and in the anation of $[Co(NH_3)_5H_2O]^{3+}$ by a series of univalent anions,[26] the values of f needed are all in the range 0.1–0.2.

[26] References 24, 25, and A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

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Contribution from the Department of Chemistry
The University of Wisconsin, Madison, Wisconsin

Studies of Ligand Exchange Reactions between Zirconium and Hafnium Chelates by Nuclear Magnetic Resonance[1]

By A. C. Adams[2] and Edwin M. Larsen

Received July 16, 1965

The n.m.r. spectra of benzene solutions containing mixtures of the metal acetylacetonates, $M(acac)_4$, and trifluoroacetylacetonates, $M(tfac)_4$, of zirconium and hafnium show six resolved methyl–proton resonances, which have been assigned to the five species $M(acac)_n(tfac)_{4-n}$. The exchange deviates somewhat from random exchange with the intermediate species favored. Equilibrium quotients (33°) for the formation of $M(acac)_3(tfac)$, $M(acac)_2(tfac)_2$, and $M(acac)(tfac)_3$ from the parent compounds are $K_1 = 24$ (19), $K_2 = 52$ (41), and $K_3 = 18$ (15), respectively, where the values for hafnium are in parentheses. The shape of the spectra change with solvent, with the methyl–proton resonances not completely resolved in carbon tetrachloride, pyridine, nitrobenzene, chlorobenzene, and bromobenzene owing to a decrease in the separation of the resonances. Also, the chemical shifts of the methyl–proton resonances in these solvents are inverted compared to benzene. At higher temperature the resonances merge because the rate of exchange increases. The zirconium complexes exchange faster than the hafnium compounds, but the rate of exchange of the trifluoroacetylacetone and acetylacetone ligands is the same.

Ligand exchange occurs in solutions containing metal acetylacetonates, $M(acac)_4$, and metal trifluoroacetylacetonates, $M(tfac)_4$, where the metal is zirconium or hafnium. The equilibrium mixtures contain the five compounds, $M(acac)_4$, $M(acac)_3(tfac)$, $M(acac)_2(tfac)_2$, $M(acac)(tfac)_3$, and $M(tfac)_4$. These species have been detected by using proton n.m.r. techniques.[1] The present paper reports the results of a more detailed study of these equilibrium systems.

Since our original note several papers have appeared in which n.m.r. is used to study the complex equilibrium mixtures resulting from ligand-exchange reactions.[3–5] These papers deal with the exchange of unidentate ligands, while the present paper is concerned with the exchange of bidentate ligands. However, the same general methods are used in both cases, and the papers in ref. 3–5 should be consulted for a more detailed discussion of the use of n.m.r. in characterizing equilibrium mixtures.

Experimental Section

The n.m.r. spectra were obtained with a Varian Associates Model A-60 spectrometer using standard Varian accessories. The chemical shifts were measured in p.p.m. relative to tetramethylsilane as an internal standard. Negative values of the chemical shift refer to resonances downfield from the tetramethylsilane resonance. The resonance areas were measured by tracing the spectra on graph paper and "counting squares." The areas were measured by this method rather than by the integrator circuit on the spectrometer because the resonances are very close together. The average separation of the methyl resonances is only 0.042 p.p.m.

The complexes were prepared by a previously reported method.[6] The purity of the complexes was checked by metal analyses and melting points.[6] The solvents were distilled and stored over drying agents (sodium metal, calcium hydride, or anhydrous magnesium sulfate). The n.m.r. samples were prepared by accurately weighing the metal complexes, $M(acac)_4$ and $M(tfac)_4$, to give a total weight of about 0.1 g. The solids were dissolved in 1.0 ml. of solvent. The nitrobenzene and carbon tetrachloride solutions contained about 0.05 g. of the metal complexes in 1 ml. of solvent because of the low solubilities of the compounds.

Discussion

Exchange in Benzene Solutions.—The n.m.r. spectra of benzene solutions containing mixtures of the zirconium or hafnium compounds have six resolved methyl resonances. The resonances have been assigned by considering the variation in the area of a given resonance as the relative concentration of the acetylacetone and trifluoroacetylacetone ligands is changed.[1] The mole fractions[7] of the different species are calculated from the areas of the resonances. A plot of the mole

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[1] Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964. For a preliminary communication see A. C. Adams and E. M. Larsen, *J. Am. Chem. Soc.*, **85**, 3508 (1963).

[2] National Science Foundation predoctoral fellow Sept. 1961–Jan. 1965.

[3] M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, **3**, 761 (1964).

[4] K. Moedritzer and J. R. Van Wazer, *ibid.*, **3**, 268 (1964).

[5] K. Moedritzer and J. R. Van Wazer, *ibid.*, **3**, 139 (1964).

[6] E. M. Larsen, G. Terry, and J. Leddy, *J. Am. Chem. Soc.*, **75**, 5107 (1953).

[7] The mole fractions are calculated without considering the solvent; in this sense, mole fraction refers to the fraction of the metal which is in a specified species.

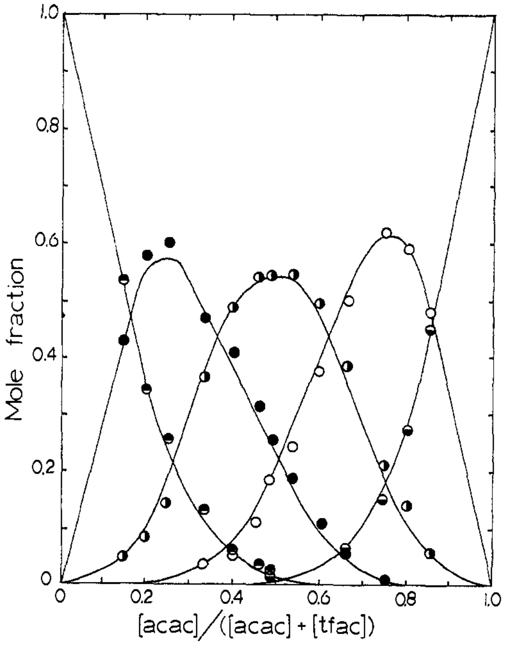

Figure 1.—Mole fraction *vs.* ligand composition: ◒, $Zr(acac)_4$; ○, $Zr(acac)_3(tfac)$; ◑, $Zr(acac)_2(tfac)_2$; ●, $Zr(acac)(tfac)_3$; ◓, $Zr(tfac)_4$. The temperature is 33°, the solvent is benzene, and the total metal concentration is 0.14 *M*.

fractions *vs.* the fraction of the ligands present as acetylacetone groups is shown in Figure 1. These data are for benzene solutions of $Zr(acac)_4$ and $Zr(tfac)_4$; however, curves which are nearly identical are obtained for benzene solutions of the hafnium compounds and for benzene solutions containing $Hf(acac)_4$ and $Zr(tfac)_4$.

It is interesting to compare the mole fractions in Figure 1 to the mole fractions calculated for a random distribution of the ligands.[8] In a random distribution, the maximum concentrations of $M(acac)_3(tfac)$, $M(acac)_2(tfac)_2$, and $M(acac)(tfac)_3$ are 0.423, 0.375, and 0.423, respectively. The experimental maximum concentrations, taken from Figure 1, are $M(acac)_3(tfac)$, 0.622; $M(acac)_2(tfac)_2$, 0.550; and $M(acac)(tfac)_3$, 0.606. This shows that the three mixed complexes are preferentially formed in the exchange reactions.[9]

The nonrandom behavior of the ligand exchange is also apparent by comparing the random and the experimental values of the equilibrium quotients for reactions 1, 2, and 3: For the random distribution, K_1 =

$$0.75M(acac)_4 + 0.25M(tfac)_4 = M(acac)_3(tfac) \quad (1)$$

$$0.50M(acac)_4 + 0.50M(tfac)_4 = M(acac)_2(tfac)_2 \quad (2)$$

$$0.25M(acac)_4 + 0.75M(tfac)_4 = M(acac)(tfac)_3 \quad (3)$$

$K_3 = 4$ and $K_2 = 6$, while the experimental equilibrium quotients (at 33°) are $K_1 = 24$ (19), $K_2 = 52$ (41), and $K_3 = 18$ (15). The values in parentheses are for the hafnium compounds; the other values are for the zirconium complexes.

The above equilibrium quotients have been found by

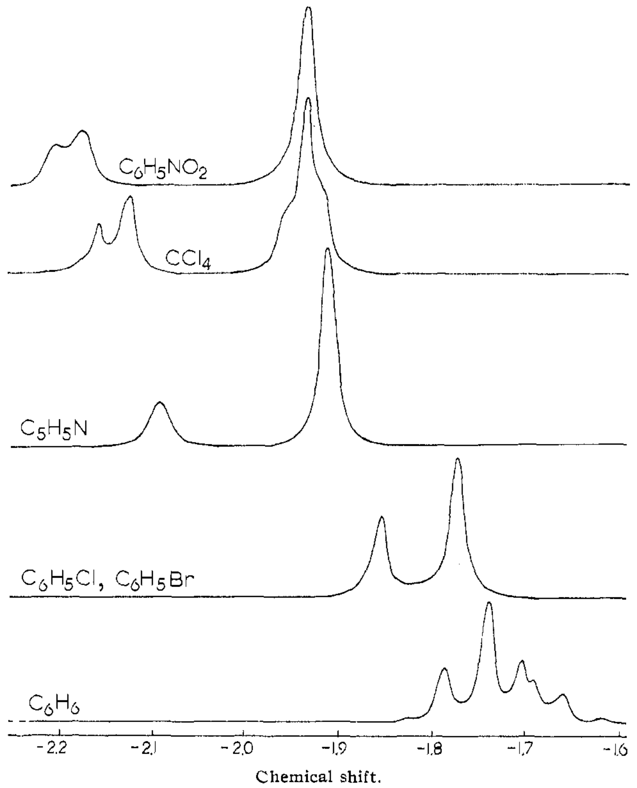

Figure 2.—Methyl resonances of $Zr(acac)_4$–$Zr(tfac)_4$ mixtures in various solvents at 33°. The total metal concentration is 0.16 *M* (for the nitrobenzene and carbon tetrachloride solutions, the total metal concentration is 0.08 *M*); [acac]/([acac] + [tfac]) is 0.52.

using the mole fractions to calculate three equilibrium quotients defined by the reactions

$$2M(acac)_x(tfac)_{4-x} = M(acac)_{x+1}(tfac)_{3-x} + M(acac)_{x-1}(tfac)_{5-x} \quad (4)$$

where x is 1, 2, or 3. Accurate values of the equilibrium quotients for reactions 4 can be obtained because the three species necessary for each calculation are present together over a large ligand composition range. On the other hand, the three compounds in reactions 1, 2, or 3 are present together over a much smaller composition range. Consequently, a direct evaluation of K_1, K_2, or K_3 leads to values with a very large uncertainty. Average values of the equilibrium quotients for reactions 4 have been calculated and an uncertainty has been computed for the 90% confidence level. The average equilibrium quotients and their uncertainties have been combined to give K_1, K_2, and K_3. The resultant uncertainty in K_1, K_2, and K_3 is ±20%. The solid lines in Figure 1 have been calculated using the reported values of the equilibrium quotients.

Solvent Effects.—Changing the solvent causes rather drastic changes in the shape of the n.m.r. spectra (Figure 2). In a particular solvent the chemical shifts of the zirconium and the hafnium complexes are the same; however, the chemical shifts change as the solvent changes. In the solvents other than benzene, the trifluoroacetylacetone methyl–proton resonances are downfield from the acetylacetone methyl–proton resonances. This assignment is confirmed by the rela-

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[8] Curves showing the mole fraction *vs.* composition for a random distribution of four ligands are given in ref. 4.

[9] T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.* **5**, 233 (1966), have shown that the preferential formation of the mixed complexes is due entirely to entropy effects.

TABLE I

CHEMICAL SHIFTS OF THE METAL COMPLEXES IN VARIOUS SOLVENTS[a]

Compound	Solvent	Chemical shift $(x - 1)$ CH_3 ($\pm$0.01)	Chemical shift $(x - 1)$ CH ($\pm$0.02)
$M(acac)_4$[b]	C_6H_6	1.83	5.34
$M(acac)_4$[c]	C_6H_5Cl	1.79	5.37
$M(acac)_4$	C_6H_5Br	1.79	5.37
$M(acac)_4$[d]	$C_6H_5NO_2$	1.91	5.57
$M(acac)_4$[d]	CCl_4	1.90	5.36
$M(tfac)_4$[e]	C_6H_6	1.62	5.74
$M(tfac)_4$[f]	C_6H_5Cl	1.83	5.85
$M(tfac)_4$	C_6H_5Br	1.84	5.85
$M(tfac)_4$[d]	$C_6H_5NO_2$	2.23	6.18
$M(tfac)_4$[d]	CCl_4	2.19	5.95

[a] Measured at 33° in p.p.m.; the concentration of the metal complex is 0.15 *M* unless otherwise noted; M is either zirconium or hafnium. [b] The chemical shift is constant over the concentration range 0.09–0.27 *M*. [c] The chemical shift is constant over the concentration range 0.11–0.23 *M*. [d] The concentration is 0.06 *M*. [e] The chemical shift is constant over the concentration range 0.06–0.19 *M*. [f] The chemical shift is constant over the concentration range 0.08–0.16 *M*.

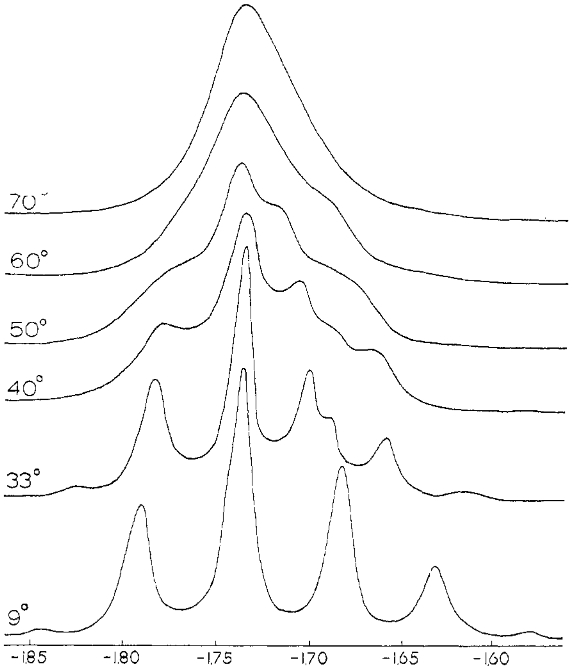
tive areas of the resonances. The chemical shifts of the $M(acac)_4$–$M(tfac)_4$ mixtures follow the same trends as are observed for solutions of pure $M(acac)_4$ or $M(tfac)_4$ (Table I).

In benzene solution, the individual methyl resonances of the five different species are observed, but in pyridine, chlorobenzene, and bromobenzene only two methyl–proton resonances are observed. The two resonances represent the average environment of the acetylacetone and trifluoroacetylacetone methyl protons. Nitrobenzene and carbon tetrachloride represent intermediate cases. In these solvents some splitting of the methyl–proton resonances is observed; however, resonances for all five species are not resolved. The lack of resolution in the solvents other than benzene may be caused by an increase in the exchange rate or a decrease in the frequency separation between the various resonances. To determine which of these factors is the most important the spectra have been recorded as a function of temperature.

Temperature Dependence.—The temperature dependence of the methyl–proton resonances of $M(acac)_4$–$M(tfac)_4$ mixtures dissolved in benzene is shown in Figures 3 and 4. As the temperature increases the rate of exchange increases and the resonances merge together. The resonances for the $Zr(acac)_4$–$Zr(tfac)_4$ mixture (Figure 3) coalesce at a lower temperature than the $Hf(acac)_4$–$Hf(tfac)_4$ resonances (Figure 4). This shows that the exchange is faster in the zirconium system.

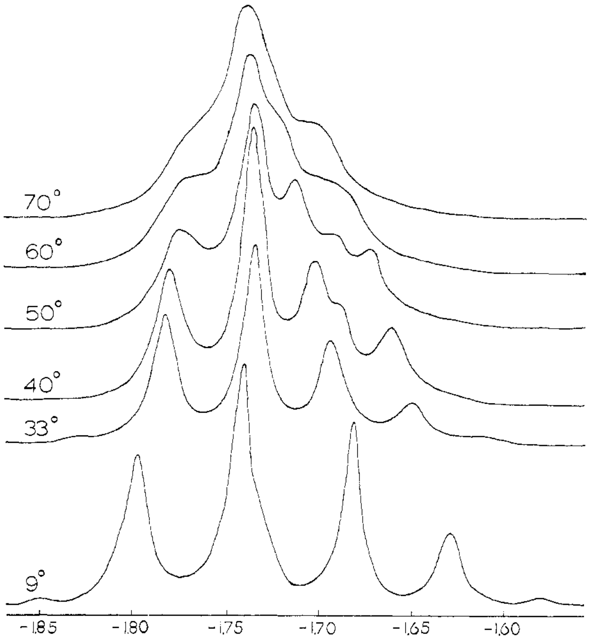
The effect of temperature on the chemical shift can be divided into two categories. The first category concerns chemical shift changes associated with the coalescence of the resonances at the higher temperatures. Using the equation[10]

$$\omega_{\text{mean}} = \Sigma p_i \omega_i \qquad (5)$$



Chemical shift.

Figure 3.—Temperature dependence of the methyl resonances for $Zr(acac)_4$–$Zr(tfac)_4$ mixtures in benzene. The total metal concentration is 0.132 *M*, [acac]/([acac] + [tfac]) is 0.532.



Chemical shift.

Figure 4.—Temperature dependence of the methyl resonances for $Hf(acac)_4$–$Hf(tfac)_4$ mixtures in benzene. The total metal concentration is 0.136 *M*, [acac]/([acac] + [tfac]) is 0.522.

(where ω_{mean} is the chemical shift of the completely coalesced resonance, ω_i is the chemical shift of species *i* when exchange is not occurring, p_i is the fractional population of species *i*, and the summation is over all the compounds undergoing exchange) it can be calculated that in the limit of very fast exchange (high temperature) there should be a single acetylacetone resonance at −1.72 p.p.m. and a single trifluoroacetylacetone reso-

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(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y.; 1959, p. 221.

TABLE II

CHEMICAL SHIFTS OF THE ZIRCONIUM COMPLEXES AT DIFFERENT TEMPERATURES[a]

Compound	Solvent	Temp., °C.	Chemical shift ($\tau - 1$) CH_3 (±0.01)	Chemical shift ($\tau - 1$) CH (±0.02)
$Zr(acac)_4$	C_6H_6	10	1.82	5.25
		40	1.82	5.31
		70	1.81	5.32
$Zr(tfac)_4$	C_6H_6	15	1.55	5.68
		40	1.59	5.70
		70	1.63	5.69
$Zr(acac)_4$	C_6H_5Cl	−3	1.78	...
		40	1.78	5.37
		70	1.78	...
$Zr(tfac)_4$	C_6H_5Cl	40	1.83	5.82
		80	1.85	5.82

[a] The concentration of metal complex is 0.13 *M*.

nance at −1.68 p.p.m.[11] The merging of the acetylacetone resonances to a single peak near −1.72 p.p.m. is seen in Figure 3. The acetylacetone resonances for $Zr(acac)_4$ and $Zr(acac)_3(tfac)$ (at −1.84 and −1.79 p.p.m.) are shifted upfield as the temperature increases. The acetylacetone resonance of $Zr(acac)_2(tfac)_2$ (at −1.74 p.p.m.) is not shifted by temperature changes, but the acetylacetone resonance for $Zr(acac)(tfac)_3$(at −1.68 p.p.m.) is shifted downfield at higher temperatures. It is expected that the trifluoroacetylacetone resonance of $Zr(acac)_3(tfac)$ (at −1.74 p.p.m.) would be shifted upfield, while the trifluoroacetylacetone resonances of $Zr(acac)(tfac)_3$ and $Zr(tfac)_4$ (at −1.63 and −1.58[12] p.p.m.) would be shifted downfield. The trifluoroacetylacetone resonance of $Zr(acac)_2(tfac)_2$ (at −1.68 p.p.m.) should be independent of temperature. Figure 3 shows that the resonance at −1.74 p.p.m. is unchanged and the other resonances are shifted downfield by increasing the temperature. This discrepancy is removed by assuming that all the trifluoroacetylacetone resonances experience a downfield shift at higher temperatures. This downfield shift, which constitutes the second category of temperature effects, is in addition to the effects associated with the coalescence of the resonances. The two effects cancel for the resonance at −1.74 p.p.m. and they reinforce each other to produce a large downfield shift for the resonances at −1.58 and −1.63 p.p.m. For the trifluoroacetylacetone resonance at −1.68 p.p.m., the general downfield shift is the only effect in operation. It is the downfield shift of the trifluoroacetylacetone signals which causes the resonance at −1.68 p.p.m. to split into a doublet at 33°. At 9° the acetylacetone resonance of Zr(acac)(tfac)$_3$ and the trifluoroacetylacetone resonance of $Zr(acac)_2(tfac)_2$ both occur at −1.68 p.p.m. At 33° the downfield shift of the trifluoroacetylacetone resonance is greater than the small downfield shift of the acetylacetone signal and both resonances are observed. The general downfield shift of the trifluoroacetylacetone resonances also causes the single resonance at 70° instead of the two resonances predicted by the coalescence of the signals. It should be noted that similar effects are observed in Figure 4 for the hafnium compounds.

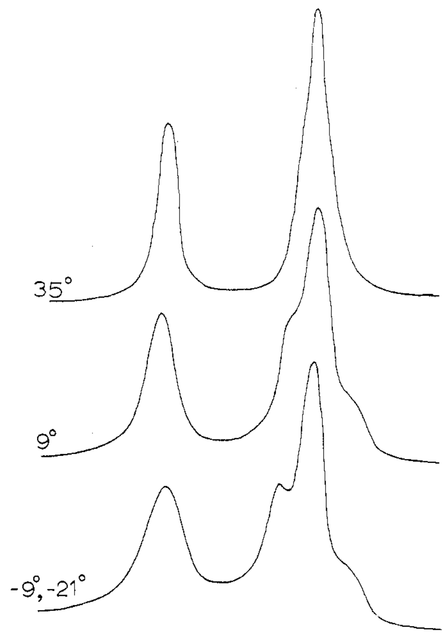

Figure 5.— Temperature dependence of the methyl resonances for $Zr(acac)_4$–$Zr(tfac)_4$ mixtures in chlorobenzene. The total metal concentration is 0.102 *M*, [acac]/([acac] + [tfac]) is 0.530.

The assumption of a general downfield shift for the trifluoroacetylacetone resonances is verified by the data in Table II. These data show that the chemical shifts of the acetylacetone methyl protons are nearly independent of temperature; however, the trifluoroacetylacetone methyl resonances are shifted downfield as the temperature increases.

The temperature dependence of the trifluoroacetylacetone resonances probably arises because of weak solvation of the trifluoroacetylacetone ligands. The downfield shift at higher temperatures reflects less solvation. This view is supported by the chemical shift data in Table I. The chemical shifts of the acetylacetone resonances are nearly the same in the different solvents. However, the changes in the chemical shifts of the trifluoroacetylacetone resonances are relatively large. These differences occur because of the changes in the solvation of the trifluoroacetylacetone ligand in the different solvents.

There is little change in the shape of the spectra for the complexes in chlorobenzene solution when the temperature is lowered from −9 to −21° (Figure 5). This shows that the separations between the different trifluoroacetylacetone methyl–proton resonances and the separations between the various acetylacetone signals are smaller when the solvent is chlorobenzene than when benzene is the solvent. Consequently, the difference in the spectra for the benzene and the chlorobenzene solutions is caused in part by the differences in the separation of the resonances. Of course the exchange rates may still be different. The present data

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[11] The chemical shifts used in this calculation are taken from the spectrum at 9° in Figure 3; the fractional populations are calculated from the data in Figure 1.

[12] The difference between the chemical shift of $Zr(tfac)_4$ reported in Figure 3 at 9° and Table II is real. Apparently the chemical shift of this compound is slightly sensitive to the composition of the solutions.

do not allow a comparison of the exchange rates in the two solvents.

It should be pointed out that no evidence for the existence of geometric isomers of these compounds has been found. Presumably, the rate of intramolecular exchange is very rapid so that only the average environment of the ligands within a molecule is observed.

Relative Rates of Acetylacetone and Trifluoroacetylacetone Exchange.—There can be two types of ligand exchange in the equilibrium system. One type involves the exchange of acetylacetone ligands with trifluoroacetylacetone groups. Examples are given in reactions 6 and 7. In reaction 6, the trifluoroacetylacetone ligand in $M(acac)_3(tfac)$ exchanges with an acetylacetone ligand in $M(acac)_2(tfac)_2$. The net result is the moving of an acetylacetone ligand from $M(acac)_2(tfac)_2$ to $M(acac)_4$ and the moving of a trifluoroacetylacetone group from $M(acac)_3(tfac)$ to $M(acac)(tfac)_3$. This process would manifest itself in the n.m.r. spectrum as the coalescence of the acetylacetone resonances of $M(acac)_4$ and $M(acac)_2(tfac)_2$ and the coalescence of the trifluoroacetylacetone resonances of $M(acac)_3(tfac)$ and $M(acac)(tfac)_3$. Since this process involves the exchange of an acetylacetone group for a trifluoroacetylacetone ligand, the rates of coalescence of the two pairs of resonances must be the same (provided that the separations between the resonances in the absence of exchange are equal). In reaction 7, the exchange process moves a ligand from one site to another identical site. This process cannot be observed in the n.m.r. spectra. However, the rates of exchange of the acetylacetone and the trifluoroacetylacetone ligands must be the same since the process again exchanges an acetylacetone for a trifluoroacetylacetone ligand.

$$M(acac)_3(tfac) + M(acac)_2(tfac)_2 = M(acac)_4 + M(acac)(tfac)_3 \quad (6)$$

$$M(acac)_3(tfac) + M(acac)_2(tfac)_2 = M(acac)_2(tfac)_2 + M(acac)_3(tfac) \quad (7)$$

A second process involves the exchange of acetylacetone ligands with different acetylacetone groups and/or the exchange of trifluoroacetylacetone ligands with other trifluoroacetylacetone ligands. Examples are given in reactions 8 and 9 where the prime is only a means of labeling one of the exchanging groups. Reaction 8 will cause the coalescence of the acetylacetone resonances of $M(acac)_3(tfac)$ and $M(acac)_2(tfac)_2$; reaction 9 will cause the trifluoroacetylacetone resonances of $M(acac)_2(tfac)_2$ and $M(acac)(tfac)_3$ to coalesce. Since reactions 8 and 9 can occur independently of each other, information concerning the relative rates of reactions 8 and 9 can be obtained by studying the rates of coalescence of the acetylacetone and the trifluoroacetylacetone resonances.

$$M(acac)_2(acac)'(tfac) + M(acac)_2(tfac)_2 = M(acac)_3(tfac) + M(acac)(acac)'(tfac)_2 \quad (8)$$

$$M(acac)_2(tfac)(tfac)' + M(acac)(tfac)_3 = M(acac)_2(tfac)_2 + M(acac)(tfac)_2(tfac)' \quad (9)$$

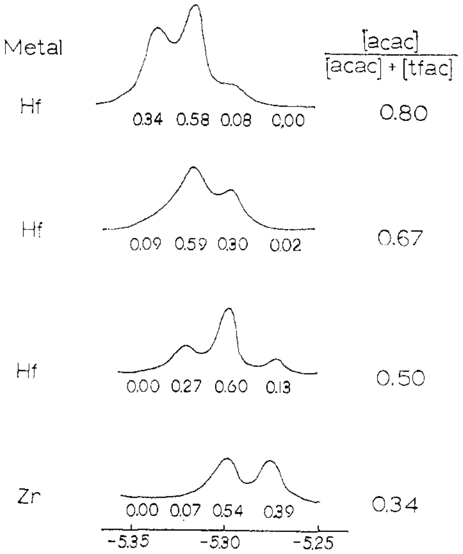

Figure 6.—The acetylacetone CH resonances for $M(acac)_4$–$M(tfac)_4$ mixtures in benzene at 33°. The total metal concentration is 0.14 *M*.

In Figure 4, the separation at 9° between the acetylacetone resonances of $Hf(acac)_3(tfac)$ (at −1.80 p.p.m.) and $Hf(acac)_2(tfac)_2$ (at −1.74 p.p.m.) is 0.06 p.p.m. This same separation is observed between the trifluoroacetylacetone resonances of $Hf(acac)_2(tfac)_2$ (at −1.69 p.p.m.) and $Hf(acac)(tfac)_3$ (at −1.63 p.p.m.). At 50° the two separations have decreased to 0.04 p.p.m., but they are still equal to each other. This shows that regardless of the exchange mechanism, the acetylacetone and the trifluoroacetylacetone ligands exchange at the same rate. These data do not indicate which of the two exchange processes is the most important.

CH Resonances.—The previous discussions have dealt with the methyl–proton resonances of the metal complexes rather than the CH resonances. In making quantitative measurements this is necessary because the methyl–proton resonances are more intense and are more nearly separated than the CH resonances. Figure 6 shows the acetylacetone CH resonances for benzene solutions containing $M(acac)_4$ and $M(tfac)_4$. The metal and the fraction of the ligands present as acetylacetone groups are indicated for each spectrum. The numbers below each resonance are the relative intensities calculated from the mole fractions in Figure 1. In making these calculations it is assumed that the resonances, starting at low field, represent the compounds $M(acac)_4$, $M(acac)_3(tfac)$, $M(acac)_2(tfac)_2$, and $M(acac)(tfac)_3$. The good agreement between the observed and the calculated intensities shows that these assignments are correct.

The trifluoroacetylacetone CH resonance is a broad singlet centered at −5.75 p.p.m. This single resonance is caused by the small separation between the different trifluoroacetylacetone signals. If this were not the case, the single resonance must result because the trifluoroacetylacetone ligands exchange at a faster rate than the acetylacetone ligands, but this has already been shown to be incorrect.

Acknowledgment.—These data have been obtained with equipment purchased on a grant from the National Science Foundation. The authors wish to thank Prof. Paul Bender for instruction in the use of the n.m.r. equipment.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Nuclear Magnetic Resonance Studies of Ligand Exchange for Some Group IVb β-Diketonates[1]

BY THOMAS J. PINNAVAIA AND ROBERT C. FAY

Received August 9, 1965

The rapid ligand exchange of β-diketonate ligands which occurs upon mixing solutions of eight-coordinated group IVb meta acetylacetonates, $\mathrm{M(acac)_4}$, and metal trifluoroacetylacetonates, $\mathrm{M(tfac)_4}$ (M = Zr, Hf, Ce, Th), has been studied by fluorine n.m.r. spectroscopy. The ligand-exchange equilibria may be described in terms of three independent equilibrium quotients. For the zirconium system, which has been studied in most detail, the equilibrium quotients in benzene and carbon tetrachloride solutions deviate by a factor of 2–3 from the values expected for a random statistical distribution of ligands. The mixed complexes $\mathrm{Zr(tfac)_3(acac)}$, $\mathrm{Zr(tfac)_2(acac)_2}$, and $\mathrm{Zr(tfac)(acac)_3}$ are favored at the expense of $\mathrm{Zr(tfac)_4}$ and $\mathrm{Zr(acac)_4}$. Deviations from a statistical distribution of ligands are due to entropy changes; enthalpy changes for the ligand exchange reactions are nearly zero. The n.m.r. spectra also indicate that the group IVb β-diketonates undergo very rapid isomerization. Attempts to detect geometrical isomers at temperatures as low as −105° have been unsuccessful. Coalescence of n.m.r. lines due to ligand exchange has been observed for mixtures of $\mathrm{Th(acac)_4}$ and $\mathrm{Th(tfac)_4}$. Proton and fluorine chemical shifts are reported for $\mathrm{M(acac)_4}$ and $\mathrm{M(tfac)_4}$ in carbon tetrachloride, chloroform, and benzene solutions.

Introduction

The coordination geometries of eight-coordinate zirconium(IV), cerium(IV), and thorium(IV) acetylacetonates have been shown by X-ray diffraction to be based on a square antiprism.[2-4] Whether or not this geometry persists in solution is not known. In attempts to investigate the stereochemistry of zirconium, hafnium, cerium, and thorium β-diketonates in solution by fluorine magnetic resonance spectroscopy, we have found that these complexes undergo remarkably rapid intramolecular rearrangement. The lability of these compounds is further indicated by rapid intermolecular ligand exchange which occurs upon mixing solutions of metal acetylacetonate, $\mathrm{M(acac)_4}$, and metal trifluoroacetylacetonate, $\mathrm{M(tfac)_4}$. A 1:1 mixture of $\mathrm{Zr(acac)_4}$ and $\mathrm{Zr(tfac)_4}$, for example, exhibits four fluorine resonance lines which are assigned to $\mathrm{Zr(tfac)_4}$ and the three mixed complexes, $\mathrm{Zr(tfac)_3(acac)}$, $\mathrm{Zr(tfac)_2(acac)_2}$, and $\mathrm{Zr(tfac)(acac)_3}$. Evidence for ligand exchange in the zirconium and hafnium systems has also been reported by Adams and Larsen using proton n.m.r. techniques.[5] The main purpose of the present paper is to describe the fluorine resonance spectra of mixtures of $\mathrm{M(acac)_4}$ and $\mathrm{M(tfac)_4}$ (M = Zr, Hf, Ce, Th) and to quantitatively characterize the ligand-exchange equilibria for the $\mathrm{Zr(acac)_4}$–$\mathrm{Zr(tfac)_4}$ system.

Experimental Section

Syntheses.—Metal acetylacetonates and trifluoroacetylacetonates used in this work were synthesized using well-known methods[6-9] with the exception of $\mathrm{Zr(tfac)_4}$ and $\mathrm{Hf(tfac)_4}$, which were prepared by refluxing the anhydrous metal chlorides with 10% excess trifluoroacetylacetone in benzene solution as suggested by Morris, Moshier, and Sievers.[10] The purity of the known compounds was checked by their melting points.[6,8,11] Cerium(IV) acetylacetonate was found to exhibit a melting point which varied with heating time due to decomposition. Rather sharp melting points were observed in the range 140–165°. Therefore, this compound was analyzed.

Anal. Calcd. for $\mathrm{Ce(C_5H_7O_2)_4}$: C, 44.61; H, 5.36; Ce, 26.04. Found: C, 44.77; H, 5.26; Ce, 26.09.

Fluorine n.m.r. spectra of the hafnium compounds indicated that the hafnium contained *ca.* 10% zirconium.

Cerium and thorium trifluoroacetylacetonates have not been previously reported but are readily prepared using methods described for the corresponding acetylacetonates.[8,9]

Tetrakis(1,1,1-trifluoro-2,4-pentanediono)cerium(IV).—This compound was obtained as dark red, needle-shaped crystals when recrystallized from 25% benzene–75% hexane; m.p. 132–132.5°.

Anal. Calcd. for $\mathrm{Ce(C_5H_4F_3O_2)_4}$: C, 31.92; H, 2.14; F, 30.30; Ce, 18.62. Found: C, 32.06; H, 2.33; F, 30.11; Ce, 18.82.

Tetrakis(1,1,1-trifluoro-2,4-pentanediono)thorium(IV).—Upon sublimation *in vacuo* at 100° this compound was obtained as white, anhydrous crystals. It is hygroscopic and must be handled in a dry atmosphere; m.p. 132.5–134° (sealed capillary).

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