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NMR STUDIES OF EQUILIBRIA BETWEEN LEWIS BASES AND TETRABENZYLZIRCONIUM OR TETRABENZYLHAFNIUM*

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Summary

Equilibrium quotients (Q) for the reaction

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

(M = Zr, B = pyridine, 4-picoline, 3,5-lutidine; M = Hf, B = tetrahydrofuran) have been obtained in chlorobenzene solvent. The value has also been obtained in 1,4-dioxane for the system $(C_6H_5CH_2)_4Zr$/4-picoline. Equilibrium quotients increase with a change of base in the order tetrahydrofuran < pyridine < 4-picoline < 3,5-lutidine. Studies of competing equilibria between $(C_6H_5CH_2)_4Zr$ and $(C_6H_5CH_2)_4Hf$ with pyridine or 3,5-lutidine indicate that $(C_6H_5CH_2)_4Hf$ gives equilibrium quotients which are 34-39 times larger than those obtained with $(C_6H_5CH_2)_4Zr$ using a common base. Effect of solvent and concentration of $(C_6H_5CH_2)_4M$ on the magnitude of Q are discussed.

Introduction

Lewis bases are known to alter the catalytic behavior of transition metal complexes [1-4]. Therefore, a systematic study of adduct formation in catalytically active organometallic systems could contribute to an understanding of factors which influence catalytic activity [5]. Because of the importance of features such as the nature of the lattice site in heterogeneous systems, a soluble organometallic catalyst is better suited for a study of acid—base behavior.

Tetrabenzylzirconium and tetrabenzylhafnium are thermally stable com-

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pounds which are known to function as homogeneous catalysts [2-4, 6-9] and to form adducts with Lewis bases [10, 11]. Ballard et al. [3, 4] have proposed a mechanism for the catalysis of styrene polymerization by tetrabenzylzirconium. According to their mechanism, the initial step involves coordination of the olefin with $(C_6H_5CH_2)_4Zr$. If this mechanism is correct, a study of factors which influence the equilibrium quotient for reaction 1 (B is an olefin,

$$(C_6H_5CH_2)_4M + B \rightleftarrows (C_6H_5CH_2)_4M \cdot B \qquad (1)$$

M is Hf or Zr) should provide insight into the relationship between the magnitude of the equilibrium quotient and catalytic activity. Unfortunately, the equilibrium quotient for reaction 1 is very small when B is an olefin and cannot be measured by NMR spectroscopy [3, 4, 10]. However, if B is a pyridine derivative, the equilibrium quotients are sufficiently large for determination by NMR technique [10]. Therefore, we have begun our studies of acid—base behavior of tetrabenzylzirconium and tetrabenzylhafnium using substituted pyridines as bases.

We have previously reported equilibrium quotients for reaction 1 (B = pyridine, M = Zr, Hf) at a single concentration of $(C_6H_5CH_2)_4M$ [10]. In this paper, we report results of additional equilibrium quotient measurements involving pyridine, 4-picoline and 3,5-lutidine with tetrabenzylzirconium and tetrahydrofuran with tetrabenzylhafnium.

Experimental

Syntheses of tetrabenzylzirconium and tetrabenzylhafnium were carried out in the manner previously described [10]. All operations were performed in a nitrogen atmosphere with extreme care taken to avoid exposure of the compounds to air or moisture. Glassware was dried at 140° and introduced into an inert atmosphere box 24 h prior to use. Samples were weighed on a Cahn Model RTL Millibalance inside the inert atmosphere box. In order to conserve tetrabenzylzirconium and tetrabenzylhafnium, only small quantities of each solution were prepared (< 1.0 ml). It was found to be more convenient to weigh small quantities of solvent accurately than to prepare small volumes of solution accurately in the inert atmosphere box. Therefore, molal concentration units were used in the preparation of solutions. Conversion to molar concentration units was accomplished through use of the density of the pure solvent.

Spectra were measured within 4 h of sample dilution on a Perkin—Elmer R-12-B 60 MHz NMR spectrometer. The low-field chlorobenzene peak (δ 7.08 ppm relative to TMS) was used as an internal standard when chlorobenzene was the solvent. The 1,4-dioxane peak was used as an internal reference in this solvent.

Pyridine (Fisher), 4-picoline (Aldrich) and 3,5-lutidine (Aldrich) were refluxed over calcium oxide or 4A molecular sieves and distilled. THF was refluxed over potassium and distilled. All bases were transferred to the inert atmosphere box under nitrogen without exposure to air following distillation. Dioxane (Fisher) was refluxed for 24 h over sodium and distilled. Chlorobenzene (Aldrich) was distilled from 4A molecular sieves.

Computation of equilibrium quotients

Previous results [10, 11] suggest that only monoadduct formation occurs to any appreciable extent when pyridine derivatives are added to tetrabenzylhafnium in aromatic solvents. If one assumes that only a monoadduct forms when tetrabenzylzirconium reacts with a Lewis base, the equilibrium quotient for reaction 1 is given by eqn. 2 [10, 12] where M_T is the total concentration of free and complexed R_4M, $\chi_{R_4M\cdot B}$ is the mole fraction of R_4M which is complexed, and *BTM* is the base to metal ratio. If rapid NMR exchange between free and complexed R_4M occurs, the value of $\chi_{R_4M\cdot B}$ is given by eqn. 3.

$$Q = \frac{\chi_{R_4M\cdot B}}{M_T(1-\chi_{R_4M\cdot B})(BTM-\chi_{R_4M\cdot B})} \tag{2}$$

$$\chi_{R_4M\cdot B} = \frac{\Delta_{obs}}{\Delta^0} \tag{3}$$

where $\Delta_{obs} = (\delta_{obs} - \delta_{R_4M})$ and $\Delta^0 = (\delta_{R_4M\cdot B} - \delta_{R_4M})$.

It was not possible to measure $\delta_{R_4M\cdot B}$ directly for most of the systems studied. Therefore, a non-linear least squares procedure [13] * was used to obtain values of Δ^0 and Q which gave the best fit of Δ_{calc} with the measured values of Δ_{obs}. Δ_{calc} was determined from trial values of Δ^0 and Q through use of eqns. 4 and 5.

$$\Delta_{calc} = \frac{\Delta^0}{2}\,[b-(b^2-4BTM)^{1/2}] \tag{4}$$

$$\text{where } b = 1 + BTM + (M_T Q)^{-1} \tag{5}$$

Calculations were performed on a Burroughs 6700 computer at the University of Delaware Computing Center. Marginal standard deviations [14-16], conditional standard deviations [14-16] and support plane confidence limits [13-17] were calculated as part of the least squares program. Sharpness of fit parameters [18] were calculated separately. The range of saturation fractions [19] used in each case are shown in Table 1.

For systems in which little adduct dissociation occurred (R_4Hf/pyridine and R_4Hf/3,5-lutidine) competing equilibria involving $(C_6H_5CH_2)_4Hf$, $(C_6H_5CH_2)_4Zr$ and the base were used to obtain Δ^0_{Hf} and Q_{Hf}/Q_{Zr} [10]. A non-linear least squares procedure [13] was used to find values of these parameters which gave the best fit between Δ^{Zr}_{obs} and Δ^{Zr}_{calc} where

$$\Delta^{Zr}_{calc} = \frac{\Delta^0_{Zr}}{1 + F(Q_{HF}/Q_{Zr})} \tag{6}$$

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* The Fortran program used was written by D.W. Marquardt and revised for the University of Delaware Systems library by T.R. Tatman. Details of the method have been described previously [13].

TABLE 1

EQUILIBRIUM QUOTIENTS (Q) AND ADDUCT CHEMICAL SHIFTS (Δ°) FOR THE REACTION $(C_6H_5CH_2)_4M + B \rightleftharpoons (C_6H_5CH_2)_4M\cdot B$ at 36.5°

M/Base	$[R_4M]^a$	Δ° (ppm)	M.D.[b]	90%C.L.[c]	Q	M.D.[b]	C.D.[d]	90%C.L.[c]	M.D./C.D.	R.S. (%)[e]
Zr/pyridine	0.012	0.88	0.02	0.04	29	1.6	0.68	4	2.8	28-83
Zr/pyridine	0.036	0.96	0.03	0.10	19	1.8	0.40	5	4.5	16-71
Zr/pyridine[f]	0.144	1.00	0.03	0.09	11	1.3	0.23	4	5.7	9-75
Zr/4-picoline	0.012	1.01	0.03	0.06	63	4.8	0.94	13	5.1	19-70
Zr/4-picoline	0.036	0.99	0.02	0.06	51	4.8	1.0	12	4.8	22-82
Zr/4-picoline (in 1,4-dioxane)	0.012	0.80	0.02	0.05	118	8.8	3.0	26	2.9	44-88
Zr/3,5-lutidine	0.012	0.94	0.02	0.06	152	13	3.4	38	3.8	47-84
Hf/THF	0.036	0.59	0.01	0.03	18	1.1	0.39	3	2.8	42-86

[a] Mol/l in chlorobenzene unless otherwise indicated. [b] Marginal deviation. [c] Uncertainty based on support plane 90% confidence limits. [d] Conditional deviation. [e] Range of saturation used [19]. [f] T = 35°. Value of 12.6 published previously [10] was based on an alternative method of calculation and molal concentration units.

TABLE 2

EQUILIBRIUM QUOTIENT RATIOS QHf/QZr OBTAINED FROM COMPETING EQUILIBRIA INVOLVING $(C_6H_5CH_2)_4Zr/(C_6H_5CH_2)_4Hf$/BASE

Base	$[R_4Zr]^a$	$[R_4Hf]^a$	Δ°_{Zr}(ppm)[b]	Δ°_{Hf}(ppm)	M.D.[c]	90%C.L.[d]	Q_{Hf}/Q_{Zr}	M.D.[c]	C.D.[e]	90%C.L.[d]	M.D./C.D.
Pyridine	0.014	0.14	0.88	0.74	0.003	0.01	34	2.0	0.70	9	2.9
Pyridine[f]	0.014	0.14	1.00	0.75	0.003	0.01	39	2.3	0.75	10	3.1
3,5-lutidine	0.036	0.11	0.94	0.74	0.004	0.02	38	3.0	1.2	10	2.5

[a] Mol/l. [b] Value of Δ°_{Zr} used in the calculation. [c] Marginal deviation. [d] Support plane 90% confidence limits. [e] Conditional deviation. [f] Previously reported results [10] were based on a different method of calculation.

$$F = \frac{\Delta^0_{Hf} - \Delta^{Hf}_{obs}}{\Delta^{Hf}_{obs}} \tag{7}$$

Only those data points in which $\Delta^{Zr}_{obs} \geqslant 0.03$ and $(\Delta^0_{Hf} - \Delta^{Hf}_{obs}) \geqslant 0.03$ were included.

Results and discussion

Results of the equilibrium studies are shown in Table 1. In all cases the sharpness of fit exceeded the recommended minimum of 20 [18]. Also the conditional standard deviations are small (< 5%), and the ratios of the marginal to conditional deviations are well below the rejection value of 12 proposed by Guidry and Drago [20]. Therefore, we believe the equilibrium quotients are reliable, in spite of the fact that the ratio of the marginal to conditional deviations are somewhat larger than the maximum value of 3 recommended by Guidry and Drago [20].

In chlorobenzene values of Δ^0 for $(C_6H_5CH_2)_4Zr \cdot B$ lie in the range 0.88-1.01, while those for $(C_6H_5CH_2)_4Hf \cdot B$ lie in the range 0.74-0.75 when B is a pyridine derivative (Table 2). All shifts are downfield from free $(C_6H_5CH_2)_4M$. Δ^0 for $(C_6H_5CH_2)_4Hf \cdot THF$ lies 0.59 ppm downfield from $(C_6H_5CH_2)_4Hf$. If the local diamagnetic term predominated, one would expect an upfield shift upon adduct formation. Althought ring currents arising from the presence of pyridine bases could contribute to the downfields shifts, this would not explain the downfield shift in $(C_6H_5CH_2)_4Hf \cdot THF$. X-ray crystal structures of tetrabenzylzirconium [21] and tetrabenzylhafnium [22] indicate that the average M—C—C bond angle is close to 93°, suggesting that interactions occur between the metal and the ring of the benzyl group. It is likely that these metal—ring interactions are partially destroyed upon adduct formation. The resulting change in geometry will affect the ring current contributions to δ_{CH_2} and could lead to the observed downfield shift.

The chemical shifts of the Si—CH$_2$—M protons in $[(CH_3)_3SiCH_2]_4Zr$ and $[(CH_3)_3SiCH_2]_4Hf$ in C_6H_6 occur at τ8.82 and τ9.43 respectively [23], while those of the C—CH$_2$—M protons in $[(CH_3)_3CCH_2]_4Zr$ and $[(CH_3)_3CCH_2]_4Hf$ occur at τ8.48 and τ8.98 [24]. Thus, the methylene protons in the hafnium derivatives appear 0.5-0.6 ppm upfield from those of the zirconium derivatives. In contrast the methylene protons in $(C_6H_5CH_2)_4Zr$ and $(C_6H_5CH_2)_4Hf$ are separated by only 0.04 ppm. Therefore, it appears that the metal—ring interaction decreases the difference in chemical shift which occurs when the metal is changed from zirconium to hafnium. The fact that the adduct chemical shifts for $(C_6H_5CH_2)_4Hf \cdot B$ appear 0.2-0.3 ppm upfield from those of $(C_6H_5CH_2)_4Zr \cdot B$ when B is a pyridine derivative is in accord with the higher resonance frequency observed for the trimethylsilylmethyl and neopentyl derivatives of hafnium compared with those of zirconium. These results support the argument that the metal—ring interaction is partly destroyed in adducts of the benzyl derivatives. The extent to which the higher adduct frequency in $(C_6H_5CH_2)_4Hf \cdot B$ reflects a difference in the strength of the metal—base interaction in going from zirconium to hafnium cannot be determined from our results.

The value of the equilibrium quotient for the reaction of $(C_6H_5CH_2)_4Zr$ with 4-picoline in 1,4-dioxane is 118 compared with a value of 63 in chlorobenzene. The smaller value in chlorobenzene undoubtedly results from the fact that solvation of tetrabenzylzirconium and/or the base occur to a larger extent in the aromatic solvent than in 1,4-dioxane. If reactions 8 and 9 compete with reaction 1, then Q, the apparent equilibrium quotient which we calculate, is related to Q_1, the actual equilibrium quotient for reaction 1,

$$(C_6H_5CH_2)_4Zr + S \overset{Q_2}{\rightleftarrows} (C_6H_5CH_2)_4Zr \cdot S \qquad (8)$$

$$S + B \overset{Q_3}{\rightleftarrows} S \cdot B \qquad (9)$$

according to eq. 10 [25]. In this equation [S] is the concentration of the

$$Q = \frac{Q_1}{(1 + Q_2\,[S])\,(1 + Q_3[S])} \qquad (10)$$

solvent. As Q_2 and Q_3 increase, Q decreases. Since association of substituted pyridines with aromatic solvents has been reported [26-28] it is likely that Q_3 is larger in chlorobenzene than in 1,4-dioxane. It is not clear which solvent will give a larger value of Q_2. However, it should be noted that no shift in the methylene resonance of $(C_6H_5CH_2)_4Hf$ in chlorobenzene occurs when when 1,4-dioxane is added [10].

The value of the equilibrium quotient obtained with pyridine in chlorobenzene decreases as the concentration of $(C_6H_5CH_2)_4Zr$ increases. Trending in previous equilibrium quotient studies has been attributed to solvation effects [29, 30], diadduct formation [31, 32] or changes in activity coefficients [33]. Self-association of the acid or base could also produce trending. Since our studies were carried out on dilute solutions, the solvent concentration should not change appreciably as the concentration of tetrabenzylzirconium is varied. Therefore, it is unlikely that solvation is responsible for the variation in Q. Furthermore, no trending in Q was observed as the concentration of pyridine was varied while holding the concentration of $(C_6H_5CH_2)_4Zr$ constant. Such a variation would be expected if diadduct formation were occurring to a significant extent. Therefore, the most likely sources of the observed trending are the neglect of activity coefficients and partial self-association of the base and/or the organometallic species. Intermolecular interactions between pyridine bases have been reported [26, 27, 34-36]. Also a small amount of a dimeric species such as $[(C_6H_5CH_2ZrH]_2$ or $[(C_6H_5CH_2C_6H_4)(C_6H_5CH_2)_2ZrH]_2$ which could be formed from the photochemical decomposition of $(C_6H_5CH_2)_4Zr$ [3, 4, 37] may be present. While the concentrations of these associated species may not be sufficient to account for the entire change in Q with concentration, their presence could be a contributing factor. Results on the system $(C_6H_5CH_2)_4Zr$/4-picoline also show a decrease in Q as the concentration of $(C_6H_5CH_2)_4Zr$ increases.

Data in Table 2 indicate that equilibrium quotients with respect to a given base are higher by a factor of 34-39 when tetrabenzylhafnium is the acid than when tetrabenzylzirconium is the acid. The Q_{Hf}/Q_{Zr} ratio is essentially the same when the base is 3,5-lutidine as when the base is pyridine. Previous results indicate that the enthalpy of adduct formation is larger for $HfCl_4$ than for $ZrCl_4$ when tetrahydrothiophene or Cl_3PO is the base [38, 39] while the enthalpies of adduct formations are similar for the two acids when the base is tetrahydrofuran [38]. $ZrCl_4$ has been found to be the stronger acid toward certain esters [40]. It is likely therefore, that Q_{Hf}/Q_{Zr} for reactions of $(C_6H_5CH_2)_4M$ with bases will also vary as the class of base changes. Since the equilibrium quotient for the reaction of $(C_6H_5CH_2)_4M$ with THF is considerably smaller ($Q_{Hf} = 18$) than that for the reaction with pyridine bases, no value of Q_{Hf}/Q_{Zr} could be obtained with THF as the base. However, Q_{Hf}/Q_{Zr} for reaction 11 is only 1.5 [41, 42].

$$MCl_4 \cdot OPCl_3 + OPCl_3 \rightleftarrows MCl_4 \cdot 2(OPCl_3) \tag{11}$$

From these results it is clear that values of Q_{Hf}/Q_{Zr} will have to be obtained with bases having a variety of donor atoms before values of the equilibrium quotient ratio for the reaction with olefins can be estimated.

Values of Q increase as the pK_a of the base increases. Previously it has been shown that enthalpies of adduct formation of $ZrCl_4$ with substituted pyridines are dependent upon the pK_a of the base also [43]. Ballard [4] has suggested that a plot of the equilibrium quotient for reaction 1 versus the basicity of a variety of ligands B could be extrapolated to determine Q for the reaction with olefins. While in principle such a procedure could be used to obtain an estimate of the stability quotients for olefin adducts, in practice a number of problems are encountered. First, if trending occurs, as was observed in the present study, uncertainty arises concerning which value of Q should be used for each base. Second, it is not obvious that a single curve will be obtained when a plot of log Q versus pK_a is constructed from data obtained with bases having different donor atoms [44]. If the curve depends on the nature of the donor atom, no extrapolation for olefin donors can be carried out. Finally, differing steric effects among bases may cause a breakdown in the relationship between log Q and pK_a [45].

The results of our study indicate that further investigations of the effects of solvent, concentration and nature of the base on equilibrium quotients are needed before one can attempt to relate the results to catalytic behavior of these organometallic compounds.

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