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# Effect of trimethylaluminum on the formation of active sites of the catalytic system bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinato]titanium(IV) dichloride—MAO and catalytic isomerization of hex-1-ene

*N. M. Bravaya,[a]★ E. E. Faingol´d,[a] O. N. Babkina,[a] L. A. Petrova,[a] V. D. Makhaev,[a]*
*S. Ch. Gagieva,[b] V. A. Tuskaev,[b] and B. M. Bulychev[b]*

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
*1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow region, Russian Federation.*
*Fax: +7 (496) 522 3507. E-mail: nbravaya@cat.icp.ac.ru*
[b] *M. V. Lomonosov Moscow State University, Department of Chemistry,*
*1 Leninskie Gory, 119992 Moscow, Russian Federation*

The transformations of bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinato]-titanium(IV) dichloride ($L_2TiCl_2$) occurring in toluene under the action of methylalumoxane (MAO) were studied by $^1$H NMR spectroscopy. The commercially available MAO containing trimethylaluminum ($AlMe_3$) and MAO free of $AlMe_3$ (the so called "dry" MAO) were used. The catalytic transformations of hex-1-ene involving the systems $L_2TiCl_2$—MAO were studied. We proposed the structures of the cationic titanium complexes formed in the absence and in the presence of hex-1-ene under the action of MAO. In the absence of olefin, neutral and cationic titanium complexes are decomposed under the action of $AlMe_3$ according to the exchange reaction of the complex ligand with the methyl groups of $AlMe_3$ to form $LAlMe_2$. The neutral complexes react considerably faster than the cationic ones. In the presence of olefin, decomposition of complexes under the action of $AlMe_3$ is suppressed. The titanium complex activated by "dry" MAO isomerizes hex-1-ene to hex-2-ene. In the presence of large amounts of TMA (commercial MAO), this reaction does not take place.

**Key words:** phenoxyimine complex, methylalumoxane, catalytic intermediates, hex-1-ene, isomerization, $^1$H NMR spectroscopy.

The catalytic systems based on the group IV transition metal bis(phenoxyimine) (FI) complexes are a novel post-metallocene generation of olefin polymerization catalysts [see Reviews 1—3]. These catalysts possess high activity in ethylene polymerization[1,4—8] and stereoselectivity in propylene polymerization.[9—14] Catalytic properties of complexes are easily modified by selection of an organic ligand, transition metal, or a certain activator (co-catalyst), and that allows one to use these modifiers for the directed synthesis of a certain polyolefin.

Among the group IV post-metallocene catalysts with varying composition, the titanium FI catalysts containing the fluorine atoms in the phenyl group of the =NPh fragments are of special interest. In the presence of polymethylalumoxane (MAO), these catalysts provide the activity in living polymerization of ethylene and propylene even at elevated reaction temperatures.[10,11,15—18] However, the presence of some substances in the reaction mixture can significantly decrease the efficiency of these catalysts. Propylene polymerization in the presence of the chelate titanium diamide complex $[ArN(CH_2)_3NAr]Ti$ in the π-donor solvent (toluene) when the catalyst is activated with MAO containing up to 30 mass.% of amphiprotic (according to Lewis) trimethylaluminum ($AlMe_3$) is characterized by a low activity, low molecular weight of the polymer, and broadened polydispersity indices.[19] Upon activation of the same catalyst in heptane or cyclohexane with "dry" MAO containing a small amount of $AlMe_3$, the catalyst exhibited a high activity in living polymerization of propylene. We observed a negative effect of trialkylaluminum on ethylene polymerization on the example of the fluorinated titanium complex, *viz.*, bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinato]titanium(IV) dichloride ($L_2TiCl_2$), activated with the commercial MAO.[20] In the presence of $AlMe_3$, retardation of the chain growth occurs and low-molecular-weight components on the molecular-weight distribution curves at the low total value of the polydispersity index $M_w : M_n$ = 1.3—1.4 appear. At the same time, when the catalyst was activated with "dry" MAO under the same conditions, the ultra-

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high-molecular-weight polyethylene insoluble in 1,2,4-trichlorobenzene at 135 °C is formed.

The important factor affecting the activity of the catalytic system is its stability in the presence of trialkylaluminum. Using NMR spectroscopy on the example of bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride activated with MAO (see Refs 21 and 22) or the system $AlMe_3—Ph_3CB(C_6F_5)_4$ (see Ref. 22), it was shown that one of the routes for deactivation of titanium FI catalysts is exchange of the phenoxyimine ligands of the complex for the methyl group of $AlMe_3$ to give $LAlMe_2$.

In the present work, we used $^1H$ NMR spectroscopy to study transformations of the tetrafluorinated FI catalysts based on bis[*N*-(3,5-di-*tert*-butylsalicylidene)-2,3,5,6-tetrafluoroanilinato]titanium(IV) dichloride, which occur in toluene in the presence of the commercial MAO and "dry" MAO, as well as catalytic isomerization of hex-1-ene to hex-2-ene under the action of this system.

## Experimental

Toluene-$d_8$ (Aldrich) and hex-1-ene dried by multiple distillation over activated molecular sieves (4Å), the commercially available MAO (Aldrich) as a 10 wt.% solution in toluene (hereafter referred to as MAO) were used in the work. "Dry" MAO (the content of $AlMe_3$ is about 5%) was prepared by evacuation of MAO at room temperature for 8 h followed by dissolution of the dry glassy product in toluene-$d_8$. The precursor ($L_2TiCl_2$) and the ligand were synthesized according to the described procedure.[23]

All procedures for the preparation of the starting reagents and reaction products were performed under dry argon using the standard operation technique in the inert atmosphere, 5 mm NMR tubes with rubber septa, gastight syringes, and glass vacuum assembly. Reagents were mixed in NMR tubes and the liquid components of the systems under study were introduced through septa by means of gastight syringes. The measurements were performed both immediately after mixing reagents (2—3 min) and after a time interval specified in the text.

$^1H$ NMR spectra were recorded with a DPX-200 (Bruker) spectrometer (200.13 MHz) at room temperature (20 °C). The chemical shifts are given in the δ scale relatively to the signals of residual protons in a deuterated solvent ($\delta_H$ 2.09).

ESR spectra were recorded with a SE/X 2544 (Radiopan) instrument for the systems $L_2TiCl_2$—MAO ($[Ti] = 2 \cdot 10^{-2}$ mol $L^{-1}$, the molar ratio $Al_{MAO} : Ti = 50 : 1$) at room temperature. The contents of the $Ti^{III}$ paramagnetic complexes were determined by comparison of the second integrals of the signals of $Ti^{III}$ with those of the organic radical TEMPO.

## Results and Discussion

**The starting dichloride complex.** Numbering scheme of the atoms in the $^1H$ NMR spectra of the $Ti^{IV}$ dichloride complex (catalyst precursor), reaction products of the ligand (LH) with MAO, the precursor with MAO (precatalyst), and catalytic intermediates that formed in the presence of hex-1-ene is given in Fig. 1 on the example of $L_2TiCl_2$.

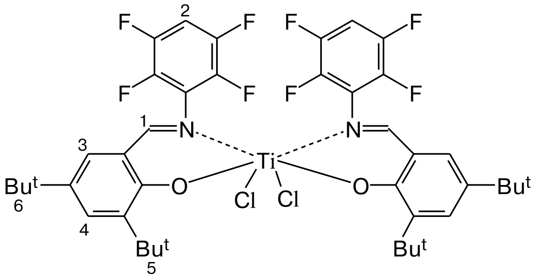

**Fig. 1.** Atomic numbering scheme in the $^1H$ NMR spectra in the ligand L on the example of $L_2TiCl_2$.

The $^1H$ NMR spectra of the ligand and precursor in toluene-$d_8$ contain narrow well-resolved signals (Table 1).

In the $^1H$ NMR spectrum of the precursor, the greatest shifts compared to those of the free ligand are observed for the signals of the groups that are the most closely adjacent to the complexing metal, namely, for the singlet signals of the imine proton and the signals of the protons H(5) of the *tert*-butyl groups (Table 1). The doublet signal of the aromatic proton H(3) and the singlet signal of the protons H(6) of the *tert*-butyl group are slightly shifted to the lower field. For the signal of aromatic protons H(2), a small shift to the higher field was observed.

**Reactions of the ligand LH with MAO.** The main deactivation products of the catalytic systems involving structurally similar titanium and zirconium FI catalysts under the action of TMA-containing activators, such as MAO or $AlMe_3—Ph_3CB(C_6F_5)_4$, are the products of exchange of the oxoimine ligand by the methyl groups of $AlMe_3$. This reaction is evidenced by the appearance of the complex $LAlMe_2$ in the reaction mixture.[21—24] A reference compound, $LAlMe_2$, required for the assignment of the signals in the NMR spectra of a multicomponent system using our precursor was synthesized by the reaction of the ligand LH with both MAO containing about 35 mol.% $AlMe_3$ and "dry" MAO containing about 5 mol.% $AlMe_3$. In the first case, the reaction was performed in a solution of MAO in toluene at the molar ratio $Al_{MAO} : LH = 20 : 1$ ($Al_{AlMe_3} : LH \approx 7 : 1$). In the second case, the reaction was carried out in a solution of "dry" MAO in deuterated toluene at $Al_{MAO} : LH = 30 : 1$ ($Al_{AlMe_3} : LH \approx 1.5 : 1$).

In both cases, in the $^1H$ NMR spectra, the signals of the protons of the starting ligand disappear and an identical set of novel signals assigned to $LAlMe_2$* appear among the reaction products. After the reaction of "dry" MAO with LH, the signal intensity of the methyl groups of the residual $AlMe_3$ decreases significantly, while the broad

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* Hereinafter in the text and in Figs 3—6, the signals assigned to $LAlMe_2$ are designated by the symbol "*".

**Table 1.** The chemical shifts of the protons in the $^1H$ NMR spectra (toluene-$d_8$) of the ligand (LH), complex ($L_2TiCl_2$), product of the $LAlMe_2$ ligand exchange, and cationic complexes **1—3** formed under the action of MAO in the absence and presence of hex-1-ene

| Compound or system | Complex | δ (*J*/Hz) | | | | | |
|---|---|---|---|---|---|---|---|
| | | H(1)<br>(s) | H(2)<br>(m) | H(3)<br>(d) | H(4)<br>(d) | H(5)<br>(s) | H(6)<br>(s) |
| LH[a] | | 8.11 | 6.09 | 7.61<br>(*J* = 2.0) | —[b] | 1.56 | 1.26 |
| $L_2TiCl_2$ | | 7.48 | 6.07 | 7.63<br>(*J* = 2.3) | 6.92<br>(*J* = 2.5) | 1.44 | 1.24 |
| $LAlMe_2$ | | 7.31 | 6.08 | 7.66<br>(*J* = 2.2) | 6.72<br>(*J* = 2.0) | 1.43 | 1.21 |
| $L_2TiCl_2$—MAO<br>("dry" MAO) | $LAlMe_2$ | 7.31 | 6.08 | 7.66<br>(*J* = 2.2) | 6.72<br>(*J* = 2.0) | 1.43 | 1.21 |
| | $L_2Ti^+Me...XMAO^-$ (**1**)[c] | 8.20 | 6.17 | 8.01<br>(*J* = 2.0) | 7.37 | 1.51 | 1.26 |
| $L_2TiCl_2$—hex-1-ene—MAO | $LAlMe_2$ | 7.31 | 6.08 | 7.66<br>(*J* = 2.2) | 6.72<br>(*J* = 2.0) | 1.43 | 1.21 |
| | $L_2Ti^+Me...(hex\text{-}1\text{-}ene)...XMAO^-$ (**2**) | 7.95 | 6.33 | 7.83 | —[b] | —[b] | —[b] |
| $L_2TiCl_2$—hex-1-ene—"dry" MAO | $L_2Ti^+Y...XMAO^-$ (**3**)[d] | 7.95 | 6.39 | 7.79 | —[b] | —[b] | —[b] |

[a] The signal of the OH group of the free ligand LH is observed at δ 13.13. [b] The signal overlaps with the signals of toluene and the signals of the other components of the catalytic system. [c] X = Cl, Me. [d] Y is alkyl, allyl, or H.

signal of the methyl groups of MAO shows no changes (Fig. 2). This fact allows one to conclude that the methyl groups of $AlMe_3$ react more readily with the ligand as compared with the methyl groups of MAO.

**Systems $L_2TiCl_2$—MAO, $L_2TiCl_2$—"dry" MAO.** In some instances, the reaction products of the titanium dichloride complex with MAO and "dry" MAO ($Al_{MAO}$ : Ti ≈ 70 : 1) were analyzed immediately after mixing reagents or after 1 h following the preparation of the system. In other cases when the changes in the spectra were slow, the analysis was conducted several hours later. Since MAO is used in reactions as a solution in toluene, in a series of experiments some signals of the products and the solvent signals overlap. Solution of pre-catalysts obtained in the reactions of the precursor with the "dry" MAO were analyzed in toluene-$d_8$, which revealed the low field signals of the protons of the reaction products overlapped in the first case with signals of toluene.

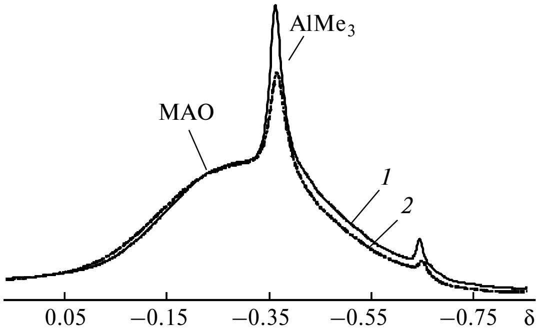


**Fig. 2.** Fragments of $^1H$ NMR spectra of "dry" MAO (*1*) and the product of its reaction with LH (*2*) at the molar ratio of $Al_{MAO}$ : LH = 30 : 1 ($Al_{AlMe_3}$ : LH ≈ 1.5 : 1).

In the systems involving $L_2TiCl_2$, MAO and "dry" MAO, cationic complexes of the same structure are formed. In the aromatic region of the spectrum obtained immediately after mixing $L_2TiCl_2$ with MAO (or "dry" MAO) two sets of signals were observed. One of them is attributable to the complex $LAlMe_2$ (see Table 1) and the second one — to a novel titanium complex, which in the low field exhibits a broad singlet of the imine proton H(1), doublets of the aromatic protons H(3) and H(4) (see Table 1 and Fig. 3, *a*, *c*). The multiplets of the protons H(2) and H(2*) overlap in the region of $\delta_H$ 5.8—6.3. In the system containing a solution of MAO in toluene, the signals of H(4), H(1*), and H(4*) are overlapped by the signals of the aromatic protons of toluene. The low field signals of the novel titanium complex are apparently related to the cationic complex $L_2Ti^+Me...XMAO^-$ (**1**, X = Cl, Me). The low field shifts of all signals compared to the signals of starting dichloride complex provide evidence in favor of this fact (see Table 1). In addition, for the system $L_2TiCl_2$—"dry" MAO in the high field spectral region, we observed the signal at $\delta_H$ 1.98 (see Fig. 3, *c*) with integral intensity 1.5-fold higher than that of the signal of the proton H(3) of complex **1**, which supports its assignment to the protons of the methyl group linked to the titanium atom.

In the case of the reaction product of $L_2TiCl_2$ with MAO, the ratio of the signal intensities for the protons H(3) and H(3*) measured immediately after mixing reagents was close to 1 : 2. Considering that, the titanium

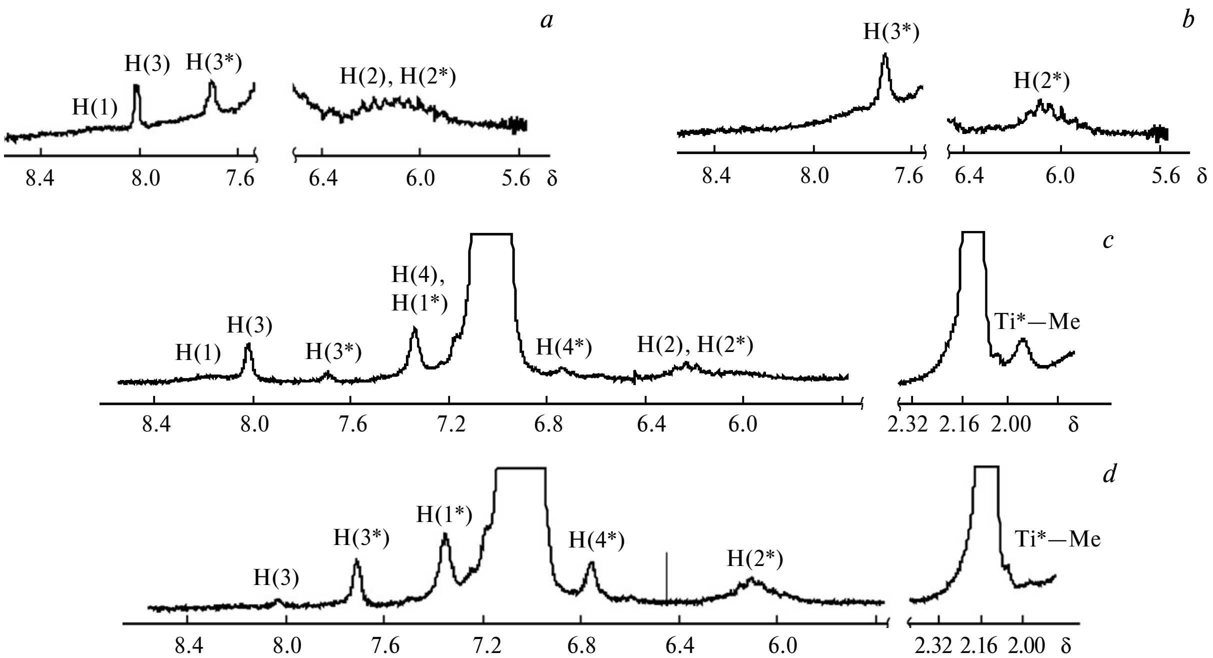


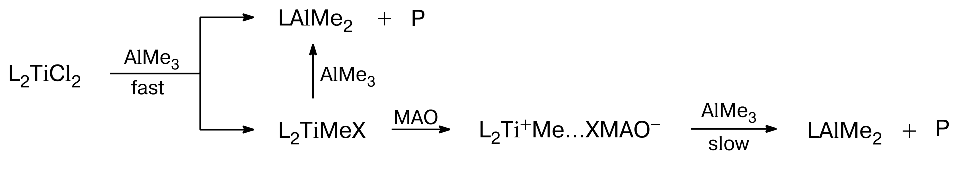
**Fig. 3.** Fragments of $^1$H NMR spectra of the systems $L_2TiCl_2$—MAO (*a*, *b*) and $L_2TiCl_2$—"dry" MAO (*c*, *d*) recorded immediately after mixing (*a*, *c*) and 4 h (*b*, *d*) after mixing reagents. The spectra (*a*, *b*) were recorded in toluene, the spectra (*c*, *d*) were recorded in toluene-$d_8$. The signals H(1)—H(3) ascribed to the cationic complex $L_2Ti^+Me...XMAO$ (**1**, X = Cl, Me).

complex **1** has two ligands and $LAlMe_2$ has one ligand, such a ratio suggests that about 65% of the titanium complex undergoes ligand exchange with $AlMe_3$ during the preparation of the complex (several minutes). During next 4 h, complex **1** quantitatively changes its ligands with the methyl groups of $AlMe_3$ to form $LAlMe_2$, which is reflected in a slow disappearance of the signal of the proton H(3) of the complex and an increase in the intensity of the signal of the proton H(3*) (see Fig. 3, *a*, *b*).

In the reaction product of $L_2TiCl_2$ and "dry" MAO, the intensity ratio of the signals of H(3) and H(3*) measured after the interval required for the sample preparation is 3 : 1, which corresponds to the transformation of only 25 mol.% of the starting pre-catalyst. These values can presumably be explained by a lower concentration of $AlMe_3$ in "dry" MAO. However, 4 h after the preparation of the system with "dry" MAO all signals of pre-catalyst **1**, as well as the signal of the Ti—Me group disappear and the spectrum exhibits only the signals of the reaction product, *viz.*, $LAlMe_2$ (see Fig. 3). Taking into account that $AlMe_3$ is a strong Lewis acid, one can expect that the attack of $AlMe_3$, which results in degradation of neutral and cationic complexes, occurs at the oxygen atom of the ligand bearing a lone pair of electrons.

The detailed mechanism of transformation of pre-catalysts requires additional studies; however, based on the experimental data (Scheme 1) one can even now make some assumptions. The processes occurring in the system $L_2TiCl_2$—MAO can be divided into relatively fast and slow. During the first minutes of the reaction, $LAlMe_2$ and $L_2Ti^+Me...XMAO$ (**1**) form due to fast processes. The formation of the cationic complex $L_2Ti^+Me...XMAO$ (**1**) should be preceded by the formation of the alkylated intermediate $[L_2TiMeX]$, whose identification by $^1$H NMR spectroscopy failed. The reason can be found in a high rate of the subsequent fragmentation. It is possible that dimethylation occurs in our system, *i.e.*, in complex **1** (X = Me). For example, according to the literature[22] the complex

**Scheme 1**



X = Cl, Me

P are the decomposition products of the precursors and pre-catalyst

$[L_2TiMe(S)]^+[MeMAO^-]$, where S is the solvent molecule, forms in the presence of the structurally close complex, bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride, under the action of MAO. The formation of $LAlMe_2$ can occur by ligand exchange of $AlMe_3$ with both dichloride and alkylated forms of the titanium complex. The cationic complex decomposes slowly (for several hours) under the action of $AlMe_3$ to give $LAlMe_2$, which was the only detected deactivation product. Thus, the neutral complex decomposes much faster than the cationic one. Decrease in the amount of $AlMe_3$ with a use of "dry" MAO leads to a decrease in the decomposition rate of both the neutral pre-catalyst and cationic complex, *i.e.*, it is $AlMe_3$ that results in decomposition of pre-catalysts.

The results outlined above agree with the NMR spectral data of the reaction products for the structurally close titanium complexes with MAO.[21,22] It was found that during the reaction mononuclear cationic complexes are formed followed by ligand exchange of the cationic complex with the methyl group of $AlMe_3$ to give $LAlMe_2$. According to our data, neutral titanium complexes more readily involved in the exchange reaction L—Me compared with the cationic ones.

Another deactivation pathway of the catalytic system is also possible, which is associated with the reduction of $Ti^{IV}$ to $Ti^{III}$ (see Ref. 22). To check this assumption, we studied the systems $L_2TiCl_2$—MAO ($[Ti] = 1.4 \cdot 10^{-2}$ mol $L^{-1}$, Al : Ti = 50 : 1) and $L_2TiCl_2$—hex-1-ene—MAO ($[Ti] = 1.5 \cdot 10^{-2}$ mol $L^{-1}$, Al : Ti = 50 : 1, hex-1-ene : Ti = 50 : 1). The organic radical TEMPO was used as the reference. It was found that 2 h after preparation, the concentration of paramagnetic compounds containing the $Ti^{III}$ atoms ($g = 1.968$) did not exceed 2 mol.% in both systems. Therefore, one can assume that if the reduction of $Ti^{IV}$ under the experimental conditions nevertheless occurs, compounds with an oxidation state less than $Ti^{III}$ are formed. Such reduction can involve neutral titanium complexes, for example, *via* the formation of thermally unstable methyl derivatives, *e.g.*, tetramethyltitanium, which decomposes at −78 °C.[24] However, we failed to obtain a direct confirmation of this assumption.

**Systems $L_2TiCl_2$—hex-1-ene—MAO and $L_2TiCl_2$—hex-1-ene—"dry" MAO.** Hex-1-ene was used to elucidate the role of a π-donor in the formation of a true catalyst and its catalytic transformations in the presence of MAO and "dry" MAO. The molar ratio hex-1-ene : Ti was about 20 : 1 in all experiments. The ternary systems were monitored at the same time intervals as in the analysis of the binary systems discussed above.

The $^1H$ NMR spectrum of a solution obtained upon mixing the components of the system $L_2TiCl_2$—hex-1-ene—MAO (Fig. 4) exhibited new signals: a broadened signal of the imine proton at $\delta_H$ 7.95 and a signal of aromatic proton H(3) at $\delta_H$ 7.83. For both these signals, small shifts to higher field compared to the signals of the cationic complex **1** were observed (see Table 1). A higher stability of the neutral complexes in the presence of olefin can be seen in a much lower content of the ligand exchange product, *viz.*, $LAlMe_2$ (the signal of H(3*)), in the ternary system than in the binary one. The conversion of this complex in the system with hex-1-ene observed 1 h after mixing components was only about 15 mol.% compared to 65 mol.% in the analogous system without hex-1-ene. No changes in the intensities of the signals of the proton H(3*) of $LAlMe_2$ and cationic titanium complexes were observed for 5 h of monitoring (see Fig. 4), which evidences a high stability of the latter in the presence of a higher olefin. No significant transformations of hex-1-ene in the presence of this catalytic system were observed for a longer interval of time. It was only 5 h after mixing reagents, when trace amounts of hex-2-ene formed in a solution. It should be noted that the chemical shifts of the protons of the cationic complexes formed in the binary and ternary systems are significantly different and the cationic complex shows a higher stability in the presence of hex-1-ene. In addition, no catalytic transformations of α-olefin occur in these systems in contrast to the system with "dry" MAO (see below). All these facts imply that the complex formed under these conditions is the olefin-separated ion pair $L_2Ti^+Me...(hex\text{-}1\text{-}ene)...MeMAO^-$ (**2**). A specific feature of this system includes the presence of

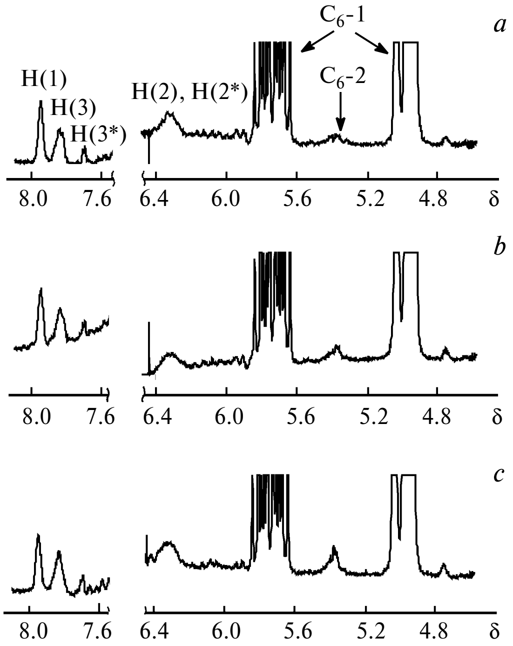


**Fig. 4.** Fragments of $^1H$ NMR spectra of the systems $L_2TiCl_2$—hex-1-ene—MAO recorded 1 (*a*), 2 (*b*), and 5 h (*c*) after the sample preparation. Hex-1-ene : Ti = 20 : 1. The signals H(1)—H(3) ascribed to the cationic complex $L_2Ti^+Me...(hex\text{-}1\text{-}ene)...XMAO$ (**2**). Here and in Figs 4 and 5 $C_6$-1 is hex-1-ene and $C_6$-2 is hex-2-ene.

hex-1-ene in the coordination sphere of the complex that hinders the exchange reaction of the phenoxyimine ligands of the complex with the methyl groups of $AlMe_3$ and, thereby, provides its enhanced stability. It is also of note that a probable coordination of $AlMe_3$ to the oxygen atom of the phenoxyimine ligand is likely to prevent catalytic transformations of hex-1-ene.

In the system $L_2TiCl_2$—hex-1-ene—"dry" MAO, the chemical shifts of the signal of the protons H(1)—H(3) in the formed cationic complex **3** (see Table 1) are close to those of complex **2**. One can note only a small high field shift of the signal of H(3) ($\Delta\delta_H = 0.04$ ppm) and a low field shift of the signal of H(2) ($\Delta\delta_H = 0.06$ ppm) compared to the corresponding signals of complex **2**. Trace amount of complex $LAlMe_2$ was detected even 24 h after the preparation of the system (Fig. 5, *a*—*c*).

A significant feature of the catalytic system with a low content of $AlMe_3$ is its ability to isomerize hex-1-ene to hex-2-ene (see Fig. 5, *d*—*f*). Catalytic activity of the system $L_2TiCl_2$—"dry" MAO in the reaction with hex-1-ene was evaluated by the integral intensities of the signals of hex-1-ene and hex-2-ene taking into account the duration of the reaction. It was revealed that at the initial reaction step, catalytic activity was about 0.3 mol ((mol Ti) min $[C_6H_{12}])^{-1}$ and it decreases exponentially with time as hex-1-ene undergoes transformation. This catalyst exhibits a very high activity in the ethylene polymerization (~60000 mol ((mol Ti) min $[C_2H_4])^{-1}$), but much lower activity in the propylene polymerization (~30 mol ((mol Ti) min $[C_3H_6])^{-1}$).[25] In the case of a more bulky hex-1-ene, the predominant catalytic reaction is isomerization proceeding at a low rate rather than insertion.

We observed slight differences in the values of the chemical shifts of the protons of the complexes with MAO and "dry" MAO in the presence of hex-1-ene and isomerization of hex-1-ene on the system with "dry" MAO as well. These facts when combined with commonly accepted concepts of the mechanism of olefin isomerization *via* formation of the metal-alkyl or allyl complexes,[26] the structure of the cationic titanium complex can be represented as the ion pair $L_2Ti^+Y...XMAO^-$ (**3**), where Y is an alkyl, hydride, or allyl group. The Ti—H bond formation is caused by hydride shift observed during isomerization.

The effect of the $AlMe_3$ content in MAO on the efficiency of hex-1-ene isomerization is shown in Fig. 6. Three types of MAO with different content of $AlMe_3$ were used for activation of the complex (see Fig. 6, *a*). The time interval of isomerization of hex-1-ene was 4 h in each experiment. It is seen from Fig. 6, *b* that an increase in the content of $AlMe_3$ is accompanied by a decrease in the efficiency of isomerization. It is obvious that $AlMe_3$ prevents isomerization, for example, due to the outersphere coordination in the cationic complex. To reveal the nature of catalytic intermediates and channels of $AlMe_3$ influence more detailed studies are required.

In conclusion, we can discuss the results outlined above. They show a specific role of the titanium phenoxyimine complex in the formation of active sites under the action of MAO. We found also that the complex is unstable in the presence of $AlMe_3$. Moreover, we succeeded to

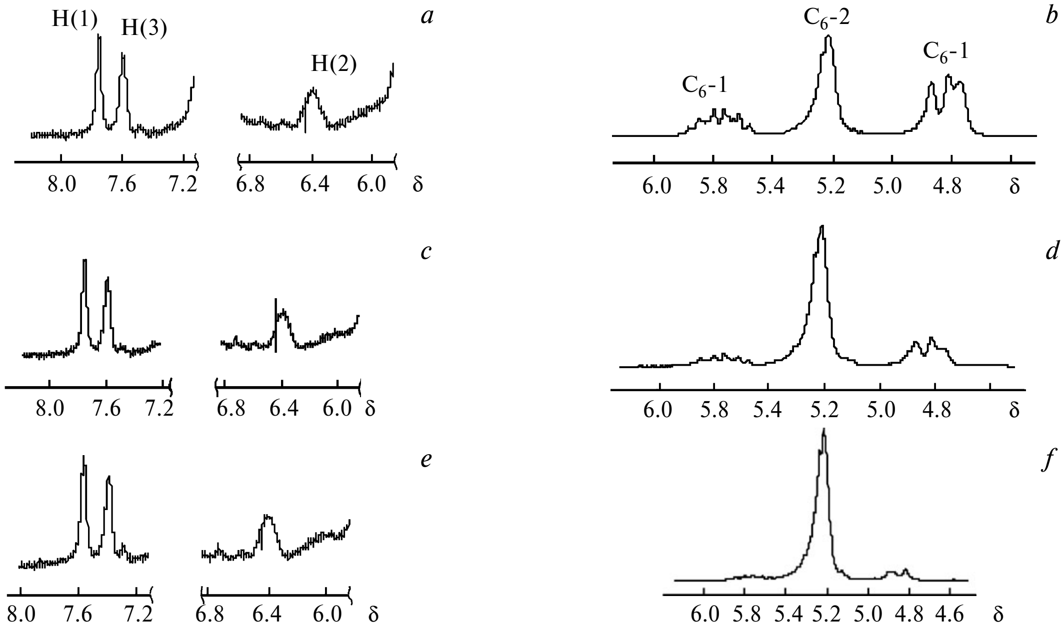


**Fig. 5.** Fragments of $^1H$ NMR spectra of the system $L_2TiCl_2$—hex-1-ene—"dry" MAO recorded 1 (*a, b*), 5 (*c, d*), and 24 h (*e,f*) after the sample preparation. Hex-1-ene : Ti = 20. The signals H(1)—H(3) ascribed to the cationic complex $L_2Ti^+Y...XMAO$ (**3**, Y = alkyl, allyl, H). *a*, *c*, *e*, The region of the signals of complex **3**; *b*, *d*, *f*, the region of the signals of the double bond in hexenes.

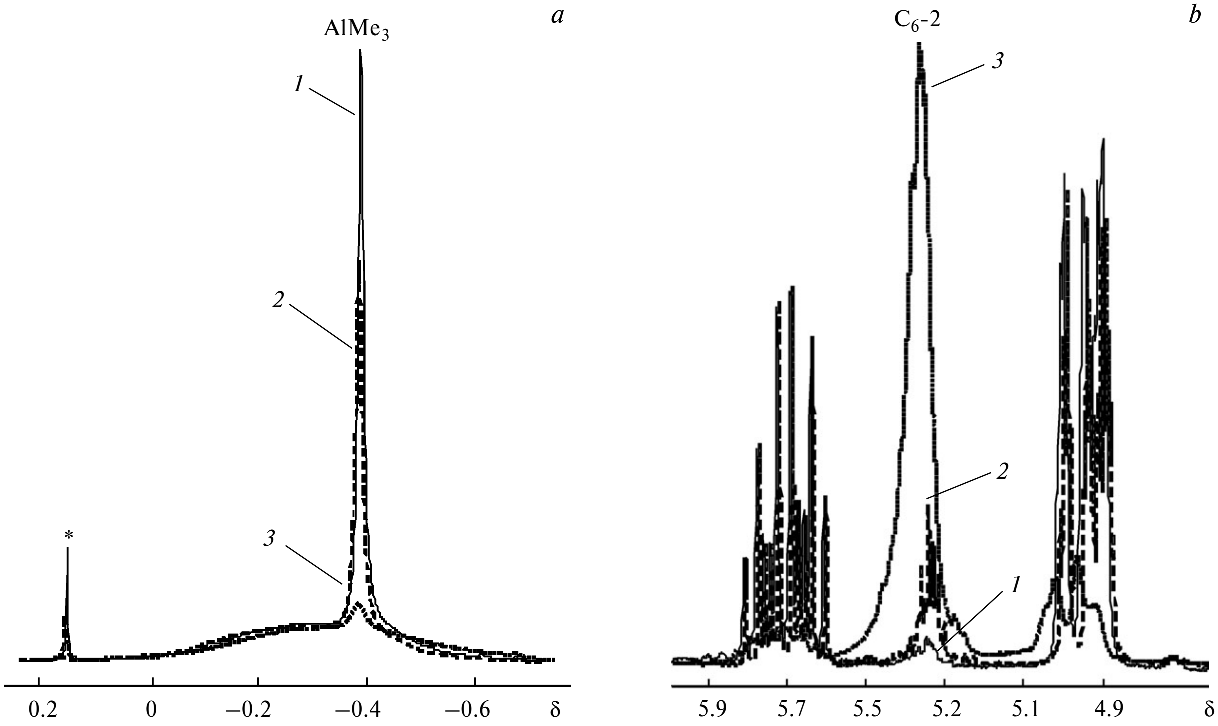


**Fig. 6.** *a*, Fragments of $^1$H NMR spectra of MAO samples containing 35 (*1*), 25 (*2*), and 5 mol.% of $AlMe_3$ (*3*). The symbol «*» designates the signal of protons of methane. *b*, The region of the signals of the double bonds in hexenes in the $^1$H NMR spectra of the catalytic system $L_2TiCl_2$—hex-1-ene—MAO at the content of $AlMe_3$ in MAO equal to 35 (*1*), 25 (*2*), 5 mol.% (*3*). The reaction time is 4 h.

disclose specific catalytic properties of the complex in the transformation of hex-1-ene and evaluate the effect of $AlMe_3$ on the catalytic processes. The reactions of $L_2TiCl_2$ with MAO at room temperature at the molar ratio Al : Ti = 70 : 1 proceed along two parallel routes. The first route is deactivation and it is realized in the presence of $AlMe_3$ and absence of olefin. Under these conditions, the exchange reaction of the phenoxyimine ligands of the neutral complexes with the methyl groups of $AlMe_3$ occurs followed by decomposition of methyl titanium derivatives. The presence of hex-1-ene hinders this exchange reaction. The second route is activation and, under the action of MAO, it leads to the formation of cationic complexes. Based on the spectral analysis and literature data[22], we assumed that the ion pair $L_2Ti^+Me...XMAO^-$ (**1**, X = Cl, Me) forms during the reaction. The cationic complexes formed undergo also exchange of the L ligand with the methyl group of $AlMe_3$ containing in MAO, but to a much lower extent than the neutral complexes.

Introduction of hex-1-ene into the system, on the one hand, suppresses transformation of both neutral and cationic complexes by the exchange reaction of L for the methyl group of $AlMe_3$. On the other hand, it favors the formation of a novel type of catalytically active cationic complexes with the proposed structure $L_2Ti^+Y...XMAO^-$ (**3**), where Y is an alkyl, hydride, or allyl group. Upon activation of the precursor with MAO free of $AlMe_3$, hex-1-ene isomerizes selectively to hex-2-ene. If $AlMe_3$ presents in the amount of 35 mol.% (commercial MAO), this process is inhibited.

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