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NUCLEAR MAGNETIC RESONANCE STUDIES OF LEWIS BASE ADDUCTS OF TETRABENZYLHAFNIUM AND TETRABENZYLZIRCONIUM

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SUMMARY

The synthesis of tetrabenzylhafnium is described. The reaction of tetrabenzylhafnium and tetrabenzylzirconium with pyridine, quinoline, 2,2′-bipyridyl, trimethylphosphine, and THF is studied by means of NMR spectroscopy. The equilibrium quotient for the reaction

$$(C_6H_5CH_2)_4M + Py \rightleftarrows (C_6H_5CH_2)_4M \cdot Py$$

in chlorobenzene solution is found to be 12.6 ± 0.6 for the zirconium compound and 460 ± 30 for the hafnium compound. No adduct formation was observed by NMR with triethylamine, tripropylamine, tributylamine, triphenylamine, *N,N,N′,N′*-tetraethylethylenediamine, diethyl ether, dioxane, triphenylphosphine, trimethyl phosphite, triethyl phosphite, *cis*-cyclooctene, cyclohexene, or 1,1-diphenylethylene.

INTRODUCTION

Although tetramethyltitanium was first reported in 1959[1], few spectroscopic studies[2] have been carried out on it or on the zirconium analog[3] because of their extreme thermal instability. Recently tetrabenzyltitanium and tetrabenzylzirconium have been reported[4]. The thermal stabilities of these compounds are such that NMR and IR studies can be conveniently carried out[4,5].

Tetramethyltitanium functions as a Lewis acid toward a variety of oxygen, nitrogen, and phosphorus donor bases[6,7]. The resulting five- and six-coordinate adducts are thermally more stable than uncomplexed $(CH_3)_4Ti$[6]. Furthermore, UV spectral studies indicate that the six-coordinate complexes with non-chelating ligands undergo partial dissociation in hexane solution to form the five-coordinate complexes[7].

We have synthesized tetrabenzylhafnium and have used NMR spectroscopy to investigate the degree of coordination of tetrabenzylhafnium and tetrabenzylzirconium with various Lewis bases in aromatic solvents.

RESULTS AND DISCUSSION

Tetrabenzylhafnium is a pale yellow, air-sensitive, crystalline solid which, if carefully purified, can be stored for months under a nitrogen atmosphere at room temperature. It is thermally more stable than the zirconium and titanium analogs.

If equimolar quantities of $(C_6H_5CH_2)_4Hf$ and $(C_6H_5CH_2)_4Zr$ are dissolved in benzene, two sharp singlets are observed in the methylene region of the NMR spectrum at room temperature and at +78°. Thus, any benzyl group exchange between these species must be slow on the NMR time scale.

The addition of pyridine, quinoline, THF, or trimethylphosphine to benzene solutions of tetrabenzylhafnium or tetrabenzylzirconium produces a single benzyl methylene resonance downfield from that for uncomplexed $(C_6H_5CH_2)_4M$ (Table 1). No peak is observed at the position of the resonance for free $(C_6H_5CH_2)_4M$. The position of the observed peak is dependent upon the base/metal ratio. This behavior is indicative of a system in which there is rapid exchange between complexed and uncomplexed organometallic compound. A plot of τ_{CH_2} *versus* B/M, the base to metal mole ratio, for mixtures of $(C_6H_5CH_2)_4Hf$ and pyridine in chlorobenzene produces a nearly straight line as the ratio varies from 0.0 to 1.0 and no change in τ_{CH_2} as B/M is

TABLE 1

OBSERVED FREQUENCY SHIFTS (ppm) IN THE METHYLENE RESONANCE OF $(C_6H_5CH_2)_4M$ IN THE PRESENCE OF LEWIS BASES

Base	B/M	$\Delta\tau_{Hf}$[a]	$\Delta\tau_{Zr}$
2,2'-Bipyridyl	< 1.0	−0.93, 0.00	−0.93, 0.00
	> 1.0	−0.93	−0.93
Quinoline	0.8	−0.46	
	1.5	−0.64	
	3.0	−0.70	
Tetrahydrofuran	0.9	−0.24	
	3.0	−0.50	
	4.0		−0.01
	6.3	−0.59	
	14.0		−0.28
Trimethylphosphine	2.8		−0.35
Pyridine[b]	0.15		−0.09
	0.40		−0.22
	0.42		−0.24
	0.83		−0.41
	0.90		−0.44
	1.56		−0.60
	1.93		−0.66
	2.50		−0.75
Pyridine[c]	0.16	−0.12	−0.02
	0.49	−0.37	−0.03
	0.79	−0.60	−0.09
	1.07	−0.68	−0.21
	1.30	−0.71	−0.33
	1.71	−0.74	−0.54
	2.04	−0.73	−0.59
	2.38	−0.74	−0.67
	2.72	−0.74	−0.68

[a] $\Delta\tau = \tau_{obs} - \tau_{R_4M}$. Benzene solutions used except for pyridine data. [b] Data for the system $(C_6H_5CH_2)_4Zr$ + Py in chlorobenzene solution. [c] Data for the system 91 mole% $(C_6H_5CH_2)_4Hf$ + 9 mole% $(C_6H_5CH_2)_4Zr$ + Py in chlorobenzene solution.

increased above 1.0 (Fig. 1). This is a good indication that a 1/1 adduct of the type $(C_6H_5CH_2)_4Hf\cdot Py$ is being formed. The linear plot indicates that little dissociation of the type:

$$(C_6H_5CH_2)_4Hf\cdot Py \rightleftharpoons (C_6H_5CH_2)_4Hf + Py \qquad (1)$$

occurs in solution[8]. The results also suggest that little or no 2/1 adduct is present. In contrast, a similar plot for mixtures of $(C_6H_5CH_2)_4Zr$ and pyridine is non-linear indicating appreciable dissociation of the type shown in eqn. (1) (Fig. 1).

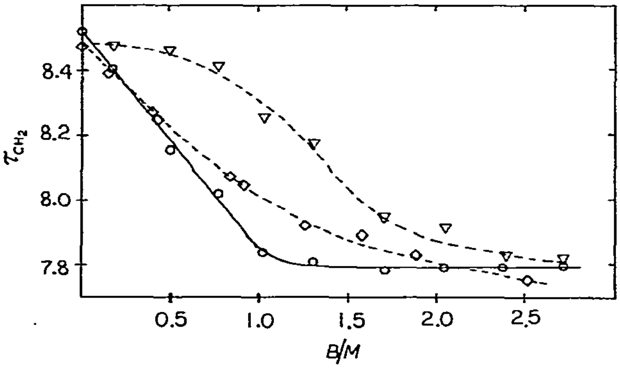

Fig. 1. Chemical shift τ (ppm) of the benzyl methylene protons as a function of the pyridine to metal mole ratio for mixtures of R_4M and pyridine in chlorobenzene. ○, $(C_6H_5CH_2)_4Hf$ in competing equilibria with 9 mole% $(C_6H_5CH_2)_4Zr$; ◇, $(C_6H_5CH_2)_4Zr$; ▽, $(C_6H_5CH_2)_4Zr$ in competing equilibria with 91 mole% $(C_6H_5CH_2)_4Hf$.

The shift in methylene resonance can be used to determine the equilibrium quotient for the reaction:

$$(C_6H_5CH_2)_4Zr + Py \rightleftharpoons (C_6H_5CH_2)_4Zr\cdot Py \qquad (2)$$

Assuming only monoadduct formation, the equilibrium quotient is given by[9]

$$Q_{Zr} = \frac{[R_4Zr\cdot Py]}{[R_4Zr][Py]}$$

$$= \frac{\chi_{R_4Zr\cdot Py}}{[R_4Zr]_0(1-\chi_{R_4Zr\cdot Py})\left(\frac{B}{M} - \chi_{R_4Zr\cdot Py}\right)}$$

where $\chi_{R_4Zr\cdot Py} = \Delta\tau_{obs}/\Delta\tau_{R_4Zr\cdot Py}$; $[R_4Zr]_0$ is the total concentration of tetrabenzylzirconium, $\Delta\tau_{obs} = \tau_{obs} - \tau_{R_4Zr}$, and $\Delta\tau_{R_4Zr\cdot Py} = \tau_{R_4Zr\cdot Py} - \tau_{R_4Zr}$.

Because of considerable dissociation at all practical ligand concentrations, the value of $\tau_{R_4Zr\cdot Py}$ cannot be observed directly. Therefore, values of Q were calculated assuming various values of $\tau_{R_4Zr\cdot Py}$ (Table 2). The calculated values of Q were plotted as a function of B/M and the least squares line obtained for each trial value of $\tau_{R_4Zr\cdot Py}$. Values of the slope and σ/Q nearest to zero were obtained for $\tau_{R_4Zr\cdot Py} = 7.52$ ppm at which point $Q_{Zr} = 12.6 \pm 0.6$. The fact that σ/Q and the absolute value of the slope of the above least-squares line go through minima at the same assumed value of $\tau_{R_4Zr\cdot Py}$ suggests that the equilibrium:

$$Py+(C_6H_5CH_2)_4Zr\cdot Py \rightleftarrows (C_6H_5CH_2)_4Zr\cdot 2Py \tag{3}$$

does not occur to a significant extent.

TABLE 2

VARIATION OF Q_{Zr} WITH $\tau_{R_4Zr\cdot Py}$ IN THE SYSTEM $(C_6H_5CH_2)_4Zr+Py$

Trial value of $\tau_{R_4Zr\cdot Py}$	$Q_{Zr}^{ave\,a}$	σ^b	σ/Q	Slope[c]
7.48	11.2	0.55	0.050	−0.372
7.50	11.8	0.53	0.045	−0.229
7.52	12.6	0.55	0.044	−0.0557
7.54	13.5	0.64	0.048	0.194
7.56	14.5	0.94	0.067	0.497

[a] Average value for the eight data points in Table 1. [b] Standard deviation. [c] Slope of line obtained in plot of Q_{Zr} *vs.* B/M.

Competing equilibria[10], in which pyridine was added to a solution containing a R_4Hf/R_4Zr ratio of 9/1, were used to obtain the value for Q_{Hf} for the reaction:

$$(C_6H_5CH_2)_4Hf+Py \rightleftarrows (C_6H_5CH_2)_4Hf\cdot Py \tag{4}$$

The equilibrium quotient is given by

$$Q_{Hf}=\frac{\chi_{R_4Hf\cdot Py}}{(1-\chi_{R_4Zr\cdot Py})[Py]}$$

where

$$[Py]=\frac{\chi_{R_4Zr\cdot Py}}{(1-\chi_{R_4Zr\cdot Py})Q_{Zr}}$$

Values of $\chi_{R_4Hf\cdot Py}$ and $\chi_{R_4Zr\cdot Py}$, the mole fractions of tetrabenzylhafnium and tetrabenzylzirconium which are complexed, are obtained from the frequencies of the methylene resonances in the mixed system. The best values of the equilibrium constant Q_{Hf} are obtained in the region $B/M=0.79$ to 1.30 (Fig. 1). In this region reasonably accurate values for both $\chi_{R_4Zr\cdot Py}$ and $\chi_{R_4Hf\cdot Py}$ can be obtained. Using values of Q_{Zr} and $\tau_{R_4Zr\cdot Py}$ obtained above and $\tau_{R_4Hf\cdot Py}=7.77$, values of Q_{Hf} of 443, 447 and 491 were obtained at $B/M=0.79$, 1.07, and 1.30 respectively giving an average of 460 ± 30. It is interesting that the shift in the methylene resonance upon adduct formation is inversely related to the magnitude of the equilibrium quotient. This has been observed previously in other systems[9]. It is also interesting that such distinctive differences in Lewis acidity arise for compounds of Hf and Zr inasmuch as these elements have such similar sizes and electronegativities.

No shift in the methylene resonance is observed when tetrabenzylhafnium is mixed with triethylamine, tripropylamine, tributylamine, triphenylamine, *N,N,N′,N′*-tetraethylethylenediamine, diethyl ether, dioxane, triphenylphosphine, trimethylphosphite, triethylphosphite, *cis*-cyclooctene, cyclohexene, or 1,1-diphenylethylene. Thus, the extent of adduct formation is too small to be observed in the NMR. Since some of these are stronger bases than those which produce adducts, steric interactions between the bulky benzyl groups and the base must play an important part in determining the strength of adduct formation. Data could not be obtained for primary amines because of decomposition of the organometallic compound.

In an attempt to determine the geometry of the monoadduct, the 220 MHz NMR spectrum of a 0.5/1 mixture of pyridine and $(C_6H_5CH_2)_4Hf$ was measured as a function of temperature in $C_6D_5CD_3$. As the temperature was lowered, the peak at τ8.16 broadened and then split into two resonances, one centered at τ8.35 due to uncomplexed $(C_6H_5CH_2)_4Hf$ and one centered at τ7.80 due to the adduct. Even at −51° the adduct peak is too broad to determine whether or not more than one kind of benzyl group is present. The 60 MHz NMR spectrum of a 1/0.5 mixture of $(C_6H_5CH_2)_4Zr$ and pyridine in $C_6D_5CD_3$ gives a single broad resonance at −70°. Thus, it is not possible to comment on the structure of the five-coordinate adduct.

If 2,2′-bipyridyl is added to a benzene solution of tetrabenzylhafnium or -zirconium a red precipitate forms. The position of the methylene resonance of free $(C_6H_5CH_2)_4M$ is unaffected, but its intensity decreases with the amount of bipyridyl added. A new peak is observed at τ 7.55 (Zr) or τ 7.59 (Hf). Because of the low solubility of the adduct in benzene, the intensity of the adduct peak remains constant as the intensity of the $(C_6H_5CH_2)_4M$ peak decreases. When the base/metal ratio is 1.0, the peak arising from uncomplexed $(C_6H_5CH_2)_4M$ disappears. The low solubility of the adduct compared with other adducts prepared suggests that the bipyridyl is functioning as a bidentate ligand to form an insoluble six-coordinate complex.

EXPERIMENTAL

All manipulations of $(C_6H_5CH_2)_4M$ were carried out in a nitrogen-filled inert atmosphere box. NMR spectra were obtained on a Varian HA-60 or a Varian HR-220 spectrometer.

Anhydrous $ZrCl_4$ and $HfCl_4$ (ROC/RIC) were obtained in glass ampules which were opened inside the inert atmosphere box and were used without further purification. Benzyl chloride (Eastman) was freshly distilled before each use. Diethyl ether was dried over sodium. The ligands THF and dioxane were refluxed over potassium or sodium and distilled under nitrogen. They were stored over sodium in an inert atmosphere and were used only if the sodium remained bright. All other ligands were distilled from CaO or Na and stored in an inert atmosphere.

Spectral grade solvents were dried over 4-A molecular sieves and degassed before being brought into the inert atmosphere box. NMR tubes were dried for 24 hours at 140° and were sealed with pressure caps after filling. Solutions were prepared by adding 0.067 mmole of $(C_6H_5CH_2)_4M$ to 0.500 g of solvent plus the desired quantity of base. In the competing equilibria experiments, 0.062 mmole of $(C_6H_5CH_2)_4Hf$ and 0.006 mmole of $(C_6H_5CH_2)_4Zr$ were diluted as above. No deterioration in the samples was noted at room temperature after tubes had been five hours in air. All NMR spectra were recorded within 90 minutes of solution preparation. Room temperature spectra were recorded at 40°.

Synthesis of tetrabenzylhafnium

A solution of $C_6H_5CH_2MgCl$ (0.1 mole) in ether was cooled to −90° in the inert atmosphere box. $HfCl_4$ (0.025 mole) was slowly stirred into the solution and the mixture allowed to warm to 0° over a period of 30 minutes with stirring. On warming, the solution gradually turned pale yellow. Ether was removed *in vacuo* and the residue extracted with four 100 ml fractions of hot hexane. The volume of the extract was reduced to 100 ml *in vacuo* and the crystals collected. The crystals were twice recrystallized from hot hexane giving 60% yield. The NMR spectrum of $(C_6H_5CH_2)_4Hf$ in C_6H_6 shows a sharp singlet at τ 8.52 due to the methylene protons and multiplets at τ 3.03 and τ 3.50 due to the ring protons. (Anal. Found: C, 61.77; H, 4.70; Hf, 32.73. m.p. 112–114°. $C_{28}H_{28}Hf$ calcd.: C, 61.93; H, 5.19; Hf, 32.90.)

Synthesis of tetrabenzylzirconium

$(C_6H_5CH_2)_4Zr$ was prepared in the same manner as $(C_6H_5CH_2)_4Hf$, m.p. 133–134° (lit.[11] 133–134°). The NMR spectrum was in good agreement with that reported previously[4].

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