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CHARGE DISTRIBUTION IN CYCLOPENTADIENYLCYCLOOCTATETRAENETITANIUM

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Summary

Metallation of $(C_5H_5)Ti(C_8H_8)$ is much more difficult than that of (C_5H_5)-$Ti(C_7H_7)$. Analysis of the products obtained after addition of CH_3I shows that substitution of $(C_5H_5)Ti(C_8H_8)$ takes place predominantly in the C_5H_5 ring, whereas $(C_5H_5)Ti(C_7H_7)$ is metallated preferentially in the C_7H_7 ring. These results indicate that in $(C_5H_5)Ti(C_8H_8)$ the C_5H_5 ring is more negatively charged than the C_8H_8 ring, which is in agreement with the results of ESCA measurements. The difference in the behaviour of $(C_5H_5)Ti(C_7H_7)$ and $(C_5H_5)Ti(C_8H_8)$ is discussed.

Introduction

We recently described the results of metallation reactions of the compounds $(C_5H_5)M(C_7H_7)$ with M = Ti, V and Cr [1,2]. It was shown that for M = Ti metallation occurred very easily and predominantly in the C_7H_7 ring [1]. In contrast, metallation of the vanadium and especially of the chromium compound was more difficult, and substitution took place preferentially in the C_5H_5 ring [2]. These results indicate that the negative charge on the C_7H_7 ring increases in the sequence $Cr < V < Ti$, whereas the charge on the C_5H_5 ring varies only slightly; in the Ti compound the negative charge on the C_7H_7 ring is even larger than that on the C_5H_5 ring. These suppositions were confirmed by ^{13}C NMR [3] and ESCA measurements [4].

Since it is often assumed that h^8-C_8H_8 rings bonded to a transition metal are negatively charged, the behaviour of $(C_5H_5)Ti(C_8H_8)$ towards metallation was investigated.

Experimental

All experiments were carried out under purified nitrogen. Solvents were purified by conventional methods and freed from oxygen by repeated degassing and saturating with nitrogen. Methyl iodide and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled before use. Commercial n-butyllithium in hexane was used without purification.

IR spectra were recorded on a Hitachi EPI-G spectrophotometer. The samples were suspended in Nujol between KBr discs. NMR spectra were obtained on a Varian A-60 high resolution instrument. CCl_4 was used as a solvent and tetramethylsilane (TMS) as an internal standard.

ESCA measurements were performed as described previously [4]. Oxidation states of the metal are calculated as described for the chromium and vanadium compounds [4]. Some of the data for the titanium compounds given in Table 1 differ slightly from our preliminary results [4], since reinvestigation showed that some of the samples carried a surface charge. Surface charge effects were eliminated by measuring samples of various thickness. It was found that the binding energy of the carbon 1*s* level in the compounds studied has an almost constant value of 284.8 ± 0.2 eV; the somewhat higher values found for thick samples are due to surface charges.

Elemental analyses were carried out by the Analytical Department of this University.

Synthesis

The compounds $(C_5H_5)Ti(C_8H_8)$ [5] and $(CH_3C_5H_4)Ti(C_8H_8)$ [6] were prepared by published procedures. $C_8H_7CH_3$ was synthesized as described by Gasteiger et al. [7] and purified by distillation. Since this compound is thermally unstable, distillation was carried out carefully (bath temperature below 55°), and the product was stored at —35°.

$(C_5H_5)TiCl_3$ [8] was used as starting material for the synthesis of $(C_5H_5)Ti$-$(C_8H_7CH_3)$. The reaction was carried out as described for the unsubstituted complex [5]. Instead of the large excess of C_8H_8 used by Van Oven, only a small excess (about 20%) of $C_8H_7CH_3$ was used. After repeated re-crystallization from hexane and sublimation at 120°/0.1 mm Hg the product was obtained pure. Yield 19%. (Found: C, 72.25, 72.31; H, 6.56, 6.71; Ti, 20.71, 20.57. $C_{14}H_{15}Ti$ calcd.: C, 72.73; H, 6.48; Ti, 20.74%.) IR absorptions: 1440m, 1340m, 1010ms, 868w, 832w, 780s, 762s, 749w, 722m.

Metallation of $(C_5H_5)Ti(C_8H_8)$

A suspension of $(C_5H_5)Ti(C_8H_8)$ (3.09 g, 13.8 mmol), n-BuLi (18.0 mmol) and TMEDA (0.4 ml, 3.6 mmol) in 50 ml of hexane was stirred at room temperature for 3 h. Then 20 mmol of CH_3I was added and the solution was stirred for 30 min. After evaporation of the volatile material the residue was washed with a few ml of n-pentane and extracted with the same solvent; yield 2.04 g of a mixture of $C_{14}H_{15}Ti$ and $C_{13}H_{13}Ti$ (from IR analysis; Ti analysis: 18.2%). Since the final mixture (mixture A) was contaminated with some LiI, it was sublimed at 120°/0.1 mmHg. The IR spectrum recorded before and after sublimation showed that the composition of mixture A with respect to the Ti compounds was not changed.

Analysis of reaction products

(i) Elemental analyses. The elemental analyses (Ti, 21.04, 21.13; C, 72.40, 72.33; H, 6.41, 6.51%) indicated that mixture A consisted of 71% of $C_{14}H_{15}Ti$ and 29% of $C_{13}H_{13}Ti$.

(ii) Reaction with CCl_4 and HCl. A part of mixture A (430 mg) was dissolved in 60 ml of freshly distilled CCl_4 at 0°. After stirring for 30 min, 24 ml of a 0.48 *M* solution of HCl in ether was added. The colour of the solution changed from yellow to yellow-green. Then the products were extracted four times with CCl_4, dried in vacuo and washed with 20 ml of n-pentane. After sublimation the products were analyzed by NMR. The NMR spectrum showed the presence of $(CH_3C_5H_4)TiCl_3$ and $(C_5H_5)TiCl_3$ in ratio 2:1.

Similar reactions were carried out for the separate compounds. In all cases $(C_5H_5)TiCl_3$ or $(CH_3C_5H_4)TiCl_3$ was isolated, reproducibly and in reasonable yields (65-70%).

(iii) Reaction with CCl_4 and air. An accurately weighed amount of (RC_5H_4)-$Ti(C_8H_7R)$ ($R = H, CH_3$) was added to 2 ml of a stirred solution of 0.25 *M* of benzene in CCl_4 at —30°. After oxidation with air the mixture was stirred for 16 h at room temperature. The NMR spectrum recorded after filtration showed the presence of C_8H_8 or $C_8H_7CH_3$. The yields of C_8H_8 and $C_8H_7CH_3$ were determined by comparing the integrated signal of benzene with those of C_8H_8 and $C_8H_7CH_3$: $(C_5H_5)Ti(C_8H_8)$, 86%; $(C_5H_5)Ti(C_8H_7CH_3)$, 46% and $(CH_3C_5H_4)Ti$-(C_8H_8), 22%.

The same reaction was carried out for a part of mixture A. The NMR spectrum recorded after filtration showed the presence of C_8H_8, while no $C_8H_7CH_3$ resonance signals were observed.

These decomposition reactions were repeated several times to check their reproducibility.

Results

Metallation of $(C_5H_5)Ti(C_8H_8)$ appeared rather difficult; only with n-BuLi/TMEDA could the compound be metallated to a substantial extent. After addition of CH_3I, evaporation of the solvents and extraction, the products were analyzed by IR spectroscopy. In addition to some starting material, the mixture contained mainly the C_5H_5 ring substituted product (frequencies: 1059, 1040, 1021, 930 and 845 cm^{-1}). Of the absorptions characteristic for the substituted C_8H_8 ring, only the strongest (1010 and 780 cm^{-1}) were detectable.

The more quantitative analysis of the reaction mixture (see Experimental) shows that substitution has taken place predominantly in the C_5H_5 ring, and that no substantial amounts of the C_8H_8 ring substituted product are present.

Discussion

The results of this investigation show that metallation of $(C_5H_5)Ti(C_8H_8)$ proceeds much less readily than that of $(C_5H_5)Ti(C_7H_7)$. Moreover, metallation of the

TABLE 1

CORE-LEVEL BINDING ENERGIES OF SOME Ti COMPOUNDS (IN eV)

Compound	Ti			C [b]	Cl		Oxidation state of titanium
	$2p_{1/2}$	$2p_{3/2}$	$3s$	$1s$	$2p_{1/2}$	$2p_{3/2}$	
$(C_5H_5)_2TiCl_2$	463.2	457.1		284.8(1.5)	199.7	198.3	+2.6
$[(C_5H_5)_2TiCl]_2$ [a]	462.1	455.9	60.8; 60.1	284.9(1.6)	200.3	198.9	+1.4
$(C_5H_5)TiCl_3$	464.1	457.9	62.1	284.7(1.6)	200.6	199.1	+3.4
$(C_5H_5)Ti(C_7H_7)$	461.7	455.6	60.3	284.6(1.6)			+1.1
$(C_5H_5)Ti(C_8H_8)$ [a]	461.1	454.9	60.6; 59.5	284.8(1.5)			+0.4
TiO_2		458.5					+4.0 [c]
Ti	460.6	454.5					+0.0 [c]

[a] Paramagnetic; multiplet splitting is observed for 3*s* of the metal, while all other lines are broadened. [b] Line widths (in eV) are given in brackets. [c] Assumed values

former compound occurs predominantly in the C_5H_5 ring, whereas $(C_5H_5)Ti(C_7H_7)$ is mainly metallated in the C_7H_7 ring.

These differences may be explained by qualitative MO considerations. The reasoning given in our recent papers [1,2] led to the conclusion that in the series of $(C_5H_5)M(C_7H_7)$ compounds (M = Ti, V, Cr) the increase of the negative charge on the C_7H_7 ring in the sequence Cr < V < Ti is due to an increase of the ligand character of the bonding molecular orbitals of δ-symmetry. These orbitals mainly consist of the e_2 orbitals of the C_7H_7 ring and the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals of the metal. Since the energy of the e_2 orbitals of the ligands decreases with increasing ring size [9]; it may be assumed that the ligand character of the bonding molecular orbitals of δ-symmetry is somewhat larger in the $Ti(C_8H_8)$ than in the $Ti(C_7H_7)$ moiety. In both $Ti(C_8H_8)$ and $Ti(C_7H_7)$ the bonding molecular orbitals of δ-symmetry are occupied by four electrons. This is two electrons more than the occupation of the corresponding orbitals in (neutral) C_8H_8, but three electrons more than the occupation of the corresponding orbitals in neutral C_7H_7. This accounts for the fact that, in spite of the somewhat larger ligand character of the molecular orbitals of δ-symmetry of $(C_5H_5)Ti(C_8H_8)$ compared with $(C_5H_5)Ti(C_7H_7)$, the negative charge on the C_8H_8 ring can be smaller than that on the C_7H_7 ring, resulting in a smaller polarity of $(C_5H_5)Ti(C_8H_8)$.

In this analysis it is assumed that the unpaired electron of $(C_5H_5)Ti(C_8H_8)$ occupies the nearly non-bonding a'_1 orbital, which has mainly $3d_{z^2}$ character. This is confirmed by ESR and PES measurements on this compound [10,11] and by the easy formation of the $[(C_5H_5)Ti(C_8H_8)]^+$ cation [12].

The expected smaller polarity of $(C_5H_5)Ti(C_8H_8)$ as compared with $(C_5H_5)Ti(C_7H_7)$ is reflected in the dipole moment and the positive charge of the metal, as determined by ESCA (Table 1). For $(C_5H_5)Ti(C_7H_7)$ a dipole moment of 1.6 D was found [1], for $(C_5H_5)Ti(C_8H_8)$ a moment of 1.2 D [6]. ESCA measurements indicate that the positive charge of the metal is considerably larger in $(C_5H_5)Ti(C_7H_7)$ than in $(C_5H_5)Ti(C_8H_8)$, viz. +1.1 and +0.4, respectively. Since it was found that the negative charge on the C_5H_5 ring has an almost constant value of about 0.3-0.4 electrons [4], the negative charge of the compound

$(C_5H_5)Ti(C_8H_8)$ will reside mainly on the C_5H_5 ring, leaving the C_8H_8 ring almost neutral. For the negative charge on the C_7H_7 ring of $(C_5H_5)Ti(C_7H_7)$, a value of about 0.7-0.8 electrons is derived [4].

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