Electric Dipole Moments and Infrared Spectral Studies of Bis(cyclopentadienyl)titanium(IV) and -zirconium(IV) Pseudohalide Complexes in Various Solvents

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Dipole moment measurements have been carried out in benzene for $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$, $(\pi\text{-}C_5H_5)_2Ti(OCN)_2$, $(\pi\text{-}C_5H_5)_2Zr(NCS)_2$ and $(\pi\text{-}C_5H_5)_2Zr(OCN)_2$' and in dioxane for $(\pi\text{-}C_5H_5)_2TiCl_2$ and $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$. The dipole moments of $(\pi\text{-}C_5H_5)_2TiCl_2$ and $(\pi\text{-}C_5H_5)_2ZrCl_2$ in benzene are known.

The measurements show that the polarity of $(\pi\text{-}C_5H_5)_2TiCl_2$ is the same in benzene and dioxane, whereas $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$ exhibits a different polarity in these solvents. Furthermore, it is shown that, in benzene,

$$\mu[(\pi\text{-}C_5H_5)_2Ti(NCS)_2]/\mu[(\pi\text{-}C_5H_5)_2TiCl_2] = \mu[(\pi\text{-}C_5H_5)_2Zr(NCS)_2]/\mu[(\pi\text{-}C_5H_5)_2ZrCl_2]$$

whereas

$$\mu[(\pi\text{-}C_5H_5)_2Ti(OCN)_2]/\mu[(\pi\text{-}C_5H_5)_2TiCl_2] \neq \mu[(\pi\text{-}C_5H_5)_2Zr(OCN)_2]/\mu[(\pi\text{-}C_5H_5)_2ZrCl_2].$$

The results of infrared spectral studies of $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$, $(\pi\text{-}C_5H_5)_2Zr(NCS)_2$, $(\pi\text{-}C_5H_5)_2Ti(OCN)_2$, and $(\pi\text{-}C_5H_5)_2Zr(OCN)_2$ in methylene chloride, benzene, and dioxane show that the thiocyanates in $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$ and $(\pi\text{-}C_5H_5)_2Zr(NCS)_2$ are N-bonded in the three solvents used, but do not shed any light on the cause of the irregularities observed in the dipole moments of the titanocene and zirconocene cyanates.

The most reasonable explanation appears to be that, contrary to the conclusions reached in an earlier work, the cyanate bonding modes in the two complexes are not the same. The titanocene cyanate most likely contains N-bonded groups, whereas those in the zirconocene cyanate are most likely O-bonded. A considerable degree of dissociation of $(\pi\text{-}C_5H_5)_2Zr(NCS)_2$ in dioxane is observed as well.

The bonding modes of various ambidentate ligands have been shown to be subject to a variety of directive influences.[1-3] The occurrence of a specific solvent effect has been noted in one example involving the coordination of the nitrite ion [4] and in five rather disparate examples involving the thiocyanate ion.[2,5-8]

In an effort to confirm the bonding patterns indicated by the results of infrared and visible-ultra violet spectral studies involving metallocene pseudo-halide complexes of the type $(\pi\text{-}C_5H_5)_2M(NCS)_2$ [M = Ti(IV), Zr(IV), Hf(IV), and V(IV)], $(\pi\text{-}C_5H_5)_2Ti(NCSe)_2$, $(\pi\text{-}C_5H_5)_2M(OCN)_2$[M = Ti(IV), Zr(IV) and Hf(IV)], $(\pi\text{-}C_5H_5)_2V(NCO)_2$, and $(\pi\text{-}C_5H_5)_2TiNCO$,[9] we have measured the dipole moments in benzene of the Ti(IV) and Zr(IV) complexes of the type $(\pi\text{-}C_5H_5)_2M(NCS)_2$ and $(\pi\text{-}C_5H_5)_2M(OCN)_2$ and in dioxane of $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$ and $(\pi\text{-}C_5H_5)_2TiCl_2$. Measurements of dipole moments of the Hf(IV) and V(IV) complexes were attempted, but the extremely low solubility in benzene and dioxane prevented these measurements from being performed. Further-more, infrared spectral measurements were carried out in methylene chloride, benzene, and dioxane for the above mentioned Ti(IV) and Zr(IV) complexes in order to permit correlation of the inferences resulting from the dipole moment measurements with those which resulted from the earlier study.[9]

EXPERIMENTAL

Preparation of complexes. The titanium(IV), zirconium(IV), hafnium(IV), and vana-dium(IV) complexes were prepared by the methods given in the literature.[9] Satisfactory C, H, and N analyses were obtained for all of the $(\pi\text{-}C_5H_5)_2ML_2$ complexes.

Analyses. Microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elsbach über Engelskirchen, West Germany.

Solvents. Dioxane [10] (Merck, *p.a.*) was treated with potassium hydroxide pellets for at least one week (50 g KOH/1000 ml dioxane). The dioxane was then decanted from the potassium hydroxide pellets, filtered, and checked for peroxide content. The peroxide free dioxane was distilled and the fraction with a boiling point of $101-102°$ was collected and kept in well closed bottles. Benzene (Merck, *p.a.*) was dried by being poured through a column of molecular sieves (BDH Laboratory Reagent, type 4A) and was then used immediately without further purification. The distilled dioxane was dried in the same way immediately before use.

Dipole moment measurements. The dielectric constant measurements were carried out at 25°C using a WTW dipolmeter model DMO1 and a cell model DFL1. Refractive indexes were measured with a high accuracy Abbe refractometer 60/ED. The dipole moments were calculated in accordance with the methods of Hedestrand,[11] Guggenheim,[12] and Smith,[13] using the following expression for the dipole moment, μ:

$$\mu^2 = \frac{27kT}{4\pi N} \times \frac{M_2}{\varrho_1(\varepsilon_1 + 2)^2}\,(a_\varepsilon - a_n)$$

where the subscript 1 refers to the solvent and subscript 2 to the solute (k = Boltzmann constant, T = absolute temperature, N = Avogadro's number, M = mol weight, ϱ = den-sity, ε = dielectric constant). a_ε is the slope of the line, $(\varepsilon_{12} - \varepsilon_1) = f(w_2)$, and a_n is the slope of the line, $(n_{12}{}^2 - n_1{}^2) = f(w_2)$ where ε_{12} and n_{12}, respectively, are the dielectric con-stant and the refractive index of the solution, and w_2 is the weight fraction of the dis-solved substance. The results and the statistical analysis of the results are shown in Table 1. The analysis has been carried out by assuming that only the term $(a_\varepsilon - a_n)$ is of importance for this analysis. The variance on a_ε and a_n were calculated according to this assumption. The dipole moments of the parent chlorides have been measured by Gid-dings *et al.*[14] and are included in Table 1 as well.

Infrared spectra. The infrared spectra of the metallocene pseudohalide complexes were measured on Perkin-Elmer 180 or 421 grating spectrophotometers in the ν_{CN} region as methylene chloride, benzene, and dioxane solutions, and with a fourfold wave number scale expansion, using matched 0.1 mm sodium chloride cells. The integrated absorption intensities of the ν_{CN} bands were determined by Ramsay's method of direct integration.[15] The results are shown in Table 2.

Table 1. Dipole moments for $(\pi\text{-}C_5H_5)_2ML_2$ complexes.[a]

$(\pi\text{-}C_5H_5)_2ML_2$	Solvent	a_ε	Variance a_ε	a_n	Variance a_n	μ Debye	$u\mu$ Debye (%)
$(\pi\text{-}C_5H_5)_2TiCl_2$	Benzene					6.26[b]	±0.39[b,c]
$(\pi\text{-}C_5H_5)_2TiCl_2$	Dioxane	17.0	1.4	1.6	2.3	5.8	±0.3 (5 %)
$(\pi\text{-}C_5H_5)_2Ti(NCS)_2$	Benzene	23.2	1.9	3.3	0.04	7.3	±0.3 (4 %)
$(\pi\text{-}C_5H_5)_2Ti(NCS)_2$	Dioxane	33.2	0.7	1.5	1.7	8.7	±0.2 (2 %)
$(\pi\text{-}C_5H_5)_2Ti(OCN)_2$	Benzene	19.8	0.3	0.7	0.01	6.8	±0.1 (2 %)
$(\pi\text{-}C_5H_5)_2ZrCl_2$	Benzene					5.90[b]	±0.38[b,c]
$(\pi\text{-}C_5H_5)_2Zr(NCS)_2$	Benzene	16.8	1.9	3.1	0.01	6.5	±0.3 (5 %)
$(\pi\text{-}C_5H_5)_2Zr(OCN)_2$	Benzene	11.1	0.5	0.3	0.01	5.5	±0.2 (3 %)

[a] 25°C. [b] Data taken from S. A. Giddings *et al.*[14] [c] 95 % confidence limits of the data.

Table 2. Infrared data for $(\pi\text{-}C_5H_5)_2ML_2$ complexes.

	Methylene Chloride (Burmeister *et al.*[9])		(This work)		Benzene		Dioxane	
	$\nu_{CN}{}^a$	$A^b \times 10^{-4}$	$\nu_{CN}{}^a$	$A^b \times 10^{-4}$	$\nu_{CN}{}^a$	$A^b \times 10^{-4}$	$\nu_{CN}{}^a$	$A^b \times 10^{-4}$
$(\pi\text{-}C_5H_5)_2Ti(NCS)_2{}^c$	2058	11	2054	10	2047	7	2052	10
	2017	20	2014	17	2009	16	2014	19
$(\pi\text{-}C_5H_5)_2Zr(NCS)_2{}^d$							2052[e]	f
	2041	11	2035	11	2030	9	2034	f
	2003	21	1998	18	1993	19	1998	f
$(\pi\text{-}C_5H_5)_2Ti(OCN)_2{}^c$	2235	13	2232	12	2230	10	2231	14
	2196	18	2194	17	2190	15	2193	22
$(\pi\text{-}C_5H_5)_2Zr(OCN)_2{}^c$	2233	12	2230	12	2229	8	2228	f
							2213	f
	2200	16	2196	15	2196	17	2198	f

[a] in cm⁻¹. [b] Integrated absorption intensity (M^{-1} cm⁻²) per mol of coordinated pseudohalide for each band of the doublet. [c] Measured on Perkin-Elmer 421 spectrophotometer. [d] Measured on Perkin-Elmer 180 spectrophotometer. [e] Most intense band. [f] Not determined due to partial decomposition of complex (*vide infra*).

DISCUSSION

It is seen from Table 1 that the error of measurement is $2-5$ %. Table 1 shows that the dipole moment and thus the polarity of $(\pi\text{-}C_5H_5)_2TiCl_2$ is the same — within experimental error — in benzene and dioxane, respectively. This finding indicates the same degree of solvation in these two solvents.

It is further seen from Table 1 that the dipole moment of $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$ is significantly different in benzene and dioxane, respectively. Table 2 shows on the other hand, that the thiocyanates in $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$ are N-bonded [9]

in methylene chloride, benzene, and dioxane, as well. The different dipole moments measured for this complex in the two solvents must then be attributed to different degrees of solvation.

The dipole moments obtained in benzene show that $\mu[(\pi\text{-}C_5H_5)_2Ti(NCS)_2]/$ $\mu[(\pi\text{-}C_5H_5)_2TiCl_2] = \mu[(\pi\text{-}C_5H_5)_2Zr(NCS)_2]/\mu[(\pi\text{-}C_5H_5)_2ZrCl_2]$ indicating that the structure of the complexes and the bonding mode of the thiocyanate ion are the same for the titanocene and zirconocene complexes. The infrared data in Table 2 for $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$ and $(\pi\text{-}C_5H_5)_2Zr(NCS)_2$ confirm that the thiocyanates are N-bonded in both complexes.[9] The infrared data in Table 2 also suggest that the $(\pi\text{-}C_5H_5)_2Zr(NCS)_2$ dissociates to a considerable extent in dioxane since the 2052 cm^{-1} band is identical to that exhibited by ionic NCS$^-$ in this solvent.

The dipole moments obtained in benzene show, on the other hand, that

$$\mu[(\pi\text{-}C_5H_5)_2Ti(OCN)_2]/\mu[(\pi\text{-}C_5H_5)_2TiCl_2]$$
$$\neq \mu[(\pi\text{-}C_5H_5)_2Zr(OCN)_2]/\mu[(\pi\text{-}C_5H_5)_2ZrCl_2]$$

indicating that the structures of the complexes and/or the bonding modes of the cyanate ion are *different* for the titanocene and zirconocene complexes. In this case, the infrared ν_{CN} frequency and integrated intensity data cannot be used to resolve the question, since no confirmed O-bonded cyanate coordination complexes exist which could be used as standards.

The original assignments [9] of O-bonding for the zirconocene and hafnocene cyanate complexes were based on their lowered (relative to the free ion) ν_{CO} stretching frequencies. The bonding modes in the only other O-bonded cyanate coordination complexes reported [16] thus far [the hexacyanates of Mo(III), Re(IV), and Re(V)] were assigned on the same basis. Conversely, the original assignment [9] of N-bonding for the vanadocene cyanate complex was based on its increased ν_{CO} stretching frequency. The ν_{CN} frequencies and their integrated intensities for all three complexes were found [9] to be quite comparable, all being increased relative to the free ion. The titanocene cyanate complex was unique in that no unequivocal ν_{CO} band assignment could be made in its infrared spectrum. Lacking any positive infrared evidence, the original assignment [9] of O-bonding was based primarily on the similarity of the mass spectrum of the titanocene cyanate complex to those of the zirconocene and hafnocene cyanates. In addition to the different dipole moment ratios, it should also be noted that the dipole moment of the zirconocene cyanate is the smallest of the six dipole moments measured in benzene (the dipole moments increase in the order chloride < cyanate < thiocyanate for the titanocene complexes, but switch to the order cyanate < chloride < thiocyanate for the zirconocenes).

In view of the foregoing, it would now appear that the most likely formulations for the metallocene cyanates are $(\pi\text{-}C_5H_5)_2M(NCO)_2$ [M = Ti(IV) and V(IV)] and $(\pi\text{-}C_5H_5)_2M(OCN)_2$ [M = Zr(IV) and Hf(IV)].

The $(\pi\text{-}C_5H_5)_2Zr(OCN)_2$ complex also undergoes a chemical change in dioxane. However, the new 2213 cm^{-1} band is not due to ionic NCO$^-$. Some bridged Zr – O – Zr species may be formed; *cf.* Coutts and Wailes.[17]

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