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^{1}H NMR study of the catalytic system (*rac*-Me_2Si(2-Me, 4-PhInd)$_2ZrCl_2$—polymethylalumoxane)—triisobutylaluminum

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The products of the reactions of polymethylalumoxane (MAO) with triisobutylaluminum (TIBA), *rac*-Me_2Si(2-Me,4-PhInd)$_2ZrCl_2$ (**1**) with MAO (**1** + MAO), and (**1** + MAO) + TIBA were studied by ^{1}H NMR at different molar ratios of the components. When the ratio Al_{TIBA}/Al_{MAO} is ~6, the reaction between MAO and TIBA involves the replacement of the methyl group of MAO by isobutyl groups and the formation of isobutylmethylalumoxane or mixed isobutylmethylalumoxane structures. When the TIBA content in the system increases to 30 mol.%, these structures are rearranged to form products with a low degree of association. With the equimolar ratio of the reactants, the main reaction products are tetraisobutylalumoxane and polyisobutylalumoxane. The **1** + MAO system with the molar ratio $Al_{MAO}/Zr = 50$ affords a MAO-bonded monomethyl monochloride derivative $[L_2ZrCl\text{-}\mu\text{-}Me]^{\delta+}[MAO]^{\delta-}$. An increase in this ratio to 150 produces intermediate binuclear complexes $[L_2ZrCl\text{-}\mu\text{-}Me\text{-}MeZrL_2]^+[MAO]^-$ and $[Me_2Al\text{-}(\mu\text{-}Me)_2\text{-}ZrL_2]^+[MAO]^-$. The addition of TIBA induces the replacement of the ZrMe groups by isobutyl groups at the first step of the interaction and formation of nonidentified reaction products at the subsequent steps.

Key words: metallocene complexes of Group IVB elements, polymethylalumoxane, triisobutylaluminum, tetraisobutylalumoxane, polyisobutylalumoxane, isobutylalumoxanes.

Metallocene cationic complexes of Group IVB elements are highly efficient catalysts for olefin homo- and copolymerization. A catalyst system is formed by the reaction of a metallocene complex with an activator (cocatalyst). The concept that catalytic intermediates (precursors of the active site) are alkylmetal cationic complexes bonded to a counterion[1—4] was confirmed by numerous spectroscopic data.[5—7] Polymethylalumoxane (MAO) -(-O—Al(Me)-)$_n$- (n = 4—30) containing a considerable amount of free or partially bound trimethylaluminum (TMA) (up to 30 mol.% with respect to aluminum) is most frequently used as a cocatalyst.[8] When activating the starting metallocene dichloride L_2ZrCl_2 (L are *hapto*-bonded cyclopentadienyl, indenyl, or fluorenyl ligands), MAO bears numerous functions: it acts as an alkylating agent (Scheme 1, reaction (1)), cation-generating agent (reaction (2)), and, in addition, purifies the reaction medium from moisture admixtures.

Scheme 1

$$L_2ZrCl_2 + MAO \longrightarrow L_2ZrMeCl \qquad (1)$$

$$L_2ZrMeCl + MAO \rightleftharpoons L_2Zr^+Me...ClMAO^- \qquad (2)$$

The MAO-activated catalysts are most active at low metallocene concentrations ($1 \cdot 10^{-5}$—$1 \cdot 10^{-7}$ mol L^{-1}) and high cocatalyst/catalyst molar ratios ($1 \cdot 10^3$—$1 \cdot 10^4$). Disadvantages of MAO are its high cost and instability during storage. Other most popular activators are fluoarylboranes and fluoaryl borates.[8] However, their use as activators is restricted, because they have no components interacting with humidity admixtures in the reaction medium and can activate only dimethylated metallocenes. Nevertheless, there are examples for the efficient activation of metallocene dichlorides by a combined activator including borates and triisobutylaluminum (TIBA).[9—13]

Some workers[14—16] propose an approach to metallocene activation based on the treatment of the metallocene dichloride complexes with small additives of MAO followed by activation with TIBA. Thus activated catalysts are efficient in propylene polymerization and show activity compatible with that of the homogeneous catalytic systems with MAO. Moreover, a good solubility of TIBA in aliphatic hydrocarbons enables polymerization to proceed under these conditions. A similar approach using TIBA is employed for the activation of the supported metallocene systems. A metallocene complex is deposited on the support surface with grafted MAO. Thus supported catalyst is efficiently activated by standard aluminum

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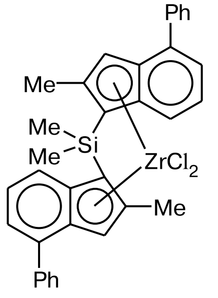
trialkyls AlR_3 at low cocatalyst/catalyst molar ratios.[17—20] However, information on the nature of forming active sites, reactions on the catalyst surface, and activation mechanisms is scarce.

The aim of this work is to reveal the activation mechanism of the metallocene complex involving the combined activator MAO and TIBA and to describe the nature of intermediates and active sites formed. Zirconocene *rac*-$Me_2Si(2\text{-}Me,4\text{-}PhInd)_2ZrCl_2$ (**1**) was used, which is highly active and isospecific in propylene polymerization.



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The efficient activation of **1** in homogeneous propylene polymerization requires very high excess MAO cocatalyst, $Al_{MAO}/Zr = 10^3—10^4$ mol mol^{-1}.[21—23] However, this catalyst can also be activated by TIBA after preactivation with MAO at low molar ratios Al_{MAO}/Zr. To reveal catalytic intermediates and the cocatalyst nature, we studied the reaction products in the MAO—TIBA, **1**—MAO, and (**1**—MAO)—TIBA systems at a varied molar ratio of the components.

Experimental

Toluene (special purity grade) was used. The solvent was distilled over $LiAlH_4$, degassed in a high-vacuum line, and stored above molecular sieves 4A under argon. ^1H NMR spectra were recorded on a Bruker DPX-200 spectrometer (200.13 MHz), using toluene-d_8 (Aldrich) as solvent, which was dehydrated by multiple distillation over activated molecular sieves 4A. Polymethylalumoxane (Witco) was used as a 10% solution in toluene, TIBA (Aldrich) was used as a 1 *M* solution in toluene, and *rac*-$Me_2Si(2\text{-}Me,4\text{-}PhInd)_2ZrCl_2$ (**1**) (Boulder Scientific Co.) was prepurified by recrystallization. The ^1H NMR spectrum of TIBA, δ: 0.34 (d, 6 H, CH_2, $J = 7.1$ Hz); 0.82 (d, 18 H, Me, $J = 6.7$ Hz); 1.86 (heptet, 3 H, CH). The ^1H NMR spectrum of compound **1**, δ: 0.94 (s, 6 H, Me_2Si); 2.09 (s, 6 H, 2-MeInd); 6.89—7.85 (m, 18 H, $C_{15}H_9$). Compound *rac*-$Me_2Si(2\text{-}Me,4\text{-}PhInd)_2ZrMe_2$ (**1** (Me)) was synthesized according to a standard procedure.[24] The ^1H NMR spectrum of compound **1** (Me), δ: −0.68 (s, 6 H, Me_2Zr); 0.91 (s, 6 H, Me_2Si); 2.02 (s, 6 H, 2-MeInd); 6.91—7.74 (m, 18 H, $C_{15}H_9$). Argon was dried by passing through a column with activated molecular sieves (5A). All procedures on the preparation of the metallocene complexes and catalysts were carried out in the presence of purified and dried argon.

Reaction MAO + TIBA. A solution of MAO was mixed with a TIBA solution to give a specified molar ratio $Al_{MAO} : Al_{TIBA}$, the mixture was stored for 1 h at room temperature, toluene (solvent) was distilled off *in vacuo*, and the resulting dry residue was evacuated for 8 h and dissolved in toluene-d_8.

Synthesis of tetraisobutylalumoxane (TIBAO). A solution of TIBA in toluene cooled to −40 °C was added by portions to ice (H_2O), and the reaction mixture was intensely stirred. The reaction product was slowly heated to room temperature, the solvent was distilled off, and the resulting dry residue was evacuated for 8 h and dissolved in toluene-d_8. The reaction was carried out at the molar ratio $AlBu^i_3 : H_2O = 2 : 1$.

Reactions 1 + MAO and (1 + MAO) + TIBA. A weighing sample of compound **1** was dissolved in toluene in the absence of oxygen. MAO was added to the resulting metallocene solution at specified molar ratios $Al_{MAO} : Zr$. The mixture was stored for 24 h at room temperature. The solvent was distilled off, and the dry residue was evacuated for 8 h and dissolved in toluene-d_8.

TIBA was added at specified $Al_{TIBA} : Zr$ molar ratios to the zirconocene + MAO mixture 24 h after the reagents were mixed. Toluene was distilled off *in vacuo*, and the dry residue was evacuated for 8 h and dissolved in toluene-d_8. The zirconocene concentration was 0.04 mol L^{-1}.

^1H NMR spectra recording. Samples were placed in NMR tubes and sealed off from the vacuum line. NMR spectra were measured in sealed 5-mm cylindrical ampules. The following conditions were used to record spectra: the spectrum sweep width 4 kHz, the pulse repetition frequency was 4 s, and the total number of pulses was 16. Signals of residual protons in toluene-d_8 (δ = 7.06, 7.10, and 7.18) were used to calculate chemical shifts.

Results and Discussion

To elucidate the character of interaction between the components of the triple catalytic system and to reveal the nature of the cocatalyst and catalytic intermediates, we analyzed the ^1H NMR spectra of the toluene-soluble reaction products of the MAO—TIBA, **1**—MAO, and (**1**—MAO)—TIBA systems. The MAO—TIBA system was studied at a varied molar ratio Al_{TIBA}/Al_{MAO}. The fragments of the obtained spectra are shown in Fig. 1.

Fragment 1, *a* represents the spectrum of MAO, and fragments 1, *b—d* are the spectra of the toluene-soluble reaction products of MAO and TIBA. The spectrum of MAO is a superposition of the broad peak (δ −0.16) corresponding to protons of the Me groups in the oligomeric MAO structures $\text{-(-O—Al(}\underline{Me}\text{)-)}_n\text{-}$ and a narrow peak (δ −0.28) of the terminal Me groups in MAO $\underline{Me_2}\text{Al-(-O—Al(Me)-)}_n\text{-O—Al}\underline{Me_2}$.[19] The spectrum agrees with the published data.[25—28] The MAO sample was prepared from the starting solution of MAO in toluene by the pre-evacuation to remove the solvent and weakly bound TMA, whose content in the starting sample reaches 30 mol.%. A white powder that formed was dissolved in toluene-d_8. The interaction between MAO and TIBA results in the transformation of the ^1H NMR spectrum of MAO that involves the disappearance of the former and appearance of new signals assigned to alumoxane structures different from MAO.

The ^1H NMR spectrum (see Fig. 1, *b*) of the soluble reaction product obtained by the reaction of MAO with TIBA ($Al_{TIBA} : Al_{MAO} \approx 1 : 15$) exhibits the following changes. The signal of protons of the terminal Me groups of the oligomeric MAO structures becomes narrower, and signals of the polyisobutylalumoxane structures appear.

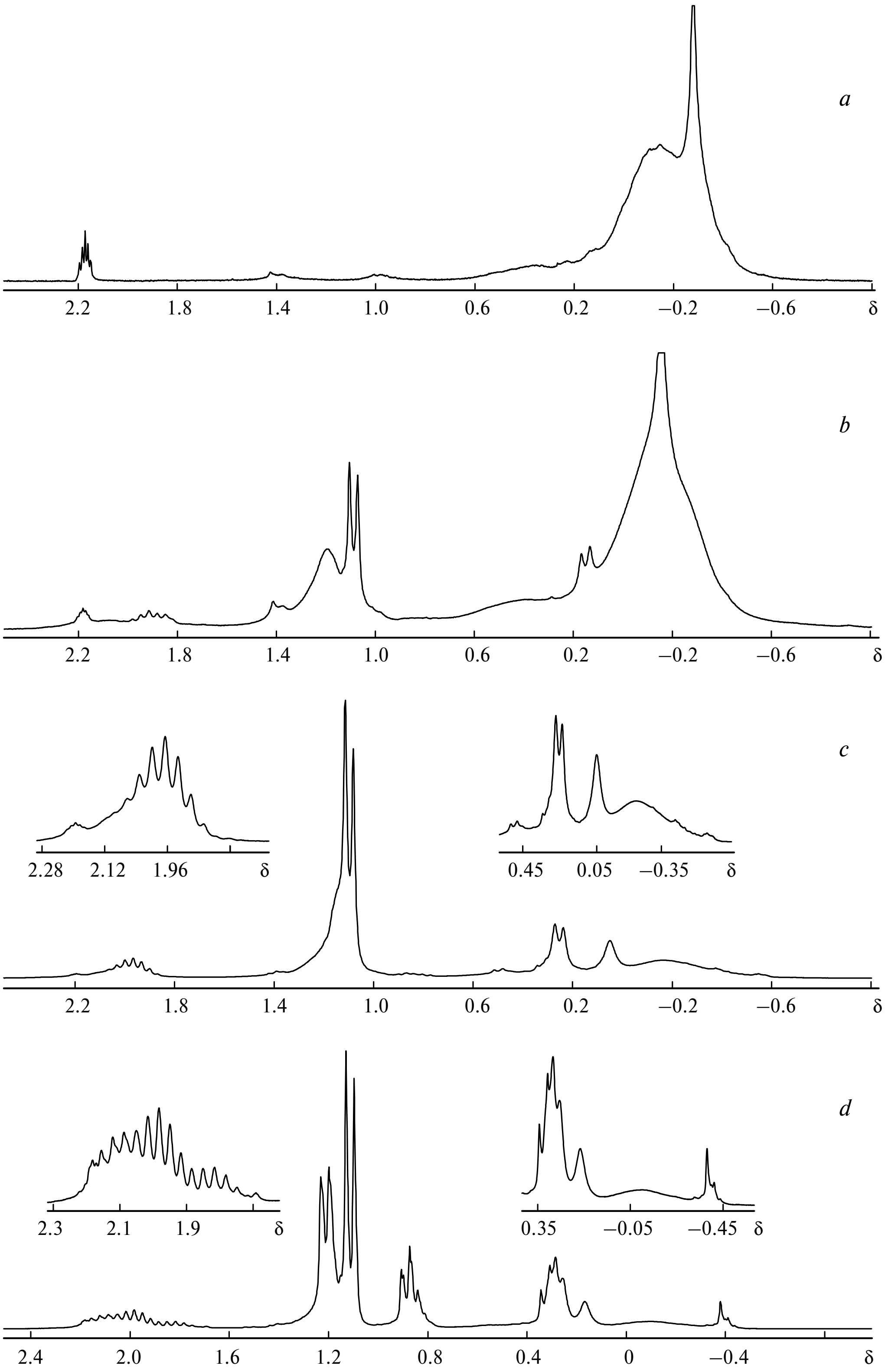
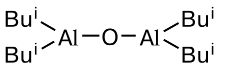


Fig. 1. Fragments of the ^{1}H NMR spectra of MAO (*a*) and the reaction systems MAO + TIBA at the varied molar ratio $Al_{TIBA} : Al_{MAO}$ = 1 : 15 (*b*), 1 : 3 (*c*), and 1 : 1 (*d*).

In addition, a broad signal of the Me protons of the isobutyl groups of the associates is observed at δ 1.2 along with the corresponding broad signal of the CH protons at δ 2.1. The spectrum contains signals of TIBAO [29]: a well resolved doublet of the Me groups at δ 1.1, a doublet of the methylenic protons at δ 0.25, and a multiplet of the CH protons of the isobutyl groups at 1.97.

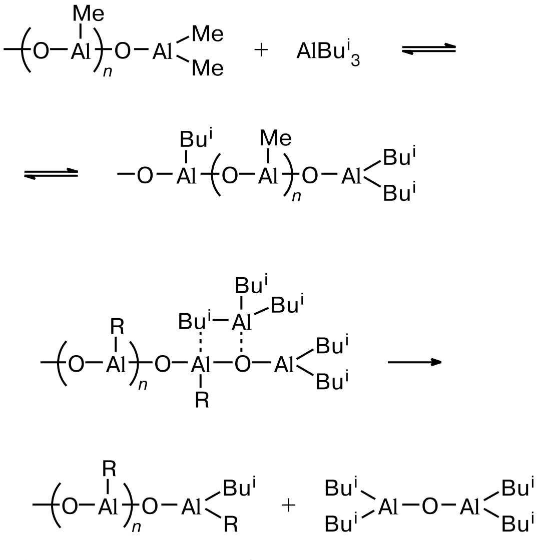


TIBAO

The resolved multiplet of the methinic protons indicates the formation of low-molecular nonassociated structures similar to higher branched alumoxanes.[30]

Thus, the introduction of even a small amount of TIBA induces significant changes in the composition and structure of MAO: the intensive replacement of the Me groups of MAO by isobutyl groups resulting simultaneously in the transformation of the polymethylalumosiloxane structures into polyisobutylalumoxanes or structures of the mixed type and a decrease in the degree of association of MAO by the action of TIBA accompanied by the simultaneous formation of TIBAO. One can readily imagine that the disappearance of the signals from the terminal Me groups of MAO due to the replacement of the Me groups of MAO by isobutyl groups, the decrease in the size of the MAO associates, and the appearance of signals of the tetraisobutylsiloxane structures are interrelated processes (Scheme 2).

Scheme 2



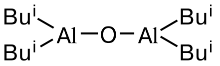
The disproportionation of MAO under the action of coordinating trimethylaluminum is known from the literature.[25]

With an increase in the Al_{TIBA} : Al_{MAO} ratio to 1 : 3 (see Fig. 1, *c*), the signals of the Me groups of MAO disappear almost completely. The signals of tetraisobutylalumoxane become predominant in the spectrum: a resolved doublet of the Me protons at δ 1.1, a doublet of the methylenic protons at δ 0.25, and a resolved multiplet of the isobutyl CH protons at δ 1.97. In addition, according to the broadening of the signals and their downfield shift, a small quantity of associated isobutylalumoxane is present.

Thus, the main soluble reaction product between MAO and TIBA (30 mol.%) is tetraisobutylalumoxane. However, the associated structures of isobutylalumoxane can be observed in the ^{1}H NMR spectrum of the soluble products. Evidence of these structures is a superposition of the broad signals in the region of the methylic and methidic protons of the isobutyl groups.

An increase in the molar ratio Al_{TIBA}/Al_{MAO} to **1** results in the appearance of signals of both tetraisobutylalumoxane and polyisobutylalumoxane in the ^{1}H NMR spectrum (see Fig. 1, *d*). All the signals of protons in this isobutylalumoxane are well resolved but downfield shifted: a multiplet of the CH protons at δ 2.1, a doublet of the Me protons at δ 1.21, and a group of signals of the methylenic protons at δ 0.87. They are partially overlap with the signals of the isobutyl protons of unreacted TIBA. The positions of the downfield chemical shifts of protons of the isobutyl groups assume that the Al atom bonded to these groups is in a more electronegative environment than in tetraisobutylalumoxane, *i.e.*, the reaction products contain isobutyl groups of the —O—Al(Bu^i)—O— fragments. The presence of the resolved multiplet of the isobutylic CH protons indicates that this compound is not associated. Since the methylenic protons in these groups are close to the Al atom, they should manifest a much greater downfield shift than the methylic and methidic protons do.

Thus, with the equimolar ratio of MAO to TIBA, the main reaction products are isobutylalumoxanes with the three-coordinated aluminum atom



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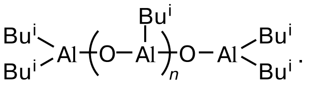

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Unsaturated coordination of tetraisobutylalumoxane gives rise to its instability[31] and a tendency to form dimers[32] and associated compounds. Our attempt to synthesize TIBAO in toluene followed by concentrating its solution afforded associates (Fig. 2, *a*). The degree of association increases with time (Fig. 2, *b*), which appears as the disappearance of the resolved multiplet of the methidic protons and downfield shift of the signals compared to TIBAO, which was synthesized in the reaction of MAO with TIBA (Fig. 2, *c*).

The formation of nonassociated isobutylalumoxanes by the reaction of MAO with TIBA can induce the activation of MAO-preactivated metallocene dichlorides in the presence of TIBA. Under conditions typical of metallocene dichloride preactivation by low molar excess MAO,

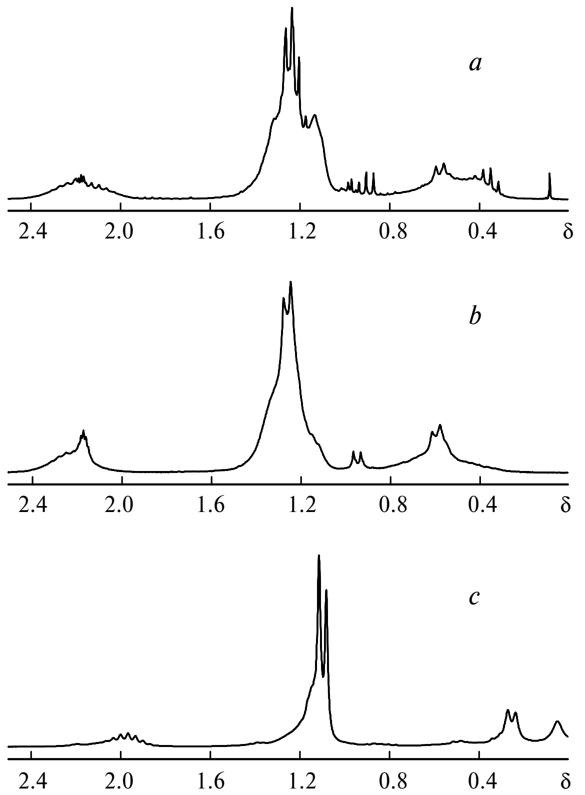

Fig. 2. Fragments of the ^{1}H NMR spectra of TIBAO obtained by the hydrolysis of TIBA (*a*, *b*) and synthesized by the reaction MAO + TIBA (Al_{TIBA} : Al_{MAO} = 1 : 1) (*c*). The spectra were recorded 1 h (*a*) and 3 days (*b*) after the synthesis.

the starting dichloride is monomethylated (see Scheme 1, reaction (1)).[5,33–36] In the presence of TIBA, the Me group is probably replaced by the isobutyl group. However, this reaction is insufficient for the subsequent formation of an active site. Monoalkyl monochloride metallocene is activated *via* the elimination of the Cl^- anion by nonassociated isobutylalumoxanes formed in the reaction of MAO with TIBA. Due to the high content of three-coordinated Al atoms,[37] nonassociated isobutylalumoxanes manifest a higher Lewis acidity than MAO and eliminate the Cl^- anion more easily (see Scheme 1, reaction (2)).[38] It is known[29,30,38–40] that branched alumoxanes can act as efficient cocatalysts for a series of metallocene complexes, and their activity is close to or even exceeds the activity of the systems with MAO.

In addition to the above-described isobutylalumosiloxanes, being the reaction products of MAO with TIBA, we observed the transformation of the methylalumoxane structures. The content of these structures decreases with an increase in the molar ratio Al_{TIBA}/Al_{MAO} but they appear in the spectra of the reaction products even at an equimolar ratio of the reactants. With an increase in the Al_{TIBA}/Al_{MAO} ratio, the signals of the terminal AlMe groups gradually disappear. The spectra (see Fig. 1, *c*, *d*) contain a signal at δ 0—0.2. The intensity of this signal also decreases with an increase in the Al_{TIBA}/Al_{MAO} ratio, and the signal shifts to δ 0.17, *i.e.*, to the region where signals of the bridged Al—Me—Al structures appear.[25–28] It is likely that the terminal Me groups are the first to exchange ligands during the interaction between TIBA and MAO, and the spectra exhibit the residual bridging Me groups, while the position of the signal depends on the degree of association of alumoxane. For the ratio Al_{TIBA} : Al_{MAO} = 1 : 1 (see Fig. 1, *d*), a low-intensity signal appears in the spectrum at δ –0.38. This signal cannot be ascribed to the terminal AlMe groups, because the Me groups are completely replaced by isobutyl groups under these conditions. The appearance of the weak signal at δ –0.58 observed on synthesizing MAO by the *in situ* hydrolysis of $AlMe_3$ has been reported previously.[34] Since this signal lies between δ –0.20 (high-molecular MAO) and δ –0.95 (dimerized tetramethylalumoxane),[41] it can be assigned to protons of the bridging Me groups of MAO with a low molecular weight. By analogy, the weak signal at δ –0.38 can be ascribed to protons of the bridging Me groups in the low-molecular-weight MAO, which is formed by MAO disproportionation with TIBA.

Let us consider the spectra of the reaction products of **1** + MAO and (**1** + MAO) + TIBA. To interpret the spectra and characterize the intermediates, we used the spectra of the dichloride and dimethyl derivatives of zirconocene **1**. The chemical shifts of the protons of the bridging groups $Me_2Si<$ and ZrMe-zirconocenes and the reaction products of zirconocene dichloride with the components of the catalytic system are presented in Tables 1 and 2.

The reaction of compound **1** with MAO was carried out at the molar ratios Al_{MAO}/Zr = 50 and 150. A comparison of the spectra of the starting compound **1** and its reaction product with MAO showed that the monomethylated zirconocene is mainly formed at the ratio Al_{MAO}/Zr = 50. Its formation is indicated by the appearance of two signals of protons of the Me groups: for both the bridging $Me_2Si<$ group and 2-Me substituent of the indenyl ligand (see Table 1). In this case, the spectrum also changes in the region where the indenyl signals appear. A broadened upfield signal appears simultaneously (δ –1.13, see Table 2), which can be assigned to protons of the bridging Me groups in the $[L_2ZrCl(\mu\text{-}Me)]^{\delta+}[MAO]^{\delta-}$ structures (**2**). The signals of

Table 1. Chemical shifts (δ) of the Me protons of the 2-Me substituents in the indenyl ligand and bridging groups $>SiMe_2$ (toluene-d_8, δ 7.06)

Catalytic system	δ	
	2-Me	$SiMe_2$
1	2.09	0.94
1—MAO (Al_{MAO}/Zr = 50)	2.11, 2.19	0.87, 0.95

Table 2. Chemical shifts (δ) of the Me protons of the ZrMe fragments in the reaction products* (toluene-d_8, δ 7.06)

Catalytic system	–δ	Assignment
1 (Me)	0.68	ZrMe
1—MAO (Al_{MAO}/Zr = 50)	1.13	Zr-μ-Me (**2**)
1—MAO (Al_{MAO}/Zr = 150)	1.66	Zr-μ-Me (**3**)
	1.46	Zr-μ-Me (**4**)
	1.13	Zr-μ-Me (**2**)
	0.95	ZrMe (**3**)
1—MAO—TIBA	1.66	Zr-μ-Me (**3**)
(Al_{MAO}/Zr = 150, Al_{TIBA}/Zr = 10)	1.46	Zr-μ-Me(**4**)
	1.13	Zr-μ-Me (**2**)
	0.95	ZrMe (**3**)

* These signals were not determined for the **1**—MAO—TIBA system (Al_{MAO}/Zr = 150, Al_{TIBA}/Zr = 50).

the nonbridging Me groups in the monomethyl monochloride derivatives are recorded in lower fields.[42]

An increase in the Al_{MAO}/Zr molar ratio to 150 is accompanied by the appearance of four upfield signals of the Me protons (see Table 2). One of them (at δ –1.13) is attributed to the monomethyl monochloride derivative coordinated to MAO. Three others correspond, most likely, to different dimeric cationic structures. This assignment is based on the fact that the signals of the Me protons of the nondimerized cationic species $L_2ZrMe^+X^-$ appear in lower fields.[43] The signals of the Me protons can be assigned by analogy to the cationic dimeric structures[2] formed by the reaction of the dimethylzirconocene derivatives and borates. The positions of the bridging (δ –2.75) and nonbridging (δ –0.89) Me protons in the dimeric structures [*rac*-$Me_2SiInd_2ZrMe(\mu\text{-}Me)MeZrInd_2SiMe_2]^+$ in CD_2Cl_2 were determined. We assume that the signals observed at δ –1.66 and –0.95 are attributed to the bridging and nonbridging Me groups in similar dimeric structures formed by the reaction between the cationic center $[MeZrL_2]^+[MAO]^-$ and monomethyl monochloride derivative $[L_2ZrCl(\mu\text{-}Me)MeZrL_2]^+[MAO]^-$ (**3**). The same intensity of the signals at δ –1.66 and –0.95 is in favor of the assumed structure. No formation of the dimethyl derivatives was observed under these conditions.[36] Therefore, no dimers of the dimethyl complex with cationic complexes should be formed in this system. Since the reaction mixture contains TMA, structures of the type $[Me_2Al(\mu\text{-}Me)ClZrL_2]^{\delta+}[MAO]^{\delta-}$ (**4**) similar to those described previously[2] can be formed, and the signal at δ –1.46 can correspond to the Me protons in a molecule of **4**. In this case, it is difficult to analyze the spectrum in the regions of signals from the >$SiMe_2$ and 2-Me groups in the indenyl ligand, because structures of several types give a complicated spectral pattern.

The influence of TIBA additives on the state of catalytic sites was studied for the ratio Al_{MAO}/Zr = 150, at which the spectrum contains the signals of the ZrMe protons in different cationic structures. The reactions were carried out at the ratios Al_{TIBA}/Zr = 10 and 50. When small quantities of TIBA (Al_{TIBA}/Zr = 10) were introduced, the ^1H NMR spectrum changed insignificantly and exhibited the same set of signals of the ZrMe protons (see Table 2), although their intensity decreased slightly. An increase in the Al_{TIBA}/Zr ratio to 50 is accompanied by the disappearance of all the four signals from the Me protons in the cationic structures along with the earlier described spectral changes related to the transformations of polymethylalumoxane. In addition to the low-intensity signal at δ –0.38, which is detected upon the interaction between MAO and TIBA, a signal at δ –0.55 appears. All the signals of the ZrMe fragment disappear, most likely, due to the replacement of the Me groups by isobutyls in the intermediates. However, the presence of several components in the catalytic system impedes the spectral pattern, and it is difficult to determine the presence of signals of the $ZrBu^i$ groups in the region of positive chemical shifts. At the same time, it is known[38] that the reaction of zirconocene dichloride with TIBA affords the isobutyl derivatives of zirconocene, which further decompose to form hydrides. A weak signal at δ –0.55 can be attributed to the bridging hydride protons or bridged structures[13] $[L_2Zr\text{-}\mu\text{-}(C_4H_7)AlBu^i{}_2]$.

The observed spectral change enables one to monitor the influence of the molar ratio of the reactants on the character of the reaction between TIBA and MAO. At a low TIBA content, the Me groups are replaced by isobutyls, and the terminal groups of MAO are exchanged especially efficiently. The polymethylalumoxane structure simultaneously decompose to form tetraisobutylalumoxane. The soluble reaction products contain weakly associated polymethylalumoxane almost without bound TMA and polyisobutylalumoxane (or mixed Me-, Bu^i-alumoxane) structures. For the molar ratio $Al_{TIBA}/Al_{MAO} \approx 0.3–1$, the main soluble reaction products are tetraisobutylalumoxane and nonassociated polyisobutylalumoxane. Based on the spectra of the reaction products, low-molecular-weight MAO also appears in small amounts. The reaction of MAO with compound **1** at the ratio Al_{MAO}/Zr = 50 produces the monomethyl monochloride zirconocene derivative. The chemical shift of the signal of ZrMe at δ –1.13 indicates the formation of associated bridged structures $[L_2ZrCl(\mu\text{-}Me)]^{\delta+}[MAO]^{\delta-}$ (**2**). An increase in the Al_{MAO}/Zr ratio to 150 induces the formation of two additional types of cationic complexes: $[L_2ZrCl(\mu\text{-}Me)MeZrL_2]^+[MAO]^-$ (**3**) and $[Me_2Al(\mu\text{-}Me)ClZrL_2]^+[MAO]^-$ (**4**). The reaction of TIBA with the cationic intermediate complexes results in the disappearance of signals of the Me protons, indicating that the Me groups were replaced by isobutyl groups at the first step of the reaction.

Thus, the activation of the metallocene precursor complexes, under the conditions of MAO preactivation at low molar ratios Al_{MAO}/M followed by activation with TIBA,[14—16] involves higher alkylalumoxanes formed in the reactions between MAO and TIBA. The main reaction products of dichloride metallocene **1** with MAO and their transformation by TIBA were determined by ^{1}H NMR spectroscopy. At the same time, a set of the metallocene complexes formed by the reaction of the starting dichloride with MAO and then with TIBA can differ from the catalytic intermediates formed in the real catalytic systems with the metallocene concentrations by three—four orders of magnitude lower than those in NMR experiments. In particular, we can suggest that at low zirconocene concentrations the probability of formation of binuclear zirconocene complexes of type **3** is low.

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