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Abstract

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APPLICATION OF THE N.M.R. METHOD TO THE STUDY OF THE NATURE OF THE TITANIUM-CYCLOPENTADIENYL BOND IN MONO- AND DICYCLOPENTADIENYL DERIVATIVES OF TITANIUM

It was reported earlier (^{1}) that some, but not all, of the cyclopentadienyl (CPD) derivatives of titanium that we studied form ferrocene in reaction with Fe^{2+}. These same compounds are readily hydrolyzed and alcoholyzed at the Ti—CPD bond. This gave us grounds to conclude that the Ti—CPD bond has different degrees of ionic character in different CPD derivatives of titanium. Other compounds studied by us do not possess these properties (^{1}).

Table 1

No.	Substance	Chemical shift of protons on the δ-scale: ring	Chemical shift of protons on the δ-scale: methyl group	Chemical shift of protons on the δ-scale: methylene group	Frequency of out-of-plane deformation vibrations C—H in C_5H_5, cm^{-1}	Frequency of antisymmetric stretching vibrations of the Ti—CPD bond, cm^{-1}	Formation of ferrocene in reaction with Fe^{2+}	Yield of C_5H_5Tl upon action of ethyl alcohol
1	$C_5H_5TiCl_3$	7.21	–	–	838	415	no	no
2	$C_5H_5Ti(OC_2H_5)Cl_2$	6.79	1.28	–	835	407	no	no
3	$C_5H_5Ti(OC_2H_5)_2Cl$	6.40	1.15	4.43	815	390	no	19%
4	$C_5H_5Ti(OC_2H_5)_3$	6.22	1.10	4.20	806	–	70%	100%

It turned out, moreover, that the i.r. spectra of compounds that transfer the CPD ring to Fe^{2+} differ from the spectra of substances that do not possess this property (2). (In the former case a shift is observed of the frequencies of the out-of-plane deformation vibrations of the C—H bonds of the CPD ring and of the antisymmetric vibrations of the Ti—CPD bond toward lower frequencies.) For $C_5H_5Ti(OC_2H_5)_3$ and $Ti(OC_2H_5)_4$, the electrical conductivity* was measured using the apparatus described in (3) at a frequency of 1000 Hz. Cells of the Jones and Bollinger type were used, with constants 0.0212 and 0.0431 cm^{-1}. It was found that for $C_5H_5Ti(OC_2H_5)_3$ the specific electrical conductivity $\chi_{25^\circ} = 7.5 \cdot 10^{-10}\ \Omega^{-1} \cdot cm^{-1}$, while for $Ti(OC_2H_5)_4$ χ_{25° is practically equal to zero.

The data obtained do not contradict our assumption that in $C_5H_5Ti(OC_2H_5)_3$ there is an ionic bond, or a bond close to it, between titanium and the CPD ring.

In the present work we report that CPD derivatives of titanium, both those that form and those that do not form ferrocene in reaction with Fe^{2+}, differ in the value of the chemical shift of the protons of the CPD rings in high-resolution n.m.r. spectra.

We proceeded from the assumption that changes in chemical shifts in compounds of one metal (in the present case titanium), differing in the nature of the atoms or groups attached to the metal, can basically be explained by changes in the electron density at the C—H bonds, and not by the magnetic anisotropy of the metal atom.

* Measurements of electrical conductivity were carried out at the Institute of Electrochemistry by Yu. M. Kessler and N. M. Allatova, to whom the authors express their deep gratitude.

Table 2

No.	Substance	Chemical shift of protons on the δ scale: ring	Chemical shift of protons on the δ scale: methyl group in the ring	Chemical shift of protons on the δ scale: methyl group in OR	Chemical shift of protons on the δ scale: methylene group in OR
1	$CH_3C_5H_4Ti(OC_2H_5)_3$	5.98	2.14	1.09	4.24
2	$CH_3C_5H_4Ti(OC_2H_5)_2Cl$	6.22	2.30	1.23	4.50
3	$CH_3C_5H_4Ti(OC_2H_5)Cl_2$	6.48	2.40	1.37	4.71
4	$CH_3C_5H_4TiCl_3$	6.72	2.36	–	–

As is evident from the results presented in Tables 1 and 2, a decrease in the number of electron-acceptor chlorine atoms attached to titanium leads to an increase in the electron density on the CPD ring. (The signal of the protons of the CPD ring is shifted substantially into the region of a stronger field.)

Fig. 1. Change in the chemical shift on the δ scale of the protons of the ring (solid line, left scale) and of the methyl protons in the ethoxy group (dashed line, right scale) in the series $CH_3C_5H_4Ti(OC_2H_5)_3$ Cl (A), and in the series $C_5H_5Ti(OC_2H_5)_3$ · Cl (B).

Figure 1: Fig. 1. Change in the chemical shift on the δ scale of the protons of the ring (solid line, left scale) and of the methyl protons in the ethoxy group (dashed line, right scale) in the series $CH_3C_5H_4Ti(OC_2H_5)_3$ Cl (A), and in the series $C_5H_5Ti(OC_2H_5)_3$ · Cl (B).

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Naturally, in the substances listed in Table 2, an additional increase in the electron density on the CPD ring is observed under the influence of the methyl group bonded to it.

The striking linearity of the changes in chemical shifts shown in Fig. 1A is noteworthy. However, in the series $C_5H_5Ti \cdot (OC_2H_5)_3$ Cl (n = from 0 to 3), deviations from additivity were observed (Fig. 1B). The nonobligatory nature of the additivity of chemical shifts in the compounds studied is also evident from the coincidence of the signal positions of the ring protons in methyl- and ethylcyclopentadienyltriethoxytitaniums.

From consideration of the data in Tables 3 and 4 it follows that substances in which, judging by the value of the chemical shift, the electron density at the C—H bonds of the CPD rings is increased form ferrocene in reaction with Fe^{2+}. In them, hydrolysis and alcoholysis of the Ti—CPD-ring bond proceed readily (only compounds with unsubstituted rings were studied).

Thus, the data obtained by the high-resolution NMR method are in agreement with the chemical behavior and with the conclusions drawn in the investigation of the IR spectra of the substances studied by us. Apparently, it may be considered established that, as the electron-acceptor properties of the groups attached to the titanium atom decrease, the Ti—CPD-ring bond becomes more ionic, and the covalent character of the bond correspondingly decreases.

The chemical shifts in high-resolution NMR spectra for the protons of the CPD ring in compounds of the type $C_5H_5Fe(CO)_2R$ were investigated by King (4). It was shown that, with weakening of the electron-acceptor properties of R, the signal of the protons of the CPD ring shifts into the region of a stronger field, which is in good agreement with the data of the present work.

It should be noted that, with an increase in the number of chlorine atoms in $C_5H_5Ti(OC_2H_5)_{3-n}Cl_n$ ($n = 0, 1, 2, 3$), the electron density decreases not only on the protons of the ring, but also on the methylene and methyl protons in the ethoxy group. In order to make sure that there is no substantial contribution to this effect from the magnetic anisotropy of the electron shell of titanium and the electrons of the cyclopentadienyl ring, we measured the chemical shifts of the protons of the CH_2- and CH_3-groups in the series $(C_2H_5O)_{4-n}TiCl_n$, where $n = 0, 1, 2, 3$. The values $\delta(CH_3)$ and $\delta(CH_2)$ are 1.16 and 4.34 for $n = 0$; 1.39 and 4.64

Table 3

No.	Substance	Ring	Methyl group in ring	Methylene group in ring	Methyl group in R	Methylene group in R	Other	Formation of ferrocene in reaction with Fe^{2+}
1	$C_5H_5TiCl_3$	7.21	–	–	–	–	–	no
2	$C_2H_5C_5H_4TiCl_3^*$	7.08	1.28	3.15	–	–	–	–
3	$(C_5H_5TiCl_2)_2O$	6.85	–	–	–	–	–	no
4	$C_5H_5Ti(OC_2H_5)Cl_2$	6.79	–	–	1.28	–	–	no
5	$CH_3C_5H_4TiCl_3^*$	6.72	2.36	–	–	–	–	–
6	$CH_3C_5H_4Ti(OC_2H_5)Cl_2^*$	6.48	2.40	–	1.37	4.71	–	–
7	$C_5H_5Ti(OCOCH_3)_3^*$	6.43	–	–	1.96	–	–	+
8	$C_5H_5Ti(OC_2H_5)_2Cl$	6.40	–	–	1.15	4.43	–	no
9	$C_5H_5Ti(OC_6H_5)_3^*$	6.27	–	–	–	–	6.94 in C_6H_5	+
10	$C_5H_5Ti(OCH_3)_3^*$	6.27	–	–	4.02	–	–	+
11	$C_5H_5Ti(OC_4H_9\text{-tert.})_3^*$	6.25	–	–	1.24	–	–	+
12	$CH_3C_5H_4Ti(OC_2H_5)_2Cl^*$	6.22	2.30	–	1.23	4.50	–	–
13	$C_5H_5Ti(OC_2H_5)_3$	6.22	–	–	1.10	4.20	–	+
14	$C_2H_5C_5H_4Ti(OC_2H_5)_3^*$	6.01	2.49	3.70	1.08	4.23	–	–
15	$CH_3C_5H_4Ti(OC_2H_5)_3^*$	5.98	2.14	–	1.09	4.24	–	–

Table 4

No.	Substance	Ring	Methyl group in ring	Methyl group in R	Other	Formation of ferrocene in reaction with Fe^{2+}
1	$(C_5H_5)_2Ti(OCOC_6H_5)_2$	6.77	–	–	7.67; 8.17 in C_6H_5	no
2	$(C_5H_5)_2TiCl_2$	6.66	–	–	–	no
3	$(C_5H_5)_2Ti(OCOCH_3)_2$	6.54	–	1.97	–	+
4	$(C_5H_5)_2Ti(OCOC_2H_5)_2^*$	6.49	–	1.03	2.16 in CH_2	+
5	$C_5H_5(CH_3C_5H_4)TiCl_2$	6.63 unsubstituted 6.36 substituted	2.45	–	–	–
6	$(CH_3C_5H_4)_2TiCl_2$	6.48	2.39	–	–	–

* Substances marked with an asterisk were obtained by us for the first time. A description of their synthesis and properties will be published in the near future.

for $n = 1$; 1.55 and 4.81 for $n = 2$; 1.68 and 4.93 for $n = 3$. As can be seen, in this series an increase in the number of chlorine atoms leads to approximately the same decrease in electron density on the CH_2- and CH_3-protons of the ethoxy group as in the analogous cyclopentadienyl derivatives of titanium (see Tables 1 and 2).

We consider extremely interesting the fact that the electron-acceptor properties of the chlorine atom are transmitted in the presence of a long chain of single bonds that includes a titanium atom, an oxygen atom, and one or two carbon atoms.

The proton-resonance spectra were recorded on a TsLA-5535 spectrometer with an operating frequency of 40 MHz and proton stabilization of the resonance conditions. The accuracy of measurement of the chemical shifts was $\pm 1 \cdot 10^{-8}$. Sealed cylindrical ampoules 4.7 mm in diameter were used; tetramethylsilane was used as the internal standard. Two of the substances we studied had previously been investigated by the NMR method (^{5}). For $(C_5H_5)_2TiCl_2$ an absolute coincidence of the chemical shift was established; the data for $C_5H_5TiCl_3$ differ by $0.07 \cdot 10^{-6}$, which is apparently connected with insufficient purity of the sample studied in (^{5}) (as the authors of that work later reported (^{6})), and also with insufficient stability of the position of the tetrahydrofuran peak taken as the standard. The spin-spin coupling constant in the ethyl- and ethoxy-substituted compounds proved to be close to 7 Hz and did not reveal any specific dependence on the structure of the molecule.

Splitting of the signals of the CPD protons was observed only in titanium CPD derivatives substituted in the ring. The magnitude of this splitting is characteristic of substituted aromatic systems. In all other cases the CPD protons gave a narrow singlet, unambiguously indicating their equivalence.

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Note: Figure translations are in progress. See original paper for figures.