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CYCLOPENTADIENYLCYCLOHEPTATRIENYLTITANIUM: SUBSTITUTION REACTIONS AND CHARGE DISTRIBUTION

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Summary

Metallation of $(C_5H_5)Ti(C_7H_7)$ occurs much more readily than that of $(C_5H_5)V(C_7H_7)$ and $(C_5H_5)Cr(C_7H_7)$. Analysis of the products obtained after addition of CH_3I shows that metallation of $(C_5H_5)Ti(C_7H_7)$ has taken place predominantly in the seven-membered ring; this is in contrast to the behaviour of the corresponding vanadium (and chromium) compounds, which are preferentially metallated in the five-membered ring. These observations are discussed in terms of qualitative molecular orbital considerations on the charge distribution in $(C_5H_5)M(C_7H_7)$ (M = Cr, V, Ti).

Introduction

An NMR and ESR study of $(C_5H_5)V(C_7H_7)$ [1] indicates that the carbon atoms of the five-membered ring are more negatively charged than those of the seven-membered ring. This explains our observation that metallation of (C_5H_5)-$V(C_7H_7)$ occurs predominantly in the five-membered ring [2]. Metallation of $(C_5H_5)Cr(C_7H_7)$ is more difficult, but again the substitution products isolated are substituted mainly in the five-membered ring [3]. In contrast, we found that metallation of $(C_5H_5)Ti(C_7H_7)$ takes place easily, and occurs preferentially in the seven-membered ring. These results are discussed in terms of molecular orbital considerations on the charge distribution in the compounds $(C_5H_5)M(C_7H_7)$ (M = Cr, V, Ti).

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 (Baker) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled before use. Commercial n-butyllithium in hexane (Merck) was used without purification. The sandwich com-

TABLE 1

DIPOLE MOMENT DATA FOR THE SANDWICH COMPOUNDS

Compound	Dipole moment (D)	Lit. value
$(C_5H_5)Ti(C_7H_7)$	1.6 ± 0.1	
$(C_5H_5)V(C_7H_7)$	1.2	
$(C_5H_5)Cr(C_7H_7)$	1.0	0.79 ± 0.05 (Ref. 3)
$(C_5H_4CH_3)Ti(C_7H_7)$	2.0	
$(C_5H_5)Ti(C_7H_6CH_3)$	1.6	

pounds $(C_5H_5)M(C_7H_7)$ (M = Ti [4], V [5], Cr [6]), $(C_5H_4CH_3)Ti(C_7H_7)$ [7] and $(C_5H_5)Ti(C_7H_6CH_3)$ [7] were prepared according to published procedures.

The NMR spectra of C_6D_6 solutions (40°) were recorded on a Varian A 60 high-resolution instrument with TMS as internal standard. The IR spectra were recorded on a Hitachi EPI-G spectrophotometer. The samples were suspended in hexachlorobutadiene or Nujol between KBr discs. The dipole moment measurements were performed at 20 ± 0.1° in benzene with a WTW dipole meter (type DM 01). Dipole moment data were calculated using the formula given by Guggenheim[8]. The dipole moments given in Table 1 are not corrected for the molecular polarizabilities of the compounds; due to the strong absorption of the compounds in the visible range it is not possible to derive their polarizabilities from refraction indices [9].

Metallation of $(C_5H_5)Ti(C_7H_7)$ with n-BuLi

To a stirred suspension of 3.53 mmol of $(C_5H_5)Ti(C_7H_7)$ in 80 ml of ether 1.70 ml of a 2.1 *M* solution of n-BuLi in hexane was added from a syringe over a period of two hours at 0°. Stirring was continued until the blue colour of the original compound had completely disappeared, then 4.02 mmol of CH_3I was added to the brown mixture at 0°. A fast reaction took place and a green-blue solution was formed. After evaporation of the solvents in vacuum the products were extracted with n-pentane; yield 2.98 mmol of $C_{13}H_{14}Ti$ (84%) which was analyzed by NMR spectroscopy (Table 2).

Metallation of $(C_5H_5)Ti(C_7H_7)$ with n-BuLi/N, N, N', N'-tetramethylethylenediamine (TMEDA)

5.48 mmol of $(C_5H_5)Ti(C_7H_7)$ was slowly added to a stirred solution of TMEDA (16.6 mmol) and n-BuLi (13.6 mmol) in 40 ml of hexane. The mixture was stirred at room temperature for three hours and 16.1 mmol of CH_3I was then added. The further procedure was as described above; yield 0.53 g of a mixture of $C_{13}H_{14}Ti$ and $C_{14}H_{16}Ti$.

TABLE 2

PROTON NMR DATA FOR $C_{13}H_{14}Ti$ IN C_6D_6 SOLUTION (40°)

	δ C_5 ring[a]	δ C_7 ring	δ CH_3	%[b]
$(C_5H_5)Ti(C_7H_6CH_3)$	4.96 (s)	5.43 (m)	2.52 (s)	95
$(C_5H_4CH_3)Ti(C_7H_7)$	4.90 (m)	5.46 (s)	1.81 (s)	5

[a] Internal standard: TMS; s, singlet; m, multiplet. [b] Determined from methyl signals.

TABLE 3

METALLATION OF $C_{13}H_{14}Ti$ WITH n-BuLi[a]

Compound	Amount (mmol)	Reaction time (h)	Yield[b] (mmol)	Products[c] (%)
$(C_5H_5)Ti(C_7H_6CH_3)$	0.85	3	0.52	$(C_5H_5)Ti[C_7H_5(CH_3)_2]$ (100)[d]
$(C_5H_4CH_3)Ti(C_7H_7)$	0.56	3	0.39	$(C_5H_4CH_3)Ti(C_7H_6CH_3)$ (28) $(C_5H_4CH_3)Ti(C_7H_7)$ (72)
$(C_5H_4CH_3)Ti(C_7H_7)$	0.78	7	0.52	$(C_5H_4CH_3)Ti(C_7H_6CH_3)$ (75) $(C_5H_4CH_3)Ti(C_7H_7)$ (25)

[a] Temperature, −10°; solvent, ether. [b] Yield after reaction with CH_3I. [c] From NMR analyses. [d] NMR data: multiplet at δ 5.40 (C_7H_5), singlet at δ 4.94 (C_5H_5), singlets at δ 2.51 and 2.48 ppm (CH_3).

Metallation of $(C_5H_4CH_3)Ti(C_7H_7)$ and $(C_5H_5)Ti(C_7H_6CH_3)$

At a temperature of −10° 0.5 ml of a 2.1 *M* solution of n-BuLi in hexane was slowly added from a syringe to a solution of 0.85 mmol of $C_{13}H_{14}Ti$ in 30 ml of ether. After the reaction times given in Table 3, 2.0 mmol CH_3I was added. Purification of the reaction products was carried out as described above. The results are summarized in Table 3.

Results

$(C_5H_5)Ti(C_7H_7)$ is easily metallated by n-BuLi. The reaction was carried out at 0°, and after about five hours the starting material was completely converted. From the NMR spectrum recorded after treatment of the lithiated products with CH_3I, it was found that two products were formed, viz $(C_5H_5)Ti(C_7H_6CH_3)$ and $(C_5H_4CH_3)Ti(C_7H_7)$. The data collected in Table 2 show that substitution has taken place predominantly in the C_7H_7 ring:

$$\begin{tikzcd}
(C_5H_5)Ti(C_7H_7) \arrow[r, "n\text{-BuLi}"] \arrow[dr] & (C_5H_5)Ti(C_7H_6Li) \arrow[r, "CH_3I"] & (C_5H_5)Ti(C_7H_6CH_3) & (95\%) \\
 & (C_5H_4Li)Ti(C_7H_7) \arrow[r, "CH_3I"] & (C_5H_4CH_3)Ti(C_7H_7) & (5\%)
\end{tikzcd}$$

Metallation of both rings of $(C_5H_5)Ti(C_7H_7)$ is also possible, but only with the use of very strong metallation agents, such as n-BuLi/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) [10]. The NMR spectrum of the reaction products showed the formation of $(C_5H_4CH_3)Ti(C_7H_6CH_3)$ (60%)* and $(C_5H_5)Ti(C_7H_6CH_3)$ (40%).

The methyl-substituted compounds $(C_5H_4CH_3)Ti(C_7H_7)$ and $(C_5H_5)Ti(C_7H_6CH_3)$, are much more soluble in ether than is $(C_5H_5)Ti(C_7H_7)$, and metallation of the substituted compounds could be performed at −10°. The data given in Table 3 show that a methyl group in the C_7H_7 ring has an accelerating effect on the electrophilic substitution. Analysis by NMR of the products isolated after addition of CH_3I shows that the "second" methyl group has entered the seven-membered ring in all cases.

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* NMR data of $(C_5H_4CH_3)Ti(C_7H_6CH_3)$: multiplets from C_7H_6 and C_5H_4 at 5.38 and 4.88 ppm respectively, singlets from CH_3 at 2.52 (C_7-ring) and 1.79 ppm (C_5-ring).

Metallation of $(C_5H_5)V(C_7H_7)$ with BuLi is much more difficult than that of the titanium compound. After 6h at room temperature, CH_3I was added. Products were then analyzed by IR spectroscopy [2]. In addition to the absorption bands of the unsubstituted C_5H_5 ring at 1012 and 1003 cm^{-1}, the spectrum showed two bands at 1039 and 1028 cm^{-1}. These absorptions are characteristic of methyl-substituted C_5H_5 [7]. The absorption bands characteristic for the C_7H_7 ring did not change. In the 3000 - 2800 cm^{-1} range we found the aliphatic C—H stretching frequencies. The bands at 1039/1028 and at 1012/1003 cm^{-1} were found to be of about equal intensities. From this it was concluded that the reaction products consisted of $(C_5H_5)V(C_7H_7)$ and of $(C_5H_4CH_3)V(C_7H_7)$ in about equal amounts.

Attempts to metallate $(C_5H_5)Cr(C_7H_7)$ in the same way as the vanadium compound were not successful; even after a reaction time of 8h at room temperature there was no indication that substitution had occurred.

Discussion

Metallation of $(C_5H_5)M(C_7H_7)$ takes place preferentially in the five membered ring for M = Cr or V, but in the seven-membered ring for M = Ti, the rate of the metallation reaction increases in the sequence M = Cr < V < Ti. We take these observations to indicate that the negative charge on the carbon atoms of the seven-membered ring increases in the same sequence.

An explanation is provided by a qualitative consideration of the molecular orbitals formed from the π-orbitals of the cyclic ligands on the one hand and the $3d$-orbitals of the metals on the other (Fig. 1). Taking the line connecting the metal with the centres of the two rings as the z-direction, the $3d_{z^2}$ and $4s$ (and $4p_z$) orbitals of the metal have σ-symmetry, as have the a_1 orbitals of the two rings. It is seen that the bonding σ-orbitals, occupied by four electrons, are essentially ligand orbitals. The d_{z^2} orbital is almost non-bonding; it is unoccupied

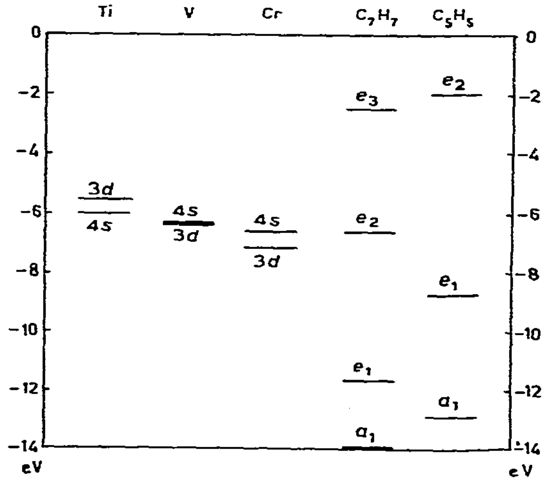

Fig. 1. Estimated energies of the $3d$ and $4s$ orbitals of Ti, V, Cr and of the π orbitals of neutral C_7H_7 and C_5H_5. Values for the metals are minus the valence orbital ionisation potentials of the neutral atoms in configuration d^ns^1[12]; values for the cyclic ligands were taken from ref. 11.

in $(C_5H_5)Ti(C_7H_7)$, occupied by one electron in the vanadium compound [1] and by two electrons in the chromium compound. Eight electrons occupy molecular orbitals of π-symmetry, made up from the e_1 orbitals of the two rings and the d_{xz} and d_{yz} (and $4p_x$, $4p_y$) orbitals of the metal. Again, the (occupied) bonding orbitals are essentially ligand orbitals, while the (empty) antibonding orbitals are metal orbitals.

The remaining four valence electrons are placed in the bonding molecular orbitals of δ-symmetry, formed by the d_{xy} and $d_{x^2-y^2}$ orbitals of the metal and the e_2 orbitals of the seven-membered ring; the e_2 orbitals of the cyclopentadienyl ligand have too high an energy and are not considered. Since the energy of the e_2 orbital of the C_7H_7 ligand is close [11] to the energy of the metal $3d$ orbitals (which increases in the sequence $Cr < V < Ti$ [12]), the ligand character of the bonding MO's of δ-symmetry will be quite sensitive to the character of the metal; it is seen that the ligand character of these (occupied) orbitals will increase in the sequence $Cr < V < Ti$.

The orbital energies shown in Fig. 1 suggest that the bonding MO's of δ-symmetry are mainly metal orbitals in $(C_5H_5)Cr(C_7H_7)$, but mainly C_7H_7 orbitals in $(C_5H_5)Ti(C_7H_7)$. This would mean that the cyclopentadienyl ligand is more negative than the cycloheptatrienyl ligand in the chromium compound, while the reverse would be true of the titanium compound. Although such a conclusion would not be very firmly based because of the uncertainties in the energies of the metal orbitals relative to the ring orbitals, it would agree with the finding of Rettig et al. [1], that the two rings carry about equal (negative) charge in $(C_5H_5)V(C_7H_7)$. According to these authors the charge of the seven-membered ring resides predominantly on the hydrogen atoms, the carbon atoms being almost neutral, while the charge of the cyclopentadienyl ring is almost evenly distributed over carbon and hydrogen atoms [1]. This is in accord with the preferred metallation of the C_5H_5 ring of $(C_5H_5)V(C_7H_7)$ which we observed [2].

In any case, our picture shows that the negative charge on the seven-membered ring of $(C_5H_5)M(C_7H_7)$ increases in the sequence $M = Cr < V < Ti$, leading to an enhanced susceptibility for metallation, while the charge on the five-membered ring is much less affected.

The crystal structures of $(C_5H_5)M(C_7H_7)$ with M = Cr [13], V [14], Ti [15] have been determined. The interatomic distances in the chromium compound [$Cr—C(C_5H_5) = 2.18$ Å; $Cr—C(C_7H_7) = 2.16$ Å] and the vanadium compound [$V—C(C_5H_5) = 2.23$ Å; $V—C(C_7H_7) = 2.25$ Å] have normal values, as have the distances $Ti—C(C_5C_5) = 2.32$ Å in the titanium compound. (The atomic radius of Ti is 0.1 Å larger than that of V). The $Ti—C(C_7H_7)$ distances of 2.19 Å, however, are abnormally short, because of the very short distance (1.49 Å) of the metal from the plane of the seven-membered ring [15]. This observation may be regarded as indicative of the enhanced importance of δ-bonding in the $Ti(C_7H_7)$ moiety; a decrease of the distance of the metal from the ring plane greatly increases the overlap of the ligand e_2 orbitals with the d_{xy} and $d_{x^2-y^2}$ orbitals of the metal.

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