Novel titanium(IV) complexes with 2,4-di-*tert*-butyl-6-(1,1,1,3,3,3-hexafluoro-2-hydroxypropan-2-yl)phenol in ethene polymerization*

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Dinuclear (**2**) and mononuclear dichloride complexes (**3**) of titanium(IV) isopropoxide with a bidentate phenol alcohol ligand, *viz.*, 2,4-di-*tert*-butyl-6-(1,1,1,3,3,3-hexafluoro-2-hydroxypropan-2-yl)phenol, were obtained. The structures of the complexes were confirmed by X-ray diffraction. The dimeric structure of complex **2** is typical of alkoxy compounds and contains the bridging fragment $Ti(\mu-OPr^i)_2Ti$; the coordination polyhedron of the Ti atom is a distorted tetragonal pyramid. In complex **3**, the Ti atom has a distorted octahedral environment made up of the O atoms of the ligand, the Cl atoms, and the O atoms of two coordinated propan-2-ol molecules. The catalytic properties of complexes **2** and **3** in ethene polymerization were studied with such promoters as polymethylaluminoxane (MAO), trimethylaluminum, triisobutylaluminum, diethylaluminum chloride, and $Et_2AlCl—MgBu_2$. Both the complexes were catalytically active (635 and 540 kg of polyethylene (PE)/(mol of Ti) h atm, respectively) only in the presence of the binary promoter $Et_2AlCl—MgBu_2$. The dichloride complexes obtained from a lithium or magnesium salt of the same ligand and $TiCl_4$ without separation from lithium and magnesium chlorides formed as by-products were catalytically active in the presence of MAO, Bu^i_3Al, and Me_3Al. For the catalytic system containing the dichloride complex and $MgCl_2$, the best promoter is Me_3Al (1082 kg of PE/(mol of Ti) h atm). The polymer obtained on all the catalytic systems is linear polyethylene characterized by high molecular weight (M_w = = 593900—2000000 g mol^{-1}) and high polydispersity indices (M_w/M_n = 2.8—15). Various conjectures were made about why lithium and magnesium chlorides have the promoting effects.

Key words: titanium(IV), coordination compounds, catalysis, organomagnesium and organoaluminum compounds, promoters, lithium chloride, magnesium chloride, ethene, polymerization.

The discovery of novel highly efficient catalysts for olefin polymerization that are based on chelate complexes of Groups 4 and 8—10 metals with imine or iminopyridyl ligands activated with polymethylaluminoxane (MAO) has given impetus to more extensive investigations in the field named "postmetallocene catalysis".[1—5] However, despite a considerable number of studies concerned with postmetallocene catalysis and appropriate catalysts, only a few papers deal with "usual" organoaluminum compounds (OAC, used in classic Ziegler catalysis) for the activation of a precatalyst and the formation of a catalyst rather than with such cocatalysts as MAO, perfluorophenylboranes, or borates traditionally employed in recent years for the same purposes. Far from pretending to have exhaustively surveyed the relevant literature data, below we cite several examples of such efficient catalytic systems for the synthesis of polyethylene (PE): bis(pyrazolyl)pyridine complexes of vanadium and diethylaluminum chloride,[6] half-sandwich complexes of Cr^{III} with salicylaldimine ligands and Et_3Al,[7] bidentate [S,P]- and [O,P=O]-complexes of Cr^{III} with Et_2AlCl,[8] bisiminopyridyl complexes of Fe^{II} with trimethylaluminum or triisobutylaluminum,[9,10] diimine complexes of Ni^{II},[9] and bisiminopyridine complex-

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es of Co^{II} with Me_3Al.[11] Much fewer literature examples refer to such an activation of Group 4 metal chelate complexes, mostly phenoxy imine complexes of zirconium activated with Me_3Al, Et_3Al,[12] and Et_2AlCl.[13]

When activated with MAO, phenoxy imine complexes of titanium form highly efficient catalysts for ethene polymerization.[14—16] Unfortunately, the polymerization kinetics on these catalysts in the presence of a trialkylaluminum is unsteady because of side reactions leading to their decomposition.[17—19] For this reason, it is desirable to use "dry" MAO free from Me_3Al for activation of the complexes. Obviously, the necessity of employing expensive MAO and, what is more, "dry" MAO makes these systems of little practical value for the synthesis of polyolefins.

The presence of an alcoholic oxygen atom in a ligand molecule, as in, *e.g.*, 1,3-dioxolane-4,5-diyldimethanol ligands (TADDOL), affords precatalysts that are inferior to phenoxy imine complexes in the synthesis of polyolefins but exhibit the steady kinetics of polymerization of lower and higher (hex-1-ene, oct-1-ene, and dec-1-ene) α-olefins even when activated with "usual" OAC (Me_3Al, Et_3Al, and Bu^i_3Al).[20]

The goal of the present work was to obtain and characterize novel titanium(IV) complexes of the formula $LTi^{4+}X_2$ ($X = OPr^i$ and Cl; L is a bidentate ligand of the phenol alcohol nature, *viz.*, 2,4-di-*tert*-butyl-6-(1,1,1,3,3,3-hexafluoro-2-hydroxypropan-2-yl)phenol) and study their catalytic properties. The presence of the highly ionized bis(trifluoromethyl) carbinol fragment in the ligand along with the phenolic O atom makes the metal atom more stable in its highest oxidation state. These complexes were activated with MAO, Me_3Al, Bu^i_3Al, Et_2AlCl or the binary mixture $3Et_2AlCl—MgBu_2$ for the formation of catalysts for ethene polymerization.

Results and Discussion

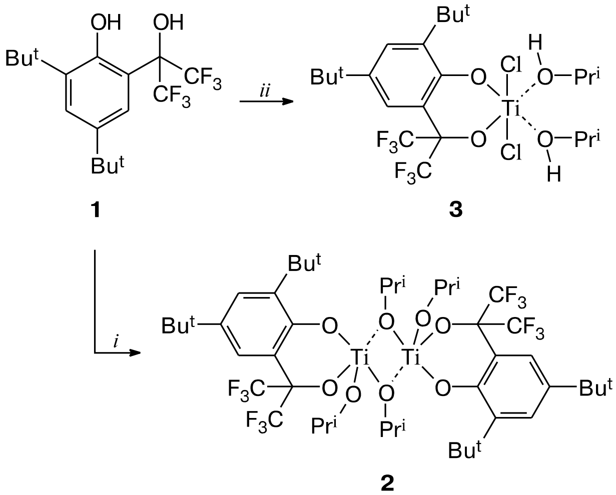
2,4-Di-*tert*-butyl-6-(1,1,1,3,3,3-hexafluoro-2-hydroxypropan-2-yl)phenol (**1**) was used as a ligand. This compound can be coordinated to a metal center through two O atoms and contains bulky trifluoromethyl and *tert*-butyl substituents, which shield well the rear part of the metal atom. Ligand **1** was prepared from perfluoroacetone and 2,4-di-*tert*-butylphenol according to a known procedure.[21]

Precursors of postmetallocene catalysts based on Group 4 metals can be obtained in several ways. The best known methods involve halides, alkyls (aryls), imines, and, less often, alkoxides of these metals as starting reagents with leaving ligands. Metal halides are most commonly used; however, their highest Lewis acidity can trigger a number of side processes that make it very difficult (or even impossible) to obtain and isolate target products in the individual state. The use of alkyl or aryl substituents causes problems associated with low chemical stability of precatalysts.

Titanium alkoxide (notably isopropoxide) complexes are widely used in organic synthesis[22,23] because of the relative ease and "unequivocal character" of the synthesis and the absence of by-products. The use of less "acidic" salts allows "mild" syntheses of precursors by direct reactions with the ligand and, moreover, substantial changes in their chemical and physical properties (*e.g.*, enhanced solubility). However, such structures are very uncommon as postmetallocene catalysts for olefin polymerization.

Direct reactions of ligand **1** with $Ti(OPr^i)_4$ (0.5 or 1 equiv.) and $TiCl_2(OPr^i)_2$ (1 equiv.) in toluene gave complexes **2** and **3**, respectively (Scheme 1). Their structures were identified by X-ray diffraction (Figs 1 and 2). Selected bond lengths and bond angles in structures **2** and **3** are listed in Tables 1 and 2.

Scheme 1



i. $Ti(OPr^i)_4$ (0.5—1 equiv.); *ii.* $TiCl_2(OPr^i)_2$ (1 equiv.).

It can be seen in Fig. 1 that tetraisopropoxytitanium reacts with ligand **1** to give a dimeric structure (typical of alkoxy compounds) with the bridging fragment $Ti(\mu\text{-}OPr^i)_2Ti$. The complex crystallizes from solution when the ratios Ti : L are (0.5—1) : 1. The coordination polyhedron of the Ti atom in structure **2** is a distorted tetragonal pyramid with the bridging O atoms in the base and the O atom of the terminal isopropoxy group in the apex. The six-membered chelate ring CCCOOTi is folded along the axis O—O, making an envelope conformation with a dihedral angle of 135°. The O...O distance in the ring is 2.52 Å. The complex is stable below 180 °C (DSC data).

The IR spectrum of complex **2** shows absorption bands at 549 and 851 cm^{-1} (Ti—O and Ti—O—Ti stretching vibrations, respectively).

The direct reaction of diisopropoxytitanium dichloride with compound **1** yields mononuclear molecular complex **3**. Its crystal structure is built from two crystallo-

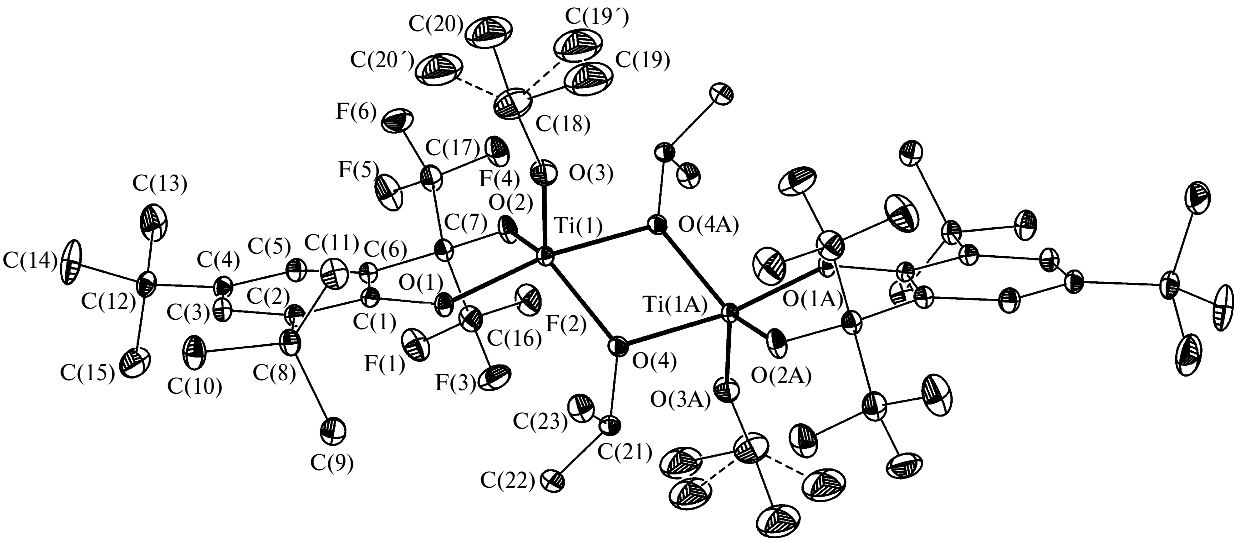


Fig. 1. Molecular structure of complex **2** with atomic displacement ellipsoids (p = 50%). The hydrogen atoms are omitted. The alternative positions of the carbon atoms in two disordered isopropyl groups are indicated with dashed lines.

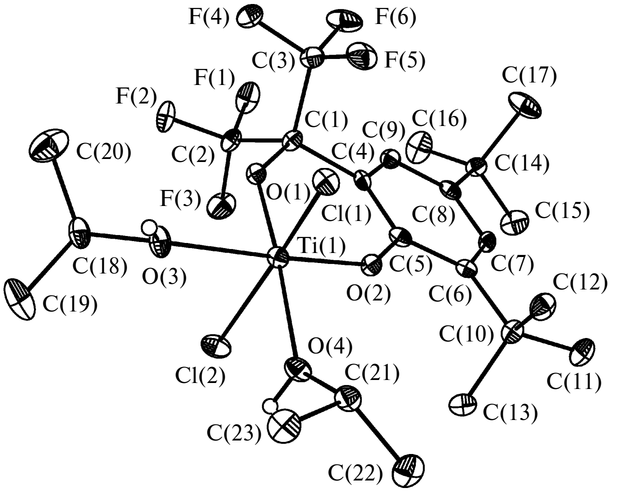


Fig. 2. One of two crystallographically independent molecules in structure **3** with atomic displacement ellipsoids (p = 50%). The hydrogen atoms are omitted.

graphically independent molecules, which are linked to each other and to an adjacent pair of complex molecules by hydrogen bonds involving the OH groups and the Cl atoms (O(3A)—H(3OA)...Cl(1) and O(3)—H(3O)...Cl(1A)).

Table 1. Selected bond lengths d in complexes **2** and **3**

Complex **2**		Complex **3**	
Bond	d/Å	Bond	d/Å
Ti(1)—O(3)	1.7560(11)	Ti(1)—Cl(1)	2.353(1)
Ti(1)—O(1)	1.8395(10)	Ti(1)—Cl(2)	2.362(1)
Ti(1)—O(2)	1.8478(10)	Ti(1)—O(1)	1.816(2)
Ti(1)—O(4)	1.9230(10)	Ti(1)—O(2)	1.786(3)
Ti(1)—O(4)#1	2.0907(10)	Ti(1)—O(3)	2.119(3)
Ti(1)...Ti(1)#1	3.1964(5)	Ti(1)—O(4)	2.121(2)

Table 2. Selected bond angles ω in complexes **2** and **3**

Angle	ω/deg
Complex **2**	
O(3)—Ti(1)—O(1)	101.49(5)
O(3)—Ti(1)—O(2)	114.41(5)
O(1)—Ti(1)—O(2)	87.05(4)
O(3)—Ti(1)—O(4)	115.12(5)
O(1)—Ti(1)—O(4)	100.56(4)
O(2)—Ti(1)—O(4)	126.98(5)
O(3)—Ti(1)—O(4)#1	94.48(5)
O(1)—Ti(1)—O(4)#1	163.83(4)
O(2)—Ti(1)—O(4)#1	84.04(4)
O(4)—Ti(1)—O(4)#1	74.50(4)
Complex **3**	
Cl(1)—Ti(1)—Cl(2)	163.55(4)
Cl(1)—Ti(1)—O(1)	98.24(8)
Cl(1)—Ti(1)—O(2)	96.97(8)
Cl(1)—Ti(1)—O(3)	82.53(7)
Cl(1)—Ti(1)—O(4)	87.16(7)
Cl(2)—Ti(1)—O(1)	93.74(8)
Cl(2)—Ti(1)—O(2)	94.53(8)
Cl(2)—Ti(1)—O(3)	86.52(7)
Cl(2)—Ti(1)—O(4)	80.65(7)
O(1)—Ti(1)—O(2)	88.7(1)
O(1)—Ti(1)—O(3)	88.7(1)
O(1)—Ti(1)—O(4)	174.4(1)
O(2)—Ti(1)—O(3)	177.3(1)
O(2)—Ti(1)—O(4)	92.3(1)
O(3)—Ti(1) O(4)	90.4(1)

In either independent molecule, the Ti atom has a distorted octahedral environment made up of the Cl atoms, two O atoms of the chelating ligand, and two O atoms of propan-2-ol molecules derived from the leaving isopropoxy groups (see Fig. 2). Since the Ti—O bonds in complex **3** differ in their nature, the Ti(1)—O(3) and Ti(1)—O(4) bonds are longer by about 0.3 Å than the Ti(1)—O(1) and Ti(1)—O(2) bonds. The corresponding C—O bond lengths also change (1.36—1.39 Å in the alkoxy groups and 1.46—1.48 Å in the coordinated propan-2-ol molecules). The geometrical parameters of the six-membered chelate ring in complex **3** are generally similar to those found in complex **2**, regardless of possible hydrogen bonding F(1)→H(9a)—C(9) (F(1)...H(9a), 2.3 Å).

The IR spectrum of complex **3** shows absorption bands at 592 and 405 cm^{-1}, which can be assigned to the Ti—O and Ti—Cl stretching vibrations, respectively. The absorption band due to the OH groups of the coordinated propan-2-ol molecules appears at 3406 cm^{-1} (for free propan-2-ol, at 3594 cm^{-1}). According to DSC data, these molecules are bound in the complex fairly strongly by both the coordination bond to the Ti atom and a system of hydrogen bonds: stepwise elimination of the propan-2-ol molecules begins only above 110 °C.

As noted above, transition metal alkoxides are sometimes used as starting reagents for the synthesis of precursors of postmetallocene catalysts for olefin polymerization (see, *e.g.*, Refs 24—28). Complex **2** isolated in the individual state proved to be inefficient in combination with such "standard" cocatalysts as MAO, Me_3Al, $Bu^i{}_3Al$, and Et_2AlCl in this reaction (Table 3) (all the precatalysts studied earlier[29] behave in a similar way). Its failure cannot be associated only with the dimeric structure and the very stable fragment $Ti(\mu\text{-}OPr^i)_2Ti$, which is inert to OAC, since nor does mononuclear dichloride complex **3** form a catalyst in the presence of the same promoters (see Table 3). It is hardly imaginable that this fact is accounted for by the coordination of propan-2-ol in complex **3** since propan-2-ol will be involved in an alcoholysis reaction with OAC present in large excess and thus leave the coordination sphere of the Ti atom. It should be noted that dimeric alkoxy complexes of titanium and zirconium with O,S,O-ligands are very efficient in ethene polymerization in the presence of all types of OAC.[26—28]

The polymerization pattern changes dramatically when individual complexes **2** and **3** react with the binary mixture $\{3Et_2AlCl + MgBu_2\}$ used previously[29] as a versatile promoter for all types of supported catalysts and homogeneous Ziegler catalysts. When dissolved in toluene, both the complexes show catalytic activity preceded by an induction period of 10 (for **3**) and 30 min (**2**). The specific performance of complexes **2** and **3** activated with the binary promoter depends on the molar ratio Al/Ti. Complex **2** was most efficient (635 kg of PE/(mol of Ti) h atm) at Al_{Et_2AlCl}/Ti = 300 : 1, while complex **3** (880 kg of PE/(mol of Ti) h atm), at Al_{Et_2AlCl}/Ti = 500 : 1. The PE samples obtained on complexes **2** and **3** in the presence of this promoter have very high molecular weights. All of them are insoluble in trichlorobenzene at 135 °C. The IR spectra of thin PE films show no absorption band at 1378 cm^{-1} (Me bending vibrations), which suggests unbranched polymer molecules.[30] Accordingly, all of these PE samples have high melting points (144—147 °C) for their degrees of crystallinity of 52—56%.

Table 3. Data on the ethene polymerization on precatalysts **2** and **3** with different promoters[a] and the melting temperatures of the polyethylene samples obtained

Entry	Pre-catalyst	Promoter	[Al]/[Ti], mol mol^{-1}	A[b]	T_m[c] /°C
1	**2**	MAO	1000	—	
2	**2**	Me_3Al	500	—	
3	**2**	$Bu^t{}_3Al$	500	—	
4	**2**	Et_2AlCl	500	—	
5	**2**	Et_2AlCl/Bu_2Mg[d]	100	Traces	
6	**2**	Et_2AlCl/Bu_2Mg	250	400	146.3
7	**2**	Et_2AlCl/Bu_2Mg	300	635	145.3
8	**2**	Et_2AlCl/Bu_2Mg	500	250	147.8
9	**3**	MAO	1000	—	
10	**3**	Me_3Al	500	—	
11	**3**	$Bu^t{}_3Al$	500	—	
12	**3**	Et_2AlCl	500	—	
13	**3**	Et_2AlCl/Bu_2Mg	100	Traces	
14	**3**	Et_2AlCl/Bu_2Mg	300	540	144.8
15	**3**	Et_2AlCl/Bu_2Mg	500	880	145.7
16	**3**	Et_2AlCl/Bu_2Mg	1000	424	144.2

[a] Conditions: toluene (50 mL), 30 °C, [Ti] = $5 \cdot 10^{-6}$ mol, ethene pressure 10 PSI (1.67 atm), polymerization time 30 min.

[b] A is the relative activity, kg of PE/(mol of Ti) h atm.

[c] The melting points was determined from DSC data.

[d] The molar ratio Al : Mg in the binary promoter is 3 : 1.

These results point to a special role of $MgCl_2$, which is produced when dichloride complexes of titanium(IV) are treated with the binary promoter,[29,31] in the formation of catalysts. According to the literature data,[32—35] similar dinuclear titanium and vanadium complexes with an O,S,O-ligand applied to $MgCl_2 \cdot 2THF$ in a ball mill also efficiently catalyze ethene polymerization, no matter whether they have been activated with MAO or OAC. Recently,[36] we have observed a similar effect of $MgCl_2$ and LiCl on ethene and propene polymerization catalyzed by a titanium dichloride complex with a dioxolanediyldimethanol O,O-ligand activated with MAO. Moreover, we have demonstrated that the solution separated from the precipitate produced in the formation of the catalyst, as well as the individual complex of TADDOL with $TiCl_4$, is inefficient, while a suspension of the precatalyst (obtained either *in situ* or by mechanical mixing of an "inert" solution of the complex with suspensions of dry

$MgCl_2$ and LiCl prepared *ex situ*) in the presence of MAO and OAC makes a medium-activity catalyst for polymerization. A similar effect has been noted earlier.[29]

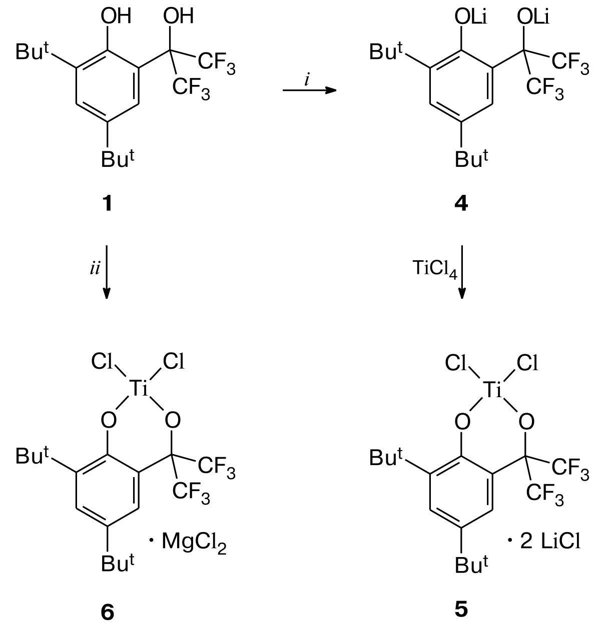
In the present work, we effected the aforesaid version of the step-by-step approach to the preparation of a catalyst, starting with the synthesis of a precatalyst accompanied by the *in situ* formation of transition and main group metal chlorides (Scheme 2). In one experiment, ligand **1** was treated with two equivalents of butyllithium, whereupon the resulting dilithium salt **4** reacted with $TiCl_4$ to give suspension **5** of the formula $\{LTiCl_2 + 2LiCl\}$. In another experiment, the ligand was deprotonated with dibutylmagnesium, which probably yields suspension **6** containing $MgCl_2$. Optimization of its composition revealed that the catalyst obtained from 2 *M* dibutylmagnesium is much more efficient than those obtained from 1 *M* $MgBu_2$ and especially from 3 *M* $MgBu_2$.

Precatalysts or suspensions **5** and **6** containing transition and main group metal chlorides, which were prepared *in situ* (Scheme 2), were activated with MAO, Me_3Al, and $Bu^i{}_3Al$ and used as catalysts for ethene polymerization. The data obtained are summarized in Table 4.

Unlike $MgCl_2$-free precatalyst **3**, precatalyst **6** can be activated with MAO (*cf.* Table 4, entries *17—19* and Table 3, entry *9*). The specific activity of the catalyst **6**/MAO increases with an increase in the molar ratio Al_{MAO}/Ti. The maximum activity of the catalyst (965 kg of PE/(mol of Ti) h atm) was achieved at $Al_{MAO}/Ti = 1000 : 1$. Also, in contrast to precatalyst **3**, precatalyst **6** forms catalysts when its suspension is treated with $Bu^i{}_3Al$ and Me_3Al (Table 3, entries *10*, *11*; Table 4, entries *19—21*), which are nearly as efficient as the MAO-activated catalysts.

The activity of LiCl-containing precatalyst **5** activated with MAO is lower by nearly one order of magnitude than the activity of the system containing precatalyst **6**, all other factors being equal (*cf.* entries *23*, *18* and *24*, *19* in Table 4).

Scheme 2



i. ^nBuLi (2 equiv.); *ii.* 1) $MgBu_2$ (2 equiv.); 2) $TiCl_4$.

However, the formation of $MgCl_2$ in precatalyst **5** (*e.g.*, upon treatment with the binary cocatalyst $Et_2AlCl—MgBu_2$) makes the system much more active (Table 4, entry *25*).

The results considered above are unambiguously indicative of the promoting effects of LiCl and especially $MgCl_2$. Note that the amount of $MgCl_2$ formed in the synthesis of precatalyst **6** is stoichiometric with respect to the titanium complex, while the use of the binary promoter leads to a molar excess of $MgCl_2$ of tens to hundreds. The activities of the resulting catalytic systems containing different cocatalysts differ insignificantly (*cf.* Table 3,

Table 4. Data on the ethene polymerization on precatalysts **5** and **6** with different promoters[a] and the molecular-weight characteristics of the polyethylene samples obtained

Entry	Pre-catalyst	Promoter	[Al]/[Ti], mol mol^{-1}	A[b]	M_w	M_n	M_w/M_n
17	**6**	MAO	200	130			
18	**6**	MAO	500	565			
19	**6**	MAO	1000	965			
20	**6**	$Bu^t{}_3Al$	500	380	846000	210000	4.1
21	**6**	Me_3Al	500	1080	906000	367000	2.5
22	**5**	MAO	110	Traces			
23	**5**	MAO	500	80			
24	**5**	MAO	1000	100	593900	38700	15.4
25	**5**	Et_2AlCl/Bu_2Mg[c]	300	706			

[a] Conditions: toluene (40 mL), 30 °C, $[Ti] = 5 \cdot 10^{-6}$ mol, ethene pressure 10 PSI (1.67 atm), polymerization time 30 min.

[b] A is the relative activity, kg of PE/(mol of Ti) h atm.

[c] The molar ratio Al : Mg in the binary promoter is 3 : 1.

entries *14* and *15* and Table 4, entries *18—21*). However, the polyethylene samples obtained on these catalytic systems have different properties. For instance, the polyethylene obtained on the system containing precatalyst **5** has a lower molecular weight and a high polydispersity index. The molecular weight distribution curves of the PE samples obtained on precatalysts **5** and **6** are shown in Fig. 3. It can be seen that the molecular weight distribution curves for $MgCl_2$-containing system **6** are virtually identical, regardless of the promoter type ($Bu^i{}_3Al$ or Me_3Al) (Fig. 3, curves *1* and *2*). The higher M_w/M_n value for the PE sample obtained in the presence of $Bu^i{}_3Al$ is due to a small contribution from the lower-molecular-weight component, which decreases the number-average molecular weight (Table 4, entries *20* and *21*). In LiCl-containing system **5**, the contribution from the lower-molecular-weight component is much greater (Fig. 3, curve *3*). Nonetheless, the main peak in curve *3* appears in the same position as the peaks in curves *1* and *2* (log(MW) ≈ 6.0). The presence of $MgCl_2$ stimulates the active sites at which high-molecular-weight PE is formed, regardless of the promoter type; in the presence of LiCl, "high-molecular-weight" active sites coexist with those forming PE with appreciably lower molecular weights. For curve *3*, the contribution from the lower-molecular-weight component with a peak at ~5.0 (M_w = 279000, M_n = 75000, M_w/M_n = 3.7) is ~40%.

It can be seen in Fig. 4 that the molecular weight distribution curves of the PE samples obtained on systems **6**/$Bu^i{}_3Al$ and **6**/Me_3Al (Fig. 3, curves *1* and *2*) can be represented as a superposition of four Flory components having close peak positions, close relative contributions to the integral GPC curve, and close molecular-weight characteristics of the corresponding peaks (Table 5). On the whole, one can note that the molecular weights of the peaks Pk2—Pk4 are higher by 10—20% than those for the system with Me_3Al. The M_w/M_n values for peaks Pk2—Pk4 are nearly unity for the systems with both promoters. Therefore, both the systems have the same set of active sites. One type of active sites is characterized by moderate activity and high efficiency of the reactions yielding low-molecular-weight PE having a broad polydispersity index (Pk1). Three other types of active sites account for ~80% of PE; their relative activities are ~1/2/0.5. The resulting high-molecular-weight PE have progressively high molecular weights (~1/2/5 for Pk2/Pk3/Pk4, respectively). Chain transfer reactions virtually do not occur on these active sites and the polydispersity indices of the corresponding Flory components are nearly unity.

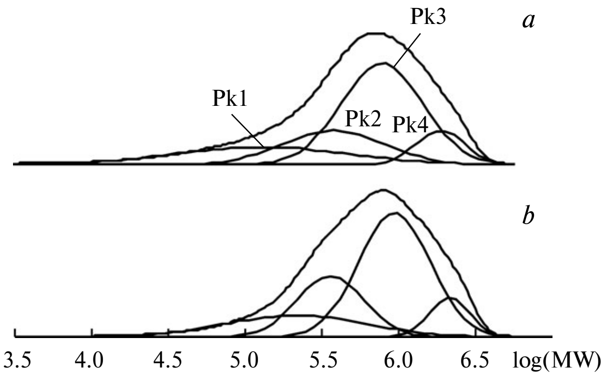


Fig. 4. Deconvolution of the GPC curves of the PE samples obtained on the systems **6**/$Bu^i{}_3Al$ (*a*) and **6**/Me_3Al (*b*) into the Flory components.

It can be inferred from the results presented above that the chemical processes associated with activation of the

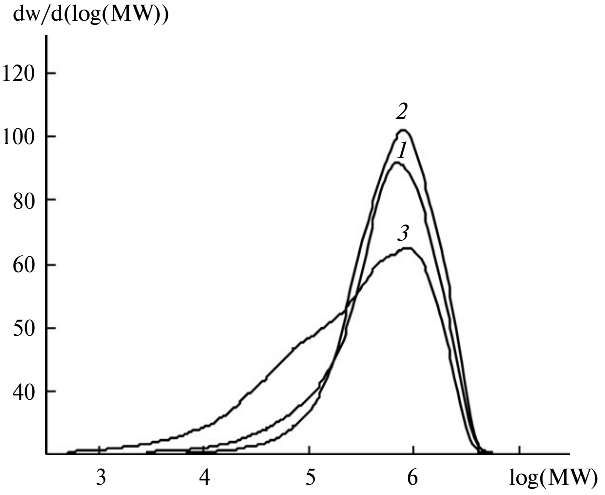


Fig. 3. Molecular weight distribution curves of the PE samples obtained on the systems **6** (*1*, *2*) and **5** (*3*). The promoters are $Bu^i{}_3Al$ (*1*), Me_3Al (*2*), and MAO (*3*) (see Table 5, entries *20*, *21*, and *23*, respectively).

Table 5. Deconvolution of the GPC curves of the PE samples obtained on the systems **6**/$Bu^i{}_3Al$ and **6**/Me_3Al into the Flory components and their molecular-weight characteristics

System	*N*[a]	Max[b]	*C*[c] (%)	M_w	M_n	M_w/M_n
6/$Bu^t{}_3Al$	Σ Pk[d]			846000	210000	4.0
	Pk1	5.1	18	289000	57000	5.1
	Pk2	5.6	23	506000	356000	1.4
	Pk3	5.9	49	940000	838000	1.1
	Pk4	6.3	10	2006000	1752000	1.2
6/Me_3Al	Σ Pk[d]			906000	367000	2.5
	Pk1	5.3	17	366000	107000	3.4
	Pk2	5.6	23	429000	410000	1.1
	Pk3	6.0	50	1078000	928000	1.2
	Pk4	6.3	10	2252000	2067000	1.1

[a] Peak number.

[b] Position of the peak maximum on the log(MW) scale.

[c] Content of the Flory component.

[d] Characteristics of the integral GPC curve.

isopropoxy complexes and the dichloride complexes obtained *in situ* are different. However, in both cases, they do not function as catalysts until the conditions in the system become favorable for the formation of magnesium or lithium chlorides. In the former case, the chloride salt is produced as soon as the organometallic components of the binary promoter are mixed (X-ray powder diffraction data);[29,31] in the latter case, a magnesium or lithium salt of the ligand reacts with $TiCl_4$ to give the corresponding chloride. Unfortunately, we failed to confirm their formation or transformations in a multicomponent system and so did Kissin *et al.*[29] All the reaction products we obtained are X-ray amorphous. Nevertheless, the unique role of the binary mixture $\{3Et_2AlCl + MgBu_2\}$ in the activation of precatalysts is not so much attributed[29] to the formation of $MgCl_2$ in the system but to the formation of the ionic salt $[MgBu]^+[AlBuEt_2Cl]^-$, which is regarded[29] as a stronger Lewis acid than its constituents. However, all the data obtained and analyzed here suggest the direct participation of main group metal chlorides in the formation of Ti-containing catalysts with saligenin ligands. In other words, we consider magnesium and lithium chlorides to be both structuring and modifying promoters (*i.e.*, promoters that increase the number of active sites and change their type).

However, this conclusion refers so far only to titanium complexes with *O,O*-ligands. Indeed, our additional experiments showed that the presence of one or another chloride salt in the system does not influence at all the properties of phenoxyimine titanium catalysts. This allows rejecting the hypothesis of possible formation of dinuclear complexes of the *ate* type with the bridges >Ti—μ-Cl—Mg< or >Ti—μ-Cl—Li<; instead, one can suggest that the Mg or Li atoms coordinate the oxygen atoms of the *O,O*-ligand spaced at ≈ 2.5 Å in complexes **2** and **3**. Either O atom bears two lone electron pairs (Fig. 5, *a*), one of which (inward) is directed toward the coordinating metal atom. As a result, at least a bimetallic *exo* complex can be formed (Fig. 5, *b*) (the role of organoaluminum compounds in the formation of active sites remains unclear and thus is left out from the present work).

Coordination with μ_2- and μ_3-O atoms (M—O, 1.8—2.2 Å) is very common in complexes with oxo ligands. As for the Mg and Li atoms, it is difficult to expect that their coordination numbers will be 4, 3, or 2 in nonsolvating media since this is atypical under these conditions. The formation of heteronuclear dimers seems to be more likely because of the maximum saturation of the coordination spheres of these atoms in such dimers (see Fig. 5, *c*).

This approach to the explanation of the role of chlorides in the formation of a catalyst helps to realize why the mixtures of alkyl complexes of titanium with $MgCl_2$ or LiCl prepared *ex situ* are less active than those formed *in situ* (*cf.* Ref. 29 and our data). Mixing of alkyl complexes with crystalline chlorides in nonsolvating media without special activation (see, *e.g.*, Refs 32—35) may be altogether futile.

The formation of trinuclear *endo*-complexes, *i.e.*, the complexes in which two Mg atoms coordinate the O atoms through their outward-looking lone electron pairs (see Fig. 5, *d*, *e*), is possible though less probable since, first, such complexes in nonsolvating media should be less stable than *exo*-complexes and, second, they should also be detected among complexes with phenoxyimine ligands, which is not the case, as mentioned above. Thus, a variety of possible ways of coordinating chlorides will give rise to active sites of various compositions and structures and hence to polymers with high polydispersity indices, which is actually observed.

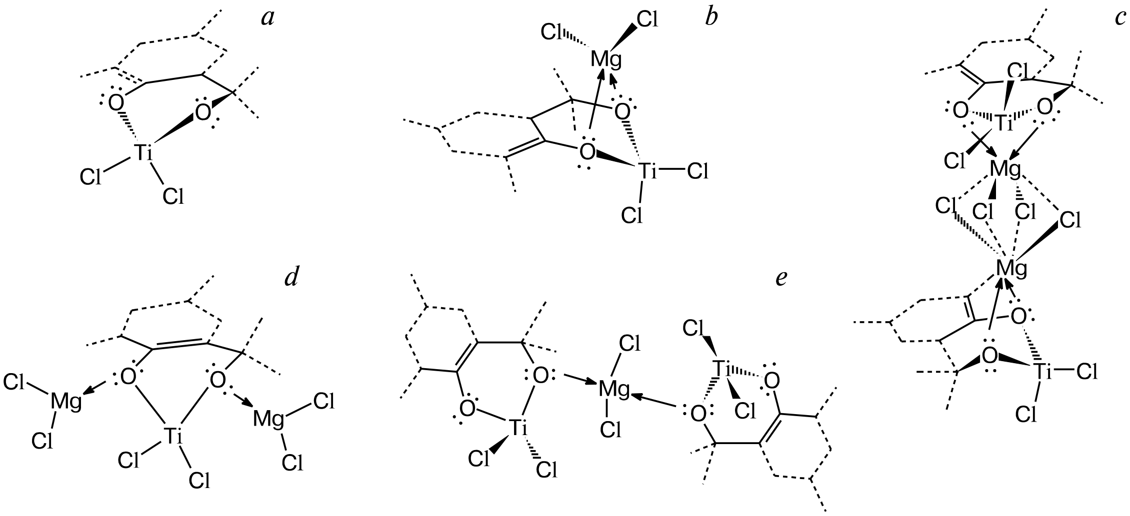


Fig. 5. Probable structures of the products of the complexation between $LTiCl_2$ and $MgCl_2$ (the trifluoromethyl and *tert*-butyl radicals are omitted).

Experimental

All manipulations involving the complexes were carried out using standard Schlenk equipment. When needed, solvents were purified and dried according to known procedures[37] and kept over 3A and 4A molecular sieves. NMR spectra were recorded on Bruker WP-600 and Bruker AMX-400 instruments. IR spectra were recorded on a Magna-IR 750 spectrophotometer. Elemental analysis was carried out on Carlo Erba-1106 and Carlo Erba-1108 instruments. Single-crystal X-ray diffraction experiments were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a CCD detector (λ(Mo-$K\alpha$) = = 0.71073 Å, graphite monochromator, ω and ϕ scan modes). Experimental data were processed and merged with the SAINT Plus program package while applying a semiempirical absorption correction.[38] Structures **2** and **3** were solved by direct methods and refined by the least-squares method in the full-matrix isotropic approximation using iterative difference electron-density maps. The non-hydrogen atoms were refined anisotropically on F^2_{hkl}. The hydrogen atoms of the OH groups were located in difference electron-density maps and refined with fixed positions. The coordinates of the other H atoms were refined using a riding model. The structures were refined with the SHELXTL 5.10 program package.[39] In the crystal of complex **2**, two terminal isopropoxy groups are disordered over two positions with an occupancy ratio of 0.7 : 0.3. Selected crystallographic parameters and the data collection and refinement statistics for structures **2** and **3** are summarized in Table 6.

Table 6. Crystallographic parameters and the data collection and refinement statistics for complexes **2** and **3**

Parameter	**2**	**3**
Molecular formula	$C_{46}H_{68}F_{12}O_8Ti_2$	$C_{23}H_{36}Cl_2F_6O_4Ti$
Molecular weight	1072.80	609.32
T/K	100(2)	100(2)
Crystal dimensions/mm	0.20×0.20×0.15	0.4×0.1×0.1
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a/Å	31.6103(11)	14.8393(11)
b/Å	10.0781(3)	21.5794(17)
c/Å	21.2079(7)	18.6004(14)
β/deg	129.357(1)	105.3985(17)
V/Å^3	5224.0(3)	5742.5(8)
Z	4	8
d_{calc}/g cm^{-3}	1.364	1.410
F(000)	2240	2528
μ/mm^{-1}	0.396	0.549
$2\theta_{max}$/deg	61	56
Number of measured reflections	33493	52301
Number of independent reflections	7958	14885
Number of reflections with $I > 2\sigma(I)$	6559	8885
Number of parameters refined	319	669
R_1	0.0398	0.0671
wR_2	0.0926	0.1182
GOOF	1.000	1.000
Residual electron density (max/min)/e Å^{-3}	0.694/–0.670	0.515/–0.505

X-ray diffraction patterns of PE samples were recorded on a DRON-2 diffractometer (CuK_α radiation, Ni filter, scan rate 1 deg (2θ)/min). The degrees of crystallinity χ of PE samples were determined from the ratio of the integral intensity of the crystalline constituent to the total intensity.

GPC curves of PE samples were recorded on a Waters GPCV-2000 chromatograph (PLgel 5 μm MIXED-C column, 1,2,4-trichlorobenzene) at 135 °C. Molecular weights were calculated from a universal calibration curve with polystyrene standards.

Thermogravimetric analysis was carried out on a NETZSCH STA Jupiter449 C instrument (argon flow rate 100 mL min^{-1}, temperature 40—300 °C, heating rate 5 deg min^{-1}).

Ethene polymerization was carried out in a 100-mL reaction vessel (Parr Instrument).

2,4-Di-*tert*-butyl-6-(1,1,1,3,3,3-hexafluoro-2-hydroxypropan-2-yl)phenol (1) was prepared as described earlier.[21] The yield was 3.7 g (90%). ^{1}H NMR (toluene-d$_8$), δ: 1.21 (s, 9 H); 1.45 (s, 9 H); 3.67 (br.s, 1 H); 7.43 (s, 1 H); 7.51 (d, 1 H, J = 2.3 Hz); 8.07 (br.s, 1 H). ^{19}F NMR (toluene-d$_8$), δ: 2.77 (s).

Di{2-[α,α-bis(trifluoromethyl)methanolato]-4,6-di-*tert*-butylphenolato}di(μ-isopropoxy)di(isopropoxy)dititanium, [LTi(OPr^i)$_2$(Pr^{i}O)]$_2$ (2). A two-necked flask fitted with a magnetic stirring bar was charged under argon with compound **1** (0.19 g, 0.50 mmol) and toluene (10 mL). Then Ti(OPr^i)$_4$ (0.16 mL, 0.5 mmol) was added and the reaction mixture was kept at 40 °C for 12 h. The red crystals that formed were filtered off, washed with toluene, and dried. The yield was 0.22 g (82%). ^{1}H NMR (toluene-d$_8$), δ: 1.97—0.71 (m, 61 H); 3.98—5.79 (m, 4 H); 7.49—7.66 (m, 2 H); 7.82—7.97 (m, 2 H). ^{19}F NMR (toluene-d$_8$), δ: 7.35—0.26 (m). Found (%): C, 51.71; H, 6.44; F, 20.91. $C_{46}H_{72}F_{12}O_8Ti_2$. Calculated (%): C, 51.50; H, 6.39; F, 21.25.

{2-[α,α-Bis(trifluoromethyl)methanolato]-4,6-di-*tert*-butylphenolato}dichlorodi(propan-2-ol)titanium, LTi(HOPr^i)$_2$Cl$_2$ (3). A two-necked flask fitted with a magnetic stirring bar was charged under argon with compound **1** (0.38 g, 1 mmol) and toluene (10 mL). Then Ti(OPr^i)$_2$Cl$_2$ (0.28 g, 1 mmol) in toluene (10 mL) was added. After the formation of a black precipitate, the mixture was heated to homogenization. On cooling, the brownish black crystals that formed were filtered off and washed with toluene. The yield was 0.4 g (59%). Found (%): C, 45.33; H, 5.62; Cl, 11.25; F, 18.55. $C_{23}H_{36}Cl_2F_6O_4Ti$. Calculated (%): C, 45.49; H, 5.64; Cl, 11.68; F, 18.77; Ti, 7.89. ^{1}H NMR (CDCl$_3$), δ: 7.59 (s, 1 H); 7.43 (d, 2 H, J = 2.2 Hz); 4.95—4.78 (m, 2 H); 3.80 (br.s, 2 H); 1.47 (s, 12 H); 1.44 (s, 9 H); 1.31 (s, 9 H). ^{19}F NMR (CDCl$_3$), δ: 4.15 (s).

2,4-Di-*tert*-butyl-6-(1,1,1,3,3,3-hexafluoro-2-hydroxypropan-2-yl)phenol, dilithium salt (4). A solution of BuLi (1.65 mL, 1.05 mmol) in hexane was added dropwise at –78 °C to a stirred solution of compound **1** (0.19 g, 0.5 mmol). The mixture was warmed to room temperature and kept for 30 min. The solvent was removed under reduced pressure. The yield was 0.18 g (92%). Found (%): C, 54.89; H, 5.41; F, 28.31. $C_{17}H_{20}F_6Li_2O_2$. Calculated (%): C, 53.14; H, 5.25; F, 29.67. ^{1}H NMR (DMSO-d$_6$), δ: 6.96 (s, 1 H); 1.31 (s, 5 H); 1.16 (s, 5 H).

{2-[α,α-Bis(trifluoromethyl)methanolato]-4,6-di-*tert*-butylphenolato}dichlorotitanium di(lithium chloride), LTiCl$_2$ · 2LiCl (5). A two-necked flask fitted with a magnetic stirring bar was charged under argon with compound **4** (0.19 g, 0.50 mmol) and toluene

(10 mL). Then $TiCl_4$ (0.05 mL, 0.50 mmol) was added at −78 °C. The mixture was slowly warmed to room temperature, stirred for 20 h, and used without further purification for ethene polymerization. To identify the compound obtained, the precipitate was filtered off, the organic layer was concentrated, and the product was recrystallized from toluene. The yield was 0.15 g (62%). Found (%): C, 41.96; H, 5.22; Cl, 14.37; Ti, 9.44. $C_{17}H_{20}Cl_2F_6O_2Ti$. Calculated (%): C, 41.75; H, 4.12; Cl, 14.50; Ti, 9.79. IR, ν/cm^{-1} (Nujol): 585 (Ti—O).

{2-[α,α-Bis(trifluoromethyl)methanolato]-4,6-di-*tert*-butylphenolato}dichlorotitanium di(magnesium dichloride), [$LTiCl_2$] · $MgCl_2$ (6). A two-necked flask fitted with a magnetic stirring bar was charged under argon with compound **1** (0.19 g, 0.50 mmol) and toluene (10 mL). Then 1 *M* $MgBu_2$ (1 mL, 1.05 mmol) in *n*-heptane was added dropwise at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 4 h. Then $TiCl_4$ (0.055 mL, 0.50 mmol) was added at −78 °C. The mixture was slowly warmed to room temperature and used further without purification for ethene polymerization. For identification, the compound obtained was dried *in vacuo* at 30 °C. ^{1}H NMR (toluene-d$_8$), δ: 7.89 (s, 1 H); 7.52 (d, 1 H, J = 2.2 Hz); 1.46 (s, 9 H); 1.27 (s, 9 H).

Ethene polymerization. A 100-mL metallic reaction vessel was evacuated and filled with ethene. Then toluene (40 mL) and an appropriate promoter were added. The vessel was kept at 30 °C for 10 min and charged with a solution of an appropriate precatalyst in toluene (10 mL). The ethene pressure was brought to a working value (10 PSI or 1.67 atm) and the polymerization was conducted for 30 min. The mixture obtained was discharged from the vessel and a mixture of ethanol and dilute HCl was added. The polymer was filtered off, washed with ethanol and water, and dried *in vacuo* with heating to a constant weight.

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