48-50</sup> If we take the mean

(46) The dipole moment calculation was based on the general procedure described in ref 38.

(47) R. C. Fay, *Ann. N. Y. Acad. Sci.*, **159**, 152 (1969).

$\text{Al-O}$  bond distance to be 1.89 Å<sup>51</sup> for the complexes in the  $\text{Al}(\text{acac})_3\text{-Al}(\text{hfac})_3$  reaction and assume that the average value of  $\Delta H$  for formation of the mixed complexes in four different solvents (-1.71 kcal/mol) is due entirely to electrostatic stabilization, then the charge difference on the donor oxygen atoms of acac and hfac is calculated to be 0.061 electron charge unit. The enthalpies observed for the formation of the mixed-ligand complexes in the  $\text{Zr}(\text{acac})_4\text{-Zr}(\text{hfac})_4$  system correspond to charge differences in the range 0.075-0.082 when the mean  $\text{Zr-O}$  bond distance is taken to be 2.20 Å.<sup>49</sup> Despite the shortcomings of the point charge model, the charge differences between acac and hfac are remarkably similar in magnitude to the differences in net charges on the oxygen atoms of the related ligands  $\text{HCOCHCOH}^-$  and  $\text{FCOCHCOF}^-$  and their metal derivatives as calculated by CNDO methods by Schuster.<sup>52</sup> In the free anions, the charge difference is 0.024 electron charge unit, but in the lithium and beryllium derivatives the charge difference increases to 0.036 and 0.046, respectively. Thus the charge differences for acac and hfac seem reasonable, and the agreement between the results for the  $\text{AlO}_6$  and  $\text{ZrO}_8$  systems indicates that electrostatic factors probably do play an important role in stabilizing the mixed-ligand complexes.

**Registry No.**  $\text{Al}(\text{acac})_3$ , 13963-57-0;  $\text{Al}(\text{acac})(\text{bzcz})_2$ , 37843-44-0;  $\text{Al}(\text{acac})_2(\text{bzcz})$ , 32158-33-1;  $\text{Al}(\text{bzcz})_3$ , 14405-36-8;  $\text{Al}(\text{acac})(\text{hfac})_2$ , 15695-78-0;  $\text{Al}(\text{acac})_2(\text{hfac})$ , 15710-98-2;  $\text{Al}(\text{hfac})_3$ , 15306-18-0;  $\text{Zr}(\text{acac})_4$ , 17501-44-9;  $\text{Zr}(\text{bzcz})_4$ , 17455-33-3;  $\text{Zr}(\beta\text{-T})_4$ , 37838-62-3;  $\text{Zr}(\text{acac})(\text{hfac})_3$ , 37838-63-4;  $\text{Zr}(\text{acac})_2(\text{hfac})_2$ , 37890-91-8;  $\text{Zr}(\text{acac})_3(\text{hfac})$ , 37838-64-5;  $\text{Zr}(\text{hfac})_4$ , 19530-02-0;  $\text{Zr}(\text{dpm})_4$ , 18865-74-2;  $\text{Zr}(\text{acac})(\text{tfac})_3$ , 37838-67-8;  $\text{Zr}(\text{acac})_2$ , 37838-68-9;  $\text{Zr}(\text{acac})_3(\text{tfac})$ , 17923-14-7;  $\text{Zr}(\text{tfac})_4$ , 17499-68-2;  $\text{Ga}(\text{acac})_3$ , 14405-43-7;  $\text{Ga}(\text{hfac})_3$ , 19648-92-1;  $\text{Ga}(\text{acac})(\text{hfac})_2$ , 37843-45-1;  $\text{Ga}(\text{acac})_2(\text{hfac})$ , 23167-14-8.

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(48) The square-antiprismatic stereochemistry referred to here seems most appropriate for the mixed zirconium complexes under consideration as it has been found for  $\text{Zr}(\text{acac})_4$  in the solid state;<sup>49</sup> the ligand-ligand distances used to determine the values of  $A$  were calculated from the equations given by Kepert.<sup>50</sup>

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