

Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711**Nuclear Magnetic Resonance Exchange Studies of 3,5-Lutidine Adducts of Tetrabenzylhafnium and Tetrabenzylzirconium**

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A study of the exchange between tetrabenzylhafnium and its 3,5-lutidine adduct has been carried out using variable-temperature 220-MHz nmr spectra in the methylene proton region. Computer line shape analysis of spectral data was carried out. Results indicate that only the monoadduct and free organometallic compound are present in the $(C_6H_5CH_2)_4Hf$ -3,5-lutidine system. Dissociation of R_4Hf -Lut is proposed as the rate-controlling step in the exchange. Activation energy for the exchange with tetrabenzylhafnium is $15.3 \text{ kcal mol}^{-1}$. Limited data obtained for the tetrabenzylzirconium-3,5-lutidine system give an activation energy of $17.1 \text{ kcal mol}^{-1}$.

Introduction

Several studies of adducts of titanium(IV), zirconium(IV), and hafnium(IV) tetraalkyls with Lewis bases have been published.¹⁻⁵ Exchange of Lewis base which is rapid on the nmr time scale often occurs in these systems.^{4,5} Several studies have been carried out on exchange reactions between Lewis bases and titanium tetrafluoride⁶ or titanium tetrachloride;⁷ however, only a few exchange studies are known which involve metal alkyls of the group IV transition metals.⁸⁻¹²

Tetrabenzylzirconium and tetrabenzyltitanium have been shown to be catalysts for the polymerization of olefins.^{13,14} Coordination of olefin with metal is considered to be one step in the polymerization process involving catalysts of this type.^{15,16} Furthermore, the presence of Lewis bases sometimes alters the behavior of catalytic systems.¹⁷ Therefore, thermodynamic and structural information on adducts of $(C_6H_5CH_2)_4M$ is of interest.

In this paper we report results of variable-temperature nmr studies in chlorobenzene solvent of acid-base exchange in the systems tetrabenzylhafnium-3,5-lutidine and tetrabenzylzirconium-3,5-lutidine.

Experimental Section

Tetrabenzylzirconium and tetrabenzylhafnium were prepared as previously described.⁴ Melting points were in agreement with literature values.^{4,18}

Spectral grade chlorobenzene (Aldrich) and 3,5-lutidine (Aldrich) were refluxed under nitrogen over 4A molecular sieve and distilled. A center fraction was transferred under nitrogen to the inert atmosphere box for use in these studies.

Sample tubes for nmr and other glassware were dried at 140° and transferred to the inert atmosphere box at least 24 hr before use. Samples were weighed in the inert atmosphere box on a Cahn millibalance (Model RTL) using an α particle source (Ventron Model U-2-500) to minimize static electricity effects. Benzyl methylene and ligand methyl peaks were integrated by nmr on weighed-out samples in solution and the ratios used to check the accuracy of weighings. Prepared samples in nmr tubes were sealed with pressure caps and kept under nitrogen in the dark at -78° while spectra were not being taken. Studies were completed within 10 hr of preparing samples. Checks showed no change in spectra obtained from the samples when stored in this manner for 1 week.

The sharp low-field peak of chlorobenzene was measured vs. TMS and found to be at 7.08 ppm over the temperature range of interest. This peak was used as an internal reference. Spectra were measured on a Varian HR-220 nmr spectrometer at the Du Pont Experimental Station in Wilmington, Del. Lifetimes of species were obtained by measurements of peak half-widths below coalescence (Table I) or, in the case of Arrhenius plots (Table II, Figure 1), by line shape analysis at all temperatures using a two-site exchange program obtained from Professor T. L. Brown and Mr. R. Guschl of the University of Illinois. Calculations were carried out on a Burroughs B-6700 computer at the University of Delaware. Temperature was determined by measuring peak separation of a methanol sample. Accuracy is estimated to be $\pm 2^\circ$.

Results

The spectrum of the benzyl methylene protons in a 3:2 mixture of $(C_6H_5CH_2)_4Hf$ and 3,5-lutidine is shown at several temperatures (Figure 2). Above coalescence, the peak at 1.96 ppm is due to methylene protons of exchanging R_4Hf and R_4Hf -Lut, while the peak at 1.75 ppm corresponds to the methyl proton resonance in 3,5-lutidine. This peak remains sharp and constant (1.74-1.76 ppm) in chemical shift over the temperature range studied. Because of the presence of the ligand peak, it was not possible to follow the exchange of 1:1 mixtures of adduct and free organometallic above coalescence. As the temperature is lowered, the methylene proton peak broadens and separates into two peaks. At -45° , relatively sharp resonances are observed at 2.17 (R_4Hf -Lut) and 1.31 ppm (R_4Hf). The small peak at 1.9 ppm is a result of about 1% decomposition of R_4Hf during sample preparation. Integration of the adduct and free R_4Hf methylene proton peaks gave a ratio of 2:1 as

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Table I. Lifetimes^a τ_{R_4Hf} and $\tau_{R_4Hf \cdot Lut}$ at -36° as a Function of Concentration

Molal concn		$\left(\frac{[R_4Hf \cdot Lut]}{[R_4Hf]}\right) \times$		
$R_4Hf \cdot Lut$	R_4Hf	$\tau_{R_4Hf \cdot Lut}^b$	$\tau_{R_4Hf}^b$	$\tau_{R_4Hf}^{b,c}$
0.0015	0.0086	0.024	0.16	0.028
0.0038	0.0062	0.025	0.032	0.020
0.0066	0.0033	0.025	0.012	0.024
0.027	0.048	0.024	0.036	0.020
0.050	0.025	0.025	0.012	0.024

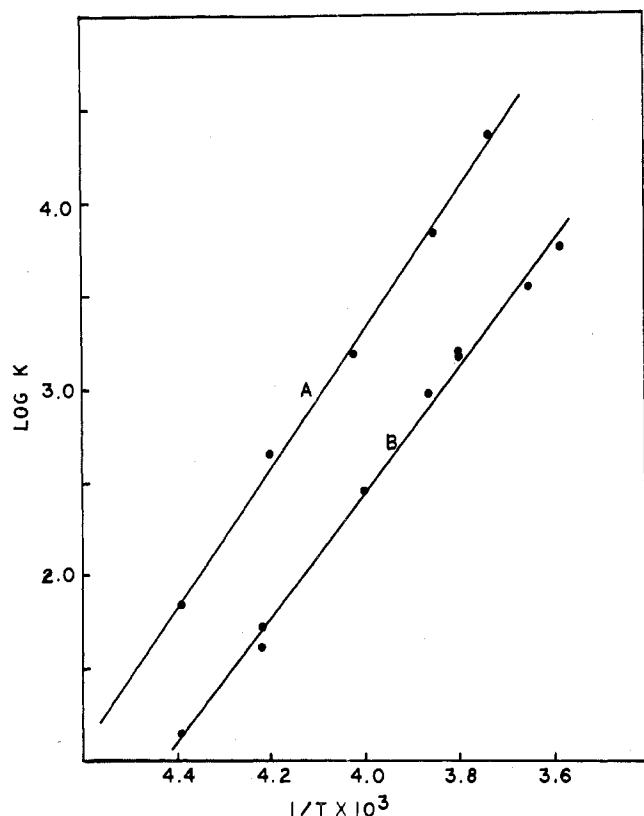
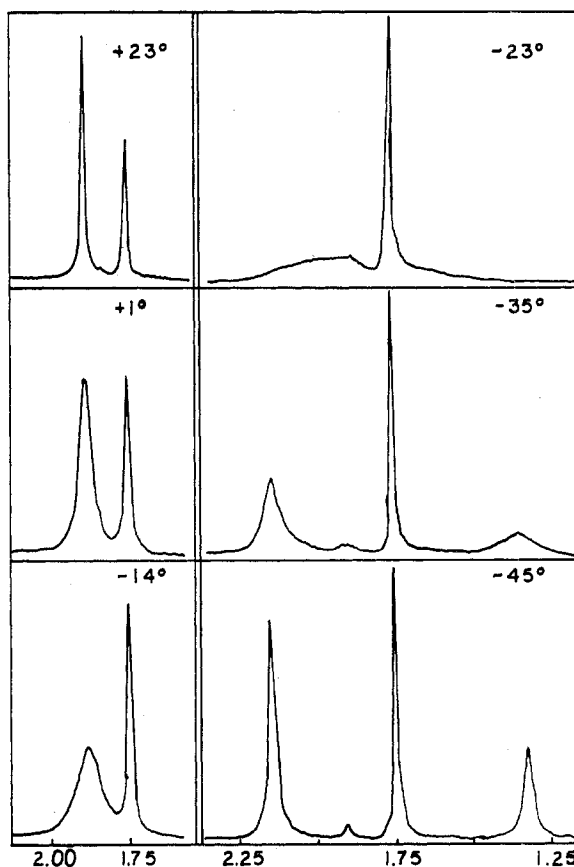
^a Determined from peak widths at half-height using the expression $\tau = 1/\pi(\Delta\nu_{1/2} - \Delta\nu_{1/2}^0)$. ^b In units of seconds. ^c See Discussion section of text.

Table II. Temperature Dependence of Lifetimes τ_e^a and $\tau_{R_4M \cdot Lut}$ Obtained from Line Shape Analysis

$T, ^\circ C$	$(C_6H_5CH_2)_4M \cdot Lut,$ mol fraction	$10^3 \tau_e, \text{ sec}$	$10^3 \tau_{R_4M \cdot Lut}, ^d \text{ sec}$
$(C_6H_5CH_2)_4Hf$-3,5-Lutidine System			
-45	0.66 ^b	24	72
-36	0.66 ^c	8.1	24
-36	0.35 ^c	14	20
-23	0.35 ^c	2.3	3.5
-14	0.66 ^c	0.35	1.1
-10	0.35 ^c	0.43	0.66
-10	0.66 ^b	0.21	0.63
+1	0.66 ^b	0.084	0.25
+6	0.66 ^b	0.058	0.17
$(C_6H_5CH_2)_4Zr$-3,5-Lutidine System			
-45	0.62 ^b	5.6	15
-35	0.60 ^b	0.91	2.2
-24	0.59 ^b	0.30	0.72
-13	0.56 ^b	0.065	0.12
-5	0.58 ^b	0.020	0.048

^a $\tau_e = (\tau_{R_4M \cdot Lut} \times \tau_{R_4M}) / (\tau_{R_4M \cdot Lut} + \tau_{R_4M})$. ^b $[R_4M \cdot Lut] + [R_4M] = 0.0106 m$. ^c $[R_4M \cdot Lut] + [R_4M] = 0.075 m$.

^d $\tau_{R_4M \cdot Lut} = \tau_e / X_{R_4M}$.

**Figure 1.** Arrhenius plots for exchange in the systems $(C_6H_5CH_2)_4Zr$ -3,5-lutidine (A) and $(C_6H_5CH_2)_4Hf$ -3,5-lutidine (B).**Figure 2.** Spectrum of a 3:2 mixture of $(C_6H_5CH_2)_4Hf$ and 3,5-lutidine at various temperatures. Chemical shifts are in parts per million relative to TMS. Peaks are identified in the text.

required if 1 equiv of 3,5-lutidine reacts with 1 equiv of R_4Hf to form 1 equiv of adduct.

It was not possible to measure $\Delta\nu_{1/2}^0(R_4Hf \cdot Lut)$, the zero exchange line width of the adduct, directly since exchange broadening occurred even at -45° ; however, a value of 3.5 Hz could be estimated from values of the observed line widths, $\Delta\nu_{1/2}(R_4Hf \cdot Lut)$, $\Delta\nu_{1/2}(R_4Hf)$, and $\Delta\nu_{1/2}^0(R_4Hf)$ at -45° . Since the value of $\Delta\nu_{1/2}^0(R_4Hf \cdot Lut)$ is much smaller than $\Delta\nu_{1/2}(R_4Hf \cdot Lut)$ at most temperatures studied, little error is introduced by a slight uncertainty in the zero exchange line width.

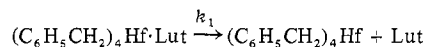
The value of $\Delta^0(\delta_{R_4Hf \cdot Lut} - \delta_{R_4Hf})$ measured at $+36.5^\circ$ (and 60 MHz) using an excess of ligand is 0.75 ppm, while at -45° $\Delta^0 = 0.88$ ppm. We assumed that Δ^0 varied linearly with temperature and used interpolated values at intermediate temperatures.

Adduct dissociation in the $(C_6H_5CH_2)_4Hf$ -3,5-lutidine system is so slight as not to be detectable by nmr integration at -45° . However, in the $(C_6H_5CH_2)_4Zr$ -3,5-lutidine system, dissociation of $R_4Zr \cdot Lut$ is considerable at -45° . Integration of a sample containing 0.85 equiv of 3,5-lutidine per equivalent of R_4Zr shows that 62% of the R_4Zr forms adduct, instead of the 85% which would be obtained if no dissociation occurred. Because of this extensive dissociation with R_4Zr , mole fractions of $R_4Zr \cdot Lut$ and R_4Zr had to be calculated above -45° assuming that the position of the exchange peak varies with the mole fractions of exchanging species. To do this, the value of δ_{R_4Zr} was measured between $+36.5$ (1.47 ppm) and -45° (1.41 ppm) and found to vary linearly with temperature. The value of $\delta_{R_4M \cdot Lut}$ at -45° (2.31 ppm) was determined by direct measurement. To obtain a value of $\delta_{R_4Zr \cdot Lut}$ at $+36.5^\circ$,

three series of spectra were taken with varying base-to-metal ratios, at total organometallic concentrations of 0.01, 0.033, and 0.132 *m*. These data were used to calculate the equilibrium concentration quotients and $\delta_{R_4M \cdot Lut}$ frequencies as previously described.⁴ Values of $\delta_{R_4Zr \cdot Lut}$ thus calculated were constant ($2.47 \pm .02$ ppm) over the concentration range from 0.0106 to 0.132 *m*. $\Delta\nu_{1/2}^0(R_4Zr)$ was observed to be 3 Hz at -45° , and $\Delta\nu_{1/2}^0(R_4Zr \cdot Lut)$ was calculated to be 4 Hz, as described for the $R_4Hf \cdot Lut$ system.

Discussion

Values of the lifetimes τ_{R_4Hf} and $\tau_{R_4Hf \cdot Lut}$ obtained from line-width measurements at -36° are given in Table I. It can be seen that $\tau_{R_4Hf \cdot Lut}$ is independent of concentration and equal to the value of $([R_4Hf \cdot Lut]/[R_4Hf])\tau_{R_4Hf}$. These results are consistent¹⁹ with a dissociative mechanism in which the reaction



is the rate-determining step. Although a solvent-assisted mechanism could lead to the same observed concentration dependence, we believe the large positive entropy of activation and large activation energy (*vide infra*) are more indicative of the dissociative process. Finally, benzyl group exchange does not occur since separate methylene resonances are observed for tetrabenzylhafnium and tetrabenzylzirconium in chlorobenzene at 36° with and without the presence of 3,5-lutidine.

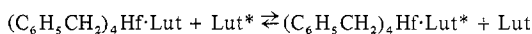
A line shape analysis (Table II) and resulting Arrhenius plot (Figure 1) give an activation energy of 15.3 ± 0.8 kcal mol⁻¹ for the $(C_6H_5CH_2)_4Hf$ -3,5-lutidine exchange. The entropy of activation was found to be 13.0 ± 1.5 eu. These values are of the same magnitude as those found for other systems involving dissociation of the adduct as the rate-determining step.²⁰ Furthermore, the activation energy is larger than the enthalpy of dissociation of $(C_6H_5CH_2)_4Hf \cdot Lut$ (~ 11 kcal mol⁻¹), estimated from equilibrium quotient measurements⁵ at three temperatures, as required if the dissociative mechanism is operative.

Line shape analyses of the variable temperature spectrum of a 1/0.85 mixture of tetrabenzylzirconium and 3,5-lutidine are shown in Table II. The activation energy (17.1 ± 0.7 kcal mol⁻¹; Figure 2) is similar to that of the hafnium system, although the entropy of activation (23.7 ± 3.0 eu) is somewhat larger. Because of the relatively rapid exchange occurring in the tetrabenzylzirconium-3,5-lutidine system even at -45° and attendant greater difficulty and uncertainty in determining $\Delta^0(R_4Zr \cdot Lut)$, $\Delta\nu_{1/2}^0(R_4Zr \cdot Lut)$, and mole fractions at intermediate temperatures, the zirconium-luti-

dine system data are subject to greater uncertainty than those for the hafnium-lutidine system. However, the similarity in activation energies between the hafnium and zirconium systems suggests that the exchange mechanism in the two cases is quite similar.

It is instructive to compare results of our studies with those obtained for the systems $(CH_3)_3Ga$ - $(CH_3)_3Ga$ -base^{19,21} and $(CH_3)_3In$ - $(CH_3)_3In$ -base²² involving an excess of free $(CH_3)_3M$. Exchange with the group III organometallics occurs by a dissociative mechanism provided the base has appreciable steric requirements. However, if a less bulky base is used, a bimolecular mechanism is observed. Furthermore, systems containing an excess of base exchange by a bimolecular process. Results published previously⁴ indicate that large steric interactions occur in adducts of tetrabenzylhafnium and tetrabenzylzirconium as a result of the presence of the bulky benzyl groups. Such steric interactions would impede a bimolecular process and would lead to the observed dissociative mechanism in the presence of excess $(C_6H_5CH_2)_4M$.

In the presence of excess 3,5-lutidine only a single base methyl resonance is observed at -45° in the tetrabenzylhafnium system. Calculations based on the lifetime of the adduct and the observed difference in chemical shift between complexed and uncomplexed 3,5-lutidine (35 Hz at 220 MHz) indicate that if the same exchange mechanism were operative with excess base as with excess organometallic, one would observe two ligand resonances at -45° with excess base added. Since only one ligand resonance is observed, rapid exchange between free and complexed 3,5-lutidine occurs under these conditions. This result may be indicative of a low-energy bimolecular exchange process of the type



in the presence of excess base.

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Registry No. $(C_6H_5CH_2)_4Hf \cdot Lut$, 40892-01-1; $(C_6H_5CH_2)_4Zr \cdot Lut$, 40881-28-5.

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