# Rearrangement processes of alkyltitanocene dichlorides under electron impact

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Mass spectra of alkyltitanocene dichlorides $(C_5H_4R)_2TiCl_2$ (R = $Me_2CH$, $Me_2CD$, $Me_3C$, and $Me_3Si$) and $(C_5Me_5)_2TiCl_2$ were studied. The participation of hydrogen atoms at the α-C atoms of substituents in the rearrangement processes were investigated using deuterium labeling.

**Key words**: alkyltitanocene dichlorides, mass spectrum.

The interest in metallocene derivatives of the titanium subgroup is associated with their use as catalysts of olefin polymerization.[1,2] A high activity of metallocene compounds is manifested in the presence of specific cocatalysts (for example, methylalumoxane (MAO)), which are responsible for the formation of ionic (polar) complexes.[3,4] The elucidation of the nature of active centers in such systems is an important problem, which opens up wide possibilities for the design of metallocene catalysts. In this work, fragmentation processes of metallocene ions have been studied by the electron impact method.

It is known that π-,σ-complexes $(C_5H_5)_2MX_2$ (M = Ti, Zr, or Hf; X = F, Cl, Br, or I) under electron impact decompose mainly with the competing loss of $C_5H_5$ and X ligands.[5–8] The interaction of a substituent in the ring with halogen atoms is also characteristic of substituted metallocenes[9,10] along with the detachment of ligands. For example, molecular ions $(C_5H_4Alk)_2ZrCl_2$ eliminate an HCl molecule, and the hydrogen atom at the α-C atom participates in this process.[11]

In this work, the elimination of HCl molecules at various stages of fragmentation of alkyltitanocene dichlorides $(C_5H_4R)_2TiCl_2$ [R = $Pr^i$ (**1**), $Bu^t$ (**2**), and $SiMe_3$ (**3**)] and $(C_5Me_5)_2TiCl_2$ (**4**) under electron impact has been studied.

## Results and Discussion

The main route of the decomposition of the molecular ion of the compound $(C_5H_4Pr^i)_2TiCl_2$ (**1**) is the consecutive elimination of HCl molecules to form $[P-HCl]^+$ and $[P-2\ HCl]^+$ ions. The intensity of the peak of the $[P-HCl]^+$ ion in the mass spectrum is maximum (Table 1). Another fragmentation process is accompanied by the loss of the cyclopentadienyl ligand. The $[P-L]^+$ ion formed decomposes *via* several directions accompanied by the consecutive elimination of HCl and $H_2$, $CH_4$ and HCl, and $CH_4$ and Cl. The decomposition of the molecular ion is accompanied to a considerably lower extent by the elimination of the chlorine atom and molecule.

Compound **4** is more resistant to the electron impact than compound **1**, and its decomposition is accompanied by the formation of $[P-Cl]^+$, $[P-Cl-HCl)^+$, $[P-L]^+$, $[P-L-HCl]^+$, and $L^+$ ions. The peak of the $L^+$ ion is the most intense in the spectrum. The elimination of an HCl molecule is difficult compared to the molecular ion due to compound **1**, which is likely associated with steric hindrances.

In the dissociative ionization of $(C_5H_4Bu^t)_2TiCl_2$ (**2**), the HCl molecule is eliminated only in the $[P-Me]^+$ and $[P-L]^+$ ions, where this process is favored by steric conditions, and the main direction of the decomposition of the molecular ion is accompanied by the elimination of the cyclopentadienyl ligand.

The peculiarity of the decomposition of the molecular ion of $(C_5H_4SiMe_3)_2TiCl_2$ (**3**) is the elimination of an $Me_3SiCl$ molecule along with the detachment of the methyl group.

Thus, the cleavage of the Ti—L and Ti—Cl bonds is typical of the fragmentation of compounds **1**—**4**. The main directions of the dissociative ionization caused by the substituent nature are the elimination of the HCl molecule (compounds **1** and **4**), methyl group (compounds **2** and **3**), and $Me_3SiCl$ molecule (compound **3**) by the molecular ion. Similar regularities of fragmentation also have been established for alkyl-substituted zirconocene dichlorides.[11]

For the study of rearrangement processes in complexes containing a hydrogen atom at the α-C atom of

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**Table 1.** Mass spectra of $(C_5H_4R)_2TiCl_2$ [R = $Pr^i$ (**1**), $Bu^t$ (**2**), and $SiMe_3$ (**3**)] and $(C_5Me_5)_2TiCl_2$ (**4**)*

| Ion | Relative intensity of peaks of ions (%) | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| $P^+$ | 8.7 | 24.1 | 10.2 | 41.7 |
| $[\mathrm{P-Cl}]^+$ | 10.6 | 28.0 | 26.8 | 37.2 |
| $[\mathrm{P-2\ Cl}]^+$ | 1.7 | — | — | 1.9 |
| $[\mathrm{P-HCl}]^+$ | 31.9 | — | — | 9.6 |
| $[\mathrm{P-2\ HCl}]^+$ | 100.0 | — | — | 0.9 |
| $[\mathrm{P-Me}]^+$ | — | 0.3 | 100.0 | — |
| $[\mathrm{P-Me-Cl}]^+$ | — | — | 17.4 | — |
| $[\mathrm{P-Me-HCl}]^+$ | — | 3.8 | — | — |
| $[\mathrm{P-2\ Cl-CH_4}]^+$ | — | 11.7 | — | — |
| $[\mathrm{P-Cl-HCl}]^+$ | — | — | — | 21.5 |
| $[\mathrm{P-Cl-HCl-2\ H}]^+$ | — | — | — | 7.1 |
| $[\mathrm{P-Cl-HCl-4\ H}]^+$ | — | — | — | 3.2 |
| $[\mathrm{P-Me_3SiCl}]^+$ | — | — | 12.7 | — |
| $[\mathrm{P-Me_3SiCl-Me}]^+$ | — | — | 16.6 | — |
| $[\mathrm{P-L}]^+$ | 50.0 | 100.0 | 49.2 | 44.5 |
| $[\mathrm{P-L-H}]^+$ | — | — | — | 15.2 |
| $[\mathrm{P-L-Cl}]^+$ | — | — | — | 29.4 |
| $[\mathrm{P-L-HCl}]^+$ | 5.2 | 15.4 | — | 42.9 |
| $[\mathrm{P-L-HCl-H}]^+$ | 8.8 | 17.8 | | — |
| $[\mathrm{P-L-HCl-2\ H}]^+$ | 28.9 | 41.2 | — | 10.8 |
| $[\mathrm{P-L-HCl-3\ H}]^+$ | — | — | — | 10.8 |
| $[\mathrm{P-L-HCl-4\ H}]^+$ | 6.2 | 11.8 | — | — |
| $[\mathrm{P-L-Me}]^+$ | — | — | 76.6 | — |
| $[\mathrm{P-L-CH_4-Cl}]^+$ | 30.6 | 51.0 | — | — |
| $[\mathrm{P-L-CH_4-HCl}]^+$ | 15.7 | 24.0 | — | — |
| $[\mathrm{P-L-CH_4-HCl-2\ H}]^+$ | — | 8.0 | — | — |
| $[\mathrm{P-L-HCl-2\ H-C_2H_2}]^+$ | 10.0 | — | — | — |
| $[\mathrm{P-L-CH_4-C_2H_2}]^+$ | 5.0 | — | — | — |
| $[\mathrm{P-L-CH_4-Cl-C_2H_2}]^+$ | 17.5 | — | — | — |
| $[\mathrm{P-L-HCl-Me-C_2H_2}]^+$ | — | 7.3 | — | — |
| $[\mathrm{P-L-HCl-CH_4-C_2H_2}]^+$ | 14.7 | — | | — |
| $Me_3Si^+$ | — | — | 11.4 | — |

* The relative intensity of the peak of each ion is the total intensity of the peaks of its isotope varieties per analogous sum of the intensities of the peaks of the ions taken as equal to 100 %. $P^+$ is the molecular ion; L is the ligand.

**Table 2.** Mass spectrum of $[C_5H_4C(D)Me_2]_2TiCl_2$ (**5**)

| Type of ion | Composition of ion | $I_{rel}$ (%) |
|---|---|---|
| $P^+$ | $C_{16}H_{20}D_2TiCl_2^+$ | 14.7 |
| $[\mathrm{P-HD}]^+$ | $C_{16}H_{21}DTiCl_2^+$ | 0.3 |
| $[\mathrm{P-2\ H-2\ D}]^+$ | $C_{16}H_{22}TiCl_2^+$ | 0.1 |
| $[\mathrm{P-Cl}]^+$ | $C_{16}H_{20}D_2\ TiCl^+$ | 8.8 |
| $[\mathrm{P-2\ Cl}]^+$ | $C_{16}H_{20}D_2Ti^+$ | 1.8 |
| $[\mathrm{P-DCl}]^+$ | $C_{16}H_{20}DTiCl^+$ | 31.1 |
| $[\mathrm{P-DCl-HCl}]^+$ | $C_{16}H_{19}DTi^+$ | 100.0 |
| $[\mathrm{P-L}]^+$ | $C_8H_{10}DTiCl_2^+$ | 69.2 |
| $[\mathrm{P-L-HD}]^+$ | $C_8H_9TiCl_2^+$ | 1.3 |
| $[\mathrm{P-L-HCl}]^+$ | $C_8H_9DTiCl^+$ | 2.3 |
| $[\mathrm{P-L-HCl-H}]^+$ | $C_8H_8DTiCl^+$ | 3.5 |
| $[\mathrm{P-L-HCl-2\ H}]^+$ | $C_8H_7DTiCl^+$ | 19.3 |
| $[\mathrm{P-L-HCl-HD}]^+$ | $C_8H_8TiCl^+$ | 8.6 |
| $[\mathrm{P-L-HCl-4\ H}]^+$ | $C_8H_5DTiCl^+$ | 2.3 |
| $[\mathrm{P-L-HCl-2\ H-HD}]^+$ | $C_8H_6TiCl^+$ | 2.0 |
| $[\mathrm{P-L-CH_4}]^+$ | $C_7H_6DTiCl_2^+$ | 2.5 |
| $[\mathrm{P-L-CH_4-Cl}]^+$ | $C_7H_6DTiCl^+$ | 24.7 |
| $[\mathrm{P-L-CH_4-HCl}]^+$ | $C_7H_5DTiCl^+$ | 9.8 |
| $[\mathrm{P-L-CH_4-DCl}]^+$ | $C_7H_6TiCl^+$ | 3.2 |
| $[\mathrm{P-L-HCl-2\ H-C_2H_2}]^+$ | $C_6H_5DTiCl^+$ | 1.9 |
| $[\mathrm{P-L-HCl-HD-C_2H_2}]^+$ | $C_6H_6TiCl^+$ | 2.3 |
| $[\mathrm{P-L-CH_4-C_2H_2}]^+$ | $C_5H_4DTiCl_2^+$ | 2.7 |
| $[\mathrm{P-L-CH_4-C_2HD}]^+$ | $C_5H_5TiCl_2^+$ | 1.1 |
| $[\mathrm{P-L-CH_4-Cl-C_2H_2}]^+$ | $C_5H_4DTiCl^+$ | 2.8 |
| $[\mathrm{P-L-CH_4-Cl-C_2HD}]^+$ | $C_5H_5TiCl^+$ | 3.5 |
| $L^+$ | $C_8H_{10}D$ | 20.0 |
| | $C_8H_{11}^+$,$C_8H_9D^+$ | 0.4 |
| | $C_8H_8D^+$, $C_8H_{10}^+$ | 3.0 |
| | $C_8H_9^+$ | 0.5 |
| | $C_8H_6D^+$ | 0.5 |
| | $C_7H_8D^+$ | 0.6 |
| | $C_7H_7D^+$, $C_7H_9^+$ | 4.2 |
| | $C_7H_6D^+$, $C_7H_8^+$ | 14.9 |
| | $C_7H_7^+$ | 4.5 |
| | $C_6H_6D^+$ | 1.8 |
| | $C_6H_5D^+$, $C_6H_7^+$ | 1.0 |
| | $C_6H_4D^+$, $C_6H_6^+$ | 1.3 |
| | $C_6H_5^+$ | 1.1 |
| | $C_5H_4D^+$ | 1.4 |
| | $C_5H_5^+$ | 1.2 |

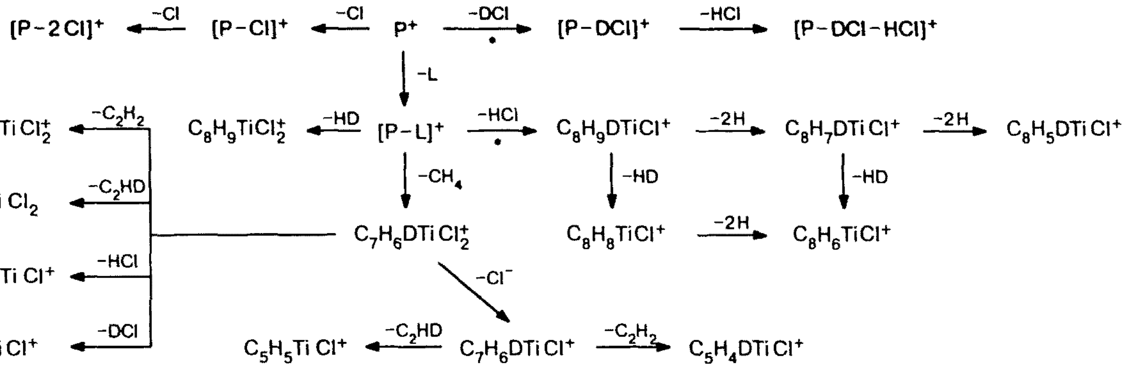
the substituent, we have synthesized a deuterated analog of compound **1**, $[C_5H_4C(D)Me_2]_2TiCl_2$ (**5**), and obtained its mass spectrum (Table 2). According to the mass-spectral data, the content of deuterium at the α-C atom is not lower than 98.5 %. The experimental and calculated values of the contents of deuterium in various ions are presented in Table 3. The fragmentation of compound **5** exhibits complete analogy with the fragmentation of the nondeuterated analog (Scheme 1).

The main route of the decomposition of the molecular ion is a consecutive loss of DCl and HCl molecules

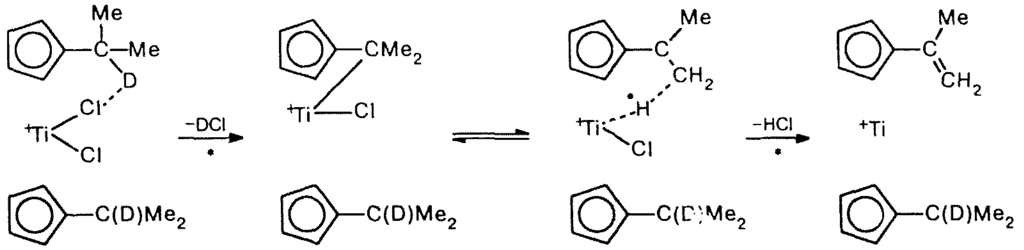
**Table 3.** Content of deuterium in ions (*D*) and their isotopic purity

| Type of ion | Experimental values | | Calculated values | | Isotope forms | | |
|---|---|---|---|---|---|---|---|
| | *D* (%) | *D*/*D*[$P^+$] | *D* (%) | *D*/*D*[$P^+$] | $d_2$ | $d_1$ | $d_0$ |
| $P^+$ | 8.95 | 1.00 | 8.95 | 1.00 | 97.6 | 1.7 | 0.7 |
| $[\mathrm{P-L}]^+$ | 8.95 | 1.00 | 8.95 | 1.00 | — | 98.4 | 1.6 |
| $L^+$ | 8.92 | 1.00 | 8.95 | 1.00 | — | 98.0 | 2.0 |
| $[\mathrm{P-DCl}]^+$ | 4.57 | 0.51 | 4.69 | 0.52 | — | 96.1 | 3.9 |
| $[\mathrm{P-DCl-HCl}]^+$ | 4.87 | 0.54 | 4.92 | 0.55 | — | 97.4 | 2.6 |

**Scheme 1**



**Scheme 2**



accompanied by the formation of the $[P-DCl]^+$ and $[P-DCl-HCl]^+$ ions (see Table 2). The content of deuterium (*D*) in the $[P-DCl]^+$ ion is equal to its halved value for the $P^+$ ion (see Table 3), which indicates unambiguously the participation of the deuterium atom of the substituent in the elimination of the hydrogen chloride molecule. The stage of the elimination of the DCl molecule probably is preceded by the agostic interaction of the deuterium of the isopropyl group. The subsequent loss of the HCl molecule from the $[P-DCl]^+$ ion involves the hydrogen atom of the methyl group (Scheme 2). This conclusion also follows unambiguously from the presented experimental and calculated values of the total content of deuterium in the $[P-DCl-HCl]^+$ ion (see Table 3).

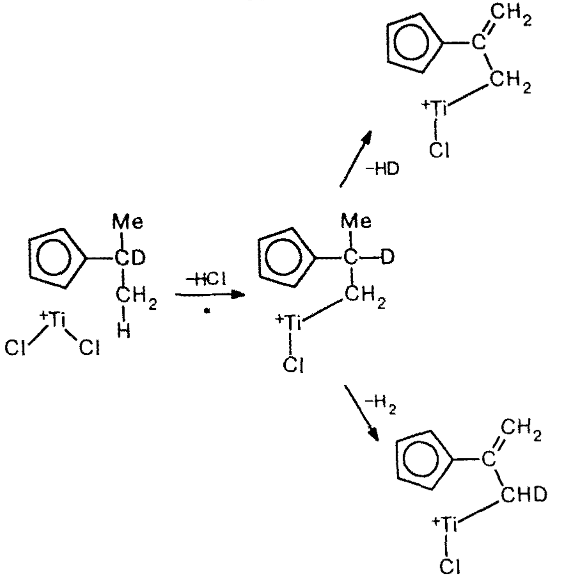
It is noteworthy that a similar sequence of elimination of DCl and HCl molecules was observed for the decomposition of the molecular ion $[C_5H_4C(D)Me_2]ZrCl_2$.[11]

The dehydrochlorination of the $[P-L]^+$ ion also involves the hydrogen atom of methyl groups. The $[P-L-HCl]^+$ ion formed eliminates hydrogen molecules of the isotope compositions $H_2$ and HD (Scheme 3).

In addition, the decomposition of the $[P-L]^+$ ion is also accompanied by the consecutive elimination of methane and hydrogen chloride (HCl, DCl), methane and acetylene molecules (see Scheme 1).

Thus, the directions of the fragmentation of alkyltitanocene dichlorides depend substantially on the nature of the substituent in the cyclopentadienyl ligand. In particular, dehydrochlorination processes are typical of titanocene derivatives with substituents containing hydrogen at the α-C atom. These derivatives probably should differ in their catalytic properties in processes with generation of cationic titanocene complexes.

**Scheme 3**



## Experimental

Alkyltitanocene dichlorides were obtained in the reaction of $TiCl_4$ with the corresponding Cp′Li in a THF—toluene medium and were purified by recrystallization from a toluene—hexane mixture. Compound **5**, $[C_5H_4C(D)Me_2]_2TiCl_2$, was synthesized in a similar way. The initial ligand was prepared by the reaction of dimethylfulvene with $LiAlD_4$.

Mass spectral measurements were carried out on an MI-1201 instrument with a sample direct inlet system into an ion source at 50 to 150 °C. The energy of ionizing electrons was 70 eV.

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