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Magnesium dichloride effect in ethylene polymerization reactions: a comparative DFT study of Mg-containing and Mg-free post-titanocene catalytic systems

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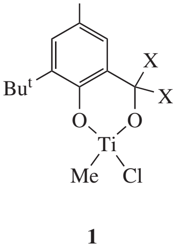
A DFT study of the bi- and trinuclear heterocomplexes of Ti, Al and Mg revealed a higher reactivity of Mg-containing compounds toward ethylene, as compared to Mg-free systems; this explains a significant activation effect of Mg-containing compounds on the catalytic activity of the Ti complexes in ethylene polymerization.

The post-metallocenes of Group IV transition metals can be activated by Al-containing compounds, mostly by methylaluminoxanes (MAO).[1] The complexes of Ti with bidentate ligands of OO-type are the rare exception[2–4] of this rule. The complexes $LTiCl_2$ with the saligenin type ligands $L = C_6H_2Bu^t_2(O–)(CX_2O–)$ ($X = CF_3$ *etc.*) considered below revealed catalytic activity in olefin polymerization reactions only if $MgCl_2$ was *in situ* formed in the course of pre-catalyst synthesis (from Grignard reagent) or its activation by a mixture of $MgBu_2 + AlEt_2Cl$.[2] However, no activity was found without $MgCl_2$ and when commercial dry $MgCl_2$ was used[4] or $MgCl_2$ was *ex situ* prepared outside the catalytic system (for instance, from the adducts of $MgCl_2$ with alcohols[5] or by the reaction of $MgBu_2$ with HCl[4]). According to experimental studies,[6,7] magnesium dichloride appeared in the mixture of $MgBu_2 + AlEt_2Cl$ as the result of the reaction

$$MgBu_2 + 2AlEt_2Cl \longrightarrow MgCl_2\downarrow + 2AlEt_2Bu. \qquad (1)$$

Based on this observation it was assumed[2] that a secondary complexation reaction between the pre-catalyst $LTiCl_2$ and single $MgCl_2$ molecules formed by reaction (1) occurred in the test catalytic system. For verifying this hypothesis, we modeled the products of such complexation reactions and their interaction with ethylene using the quantum chemical DFT method[8] for the model compounds LTi(Me)Cl **1**, with different substituents X = H (**a**), Me (**b**), CF_3 (**c**) and Ph (**d**). The most stable products of $MgCl_2$ binding to **1** are binuclear heterocomplexes **2** and **3** with oxygen and chlorine bridges between Ti and Mg atoms.[8] Trinuclear compounds **4** and **5** (Scheme 1), in which the coordination vacancy of the Mg atom is filled with one activator molecule of AlR_2Cl, are considered as probable active sites for ethylene polymerization.[9]



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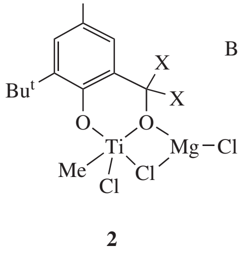

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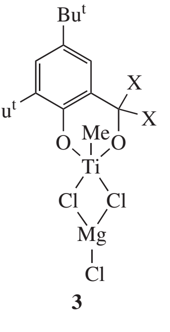

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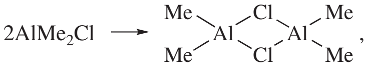
The Al-containing activators can also form binuclear heterocomplexes with Group IV transition metal compounds (for instance, structures **6** and **7** in Scheme 1). The main question of this work concerns the formation of Ti and Al heterocomplexes in the test catalytic systems and their competition with Mg-containing compounds as catalytic particles in ethylene polymerization reactions. The aim of this work was to explain the experimental inactivity of the system without Mg-containing compounds. Here, we present the results of the DFT modeling of the reactions of AlR_2Cl (R = Me) with complexes **1** and the reactions of the products with ethylene.

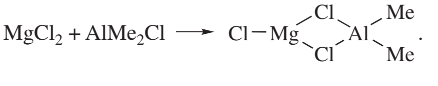
Calculations were carried out using the PBE functional[10] and the PRIRODA program.[11] Gaussian-type basis sets were used to solve the Kohn–Sham equations and to expand electron density in an auxiliary basis set. The orbital basis sets used have the following contraction schemes: (5*s*1*p*)/[3*s*1*p*] for H, (11*s*6*p*2*d*)/[6*s*3*p*2*d*] for C, O and F, (14*s*10*p*)/[9*s*5*p*] for Mg, (15*s*11*p*2*d*)/[10*s*6*p*2*d*] for Al and Cl, (17*s*13*p*8*d*)/[12*s*9*p*4*d*] for Ti. The auxiliary basis sets represent the following uncontracted sets of Gaussian functions: (5*s*2*p*) for H, (10*s*3*p*3*d*1*f*) for C, O and F, (14*s*3*p*2*d*) for Mg, (14*s*3*p*3*d*1*f*1*g*) for Al and Cl, (18*s*6*p*6*d*5*f*5*g*) for Ti. Complete geometry optimization was performed for all stable and transition states without imposing symmetry or other restrictions. The vibrational spectra of transition states revealed only one imaginary mode corresponding to the reaction coordinate. No imaginary modes were found in the vibrational spectra of stable states. Free energies *G* were calculated at *T* = 298.15 K using ideal gas, rigid rotator and harmonic oscillator approximations; the results of such calculations should be considered as rough estimates.

The calculated energy effects of activator dimerization reaction (2) are $\Delta E^{dim} = -26.8$ and $\Delta G^{dim} = -11.3$ kcal mol^{-1}.



$$2AlMe_2Cl \longrightarrow Me_2Al(\mu\text{-}Cl)_2AlMe_2, \qquad (2)$$

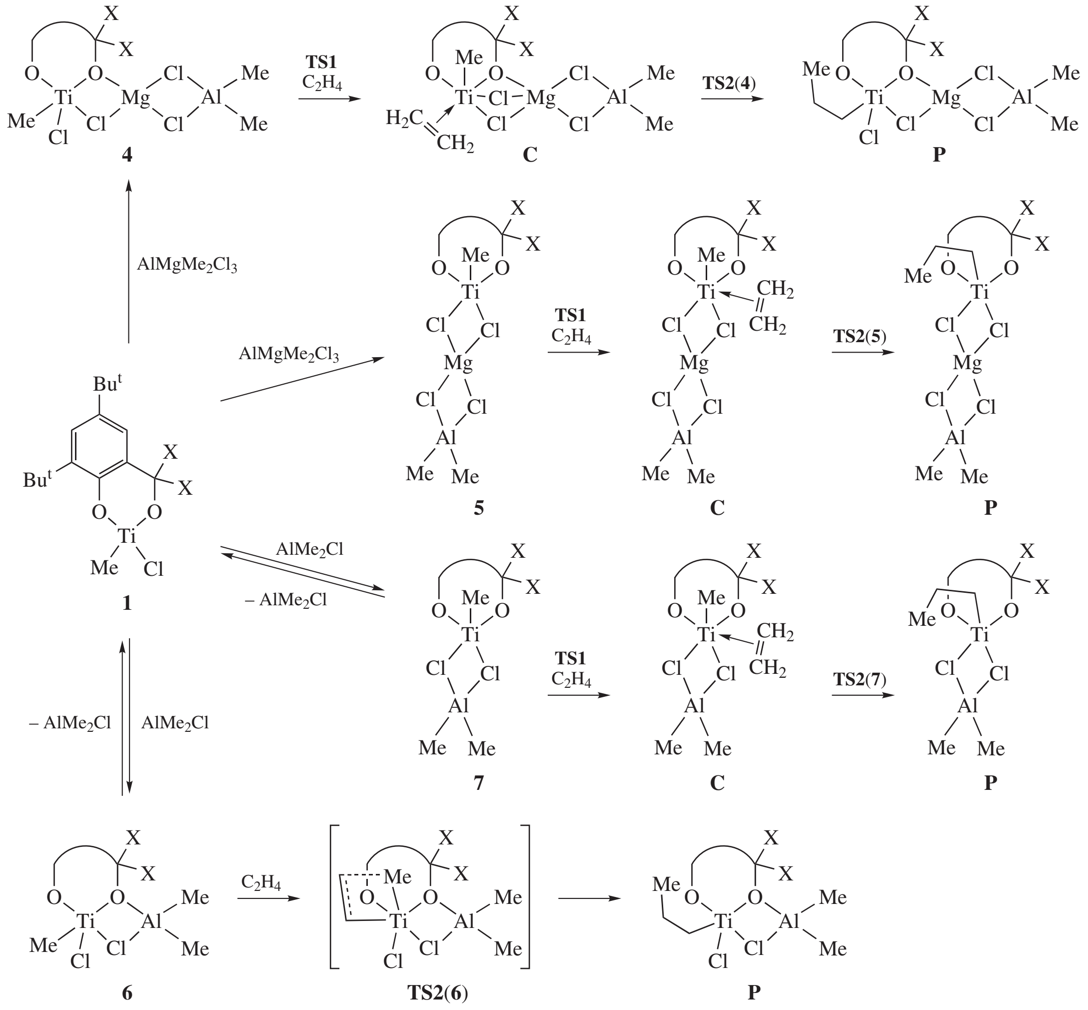
$Al_2Me_4Cl_2$



$$MgCl_2 + AlMe_2Cl \longrightarrow Cl{-}Mg(\mu\text{-}Cl)_2AlMe_2. \qquad (3)$$

$AlMgMe_2Cl_3$

Binuclear heterocomplex $AlMgMe_2Cl_3$ formation in reaction (3) is an even more exergonic process with energy effects of –32.9 (ΔE) and –20.8 (ΔG) kcal mol^{-1}. Therefore, reactions (2) and (3) were taken into consideration in this study.



Scheme 1 Formation of model compounds **4**–**7** and their reactions with ethylene.

According to our data, complex **1** can form a number of products with $MgCl_2$ and $AlMe_2Cl$ (or $AlMgMe_2Cl_3$). Products **4** and **5** have the lowest energy. The addition of $AlMe_2Cl$ (or $^1/_2Al_2Me_4Cl_2$) to **1** leads to the formation of the most stable products **6** and **7**, whose structures are similar to those of compounds **4** and **5**, respectively. There is the Ti–O–M bridge bond (M = Mg or Al) in **4** or **6**, while there is no such bond in **5** or **7**.

Table 1 summarizes the calculated total ΔE^f and free ΔG^f energies of **4**–**7** formation from **1** and non-transition metal chlorides. We assume that the energies ΔE^f and ΔG^f are related

Table 1 Total and free energies (kcal mol^{-1}) of the formation of compounds **4**–**7** (ΔE^f and ΔG^f, respectively) and of transition states **TS2** of their reactions with ethylene.

Compound	Parameter	$AlMgMe_2Cl_3$		$Al_2Me_4Cl_2$ ($AlMe_2Cl$)[a]		$AlMgMe_2Cl_3$		$Al_2Me_4Cl_2$ ($AlMe_2Cl$)[a]	
		4 (*E*)[b]	**5** (*E*)[b]	**6** (*E*)	**7** (*E*)	**4** (*G*)	**5** (*G*)	**6** (*G*)	**7** (*G*)
a (X = H)	$\Delta E^f/\Delta G^f$	–26.0[a]	–22.2	–10.3 (–23.7)	–3.4 (–16.8)	–13.0	–9.3	–2.8 (–8.5)	2.5 (–3.2)
	$\delta\Delta E^f/\delta\Delta G^f$	0[c]	3.8	0	6.9	0	3.7	0	5.3
	ΔE(**TS2**)/ΔG(**TS2**)	**11.0**[d]	17.6	**15.5**	22.1	**27.6**	31.7	**30.0**	35.7
b (X = Me)	$\Delta E^f/\Delta G^f$	–24.3	–22.6	–7.2 (–20.6)	–3.7 (–17.1)	–10.3	–9.7	2.2 (–3.5)	2.2 (–3.5)
	$\delta\Delta E^f/\delta\Delta G^f$	0	1.7	0	3.5	0	0.6	0	0
	ΔE(**TS2**)/ΔG(**TS2**)	**12.9**	16.3	**16.8**	19.9	**28.8**	29.8	31.7	**31.4**
c (X = CF_3)	$\Delta E^f/\Delta G^f$	–25.0	–23.2	–0.8 (–14.2)	–4.5 (–17.9)	–9.2	–9.5	8.1 (2.4)	2.0 (–3.7)
	$\delta\Delta E^f/\delta\Delta G^f$	0	1.8	3.7	0	0	–0.3	6.1	0
	ΔE(**TS2**)/ΔG(**TS2**)	**12.1**	15.7	19.8	**15.7**	**27.0**	28.6	38.6	**29.7**
d (X = Ph)	$\Delta E^f/\Delta G^f$	–26.0	–22.2	–7.1 (–20.5)	–3.2 (–16.6)	–10.4	–9.9	2.2 (–3.4)	2.0 (–3.6)
	$\delta\Delta E^f/\delta\Delta G^f$	0	3.8	0	3.9	0	0.5	0	–0.2
	ΔE(**TS2**)/ΔG(**TS2**)	**11.6**	17.2	20.7	**19.3**	**26.5**	29.3	36.0	**30.7**

[a] ΔE^f and ΔG^f values are calculated with respect to the sum of energies of **1** and $AlMgMe_2Cl_3$ or **1** and $Al_2Me_4Cl_2$. Values in parentheses are calculated with respect to the sum of energies of **1** and $AlMe_2Cl$. [b] Data presented in the columns have been published previously.[9] [c] $\delta\Delta E^f$ and $\delta\Delta G^f$ are the relative energies of two isomers calculated with respect to the most stable of them, *i.e.*, the isomer for which $\delta\Delta E^f = 0$. [d] ΔE(**TS2**) and ΔG(**TS2**) values are calculated with respect to the sum of energies of ethylene and an isomer for which $\delta\Delta E^f = 0$. The minimal ΔE(**TS2**) and ΔG(**TS2**) values for Mg-containing and Mg-free systems are boldfaced.

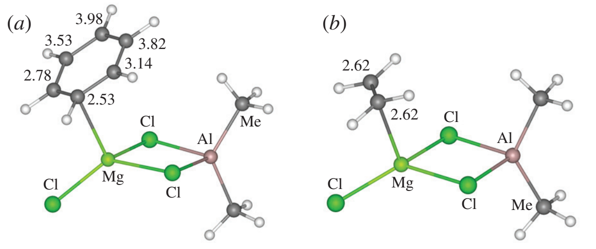


Figure 1 Optimized structures of binuclear heterocomplex $AlMgMe_2Cl_3$ adducts with (*a*) benzene and (*b*) ethylene. Distances Mg–C are given in Å.

to a number of particles of each type generated in the system: the more stable is the particle (*i.e.*, the more negative are its ΔE^f and ΔG^f values), the more probable is its formation. In Table 1, the data in parentheses are calculated ignoring activator dimerization reaction (2). The energy effects of **6** and **7** formation in the reactions of $AlMe_2Cl$ (or $^1/_2Al_2Me_4Cl_2$) with complex **1** are always smaller than the energies of **4** and **5** formation from **1** and $AlMgMe_2Cl_3$. Our estimates for ΔG^f (Table 1) show that the formation of compounds **4** and **5** always decreases the free energy of the system ($\Delta G^f < 0$). However, the formation of complexes **6** and **7**, calculated with respect to activator dimer, in most cases (with only one exception **6a**) increases the free energy of the system ($\Delta G^f > 0$). Thus, since the equilibrium between the reagents (**1** and $Al_2Me_4Cl_2$) and **6** (or **7**) is shifted toward the reagents, complexes **6** and **7** are probably not produced in noticeable amounts.

The coordination number of the magnesium atom in compounds **4** and **5** is four, while it is only three in the reagent $AlMgMe_2Cl_3$. This allows us to suggest that the Mg atom of $AlMgMe_2Cl_3$ is capable of coordinating a solvent or monomer molecule S to fill the coordination vacancy. Optimized structures of such adducts are shown in Figure 1. Calculated energies of S binding to $AlMgMe_2Cl_3$ are $\Delta E^S = -9.5$ and $\Delta G^S = 1.0$ kcal mol^{-1} for S = C_6H_6, and $\Delta E^S = -10.5$ and $\Delta G^S = 0.5$ kcal mol^{-1} for S = C_2H_4. The free energies ΔG^f of **4** and **5** formation from **1** and $AlMgMe_2Cl_3$ or its adducts with S are the same to within 1 kcal mol^{-1}. Thus, taking into consideration the three-coordinated Mg atom interaction with a solvent or monomer molecule, we obtained a similar result as that when we ignored this interaction.

The relative energies $\delta\Delta E^f$ and $\delta\Delta G^f$ presented in Table 1 are differences between the energies of two isomers calculated with respect to the most stable of them. Isomers **4** have lower energies *E* than **5** for all the substituents X. Compounds **6** also have lower energies *E* than **7**. The only exception is **6c**, whose energy is higher than that of **7c**. This can be explained by the repulsion between the methyl groups of the $AlMe_2$ fragment and the F atoms of the CF_3 groups. In the case of Mg-containing compound **4c**, the intramolecular interaction C–F–Mg[9] compensates this repulsion, whereas in **6c** there is no intramolecular contacts C–F–Al to compensate it.

Free energies *G* of isomers **4b**,**c** and **5b**,**c** are close, although for total energies *E* it has been found that they are always substantially lower for complexes of type **4**. This is due to a greater entropy of complexes **5b**,**c**, as compared to that of **4b**,**c**. The less sterically hindered complex **4a** (X = H) is the exception because it has significantly lower free energy than **5a**. Thus, the structure of the substituent X influences the total and free energy differences of isomers **4** and **5**. The same regularities are revealed for compounds **6** and **7**: (1) **6a** has lower total and free energies than **7a**; (2) the total energies of **6b**,**d** are lower than the energies of **7b**,**d**, but their free energies are close; (3) **6c** has higher total and free energies than **7c**.

To compare the relative stability of Mg-containing and Mg-free systems, we calculated the energy characteristics of the interaction of complexes **6** and **7** with $MgCl_2$ to form compounds **4** and **5**. For instance, the energy effects of transformation (4), calculated from the total energies of **4**, **6** and $MgCl_2$, are –35.2, –36.6, –43.7, and –38.4 kcal mol^{-1} for **a**, **b**, **c** and **d**, respectively. The free energy effects of reaction (4) are –25.3, –27.6, –32.5 and –27.9 kcal mol^{-1} for **a**, **b**, **c** and **d**, respectively. Therefore, transformation (4) is favorable from the thermodynamic point of view.

$$\mathbf{6} + \mathrm{MgCl_2} \longrightarrow \mathbf{4}. \tag{4}$$

The reason why $MgCl_2$ should be formed *in situ* to promote ethylene polymerization may be that only single $MgCl_2$ molecules can bind to Ti complex **1**. Otherwise, energy expenses for the molecule extraction from the crystalline solid, which is insoluble in nonpolar media, exceed the energy effects of the formation of active particles (in particular, of type **4** or **5**).

According to our previous study,[8] the interaction of active center **2** (formed in the **1** + $MgCl_2$ system) with ethylene consists of two steps: (1) ethylene molecule binding to active center **2** forms complex **C**, and (2) the C–C bond formation in **C** leads to primary product **P**. The energy barrier **TS2** of the second step is the highest energy point on the reaction pathway. Therefore, we suggest that the energies ΔE(**TS2**) and ΔG(**TS2**), which are differences between the energies of **TS2** and non-interacting reagents (active particle + ethylene molecule), can serve as a measure of the active centers **4**–**7** reactivity with respect to ethylene.[8,9]

Geometry parameters were optimized and energies were calculated for the transition state of the C–C bond formation (**TS2**) in the reactions of complexes **4**–**7** with ethylene. The interesting feature of the structure of **TS2**(**4**), formed by isomers **4**, is the three bridge bonds (–O–, –Cl–, –Cl–) connecting Ti and Mg atoms [Figure 2(*a*)]. In complex **4**, one of two chlorine

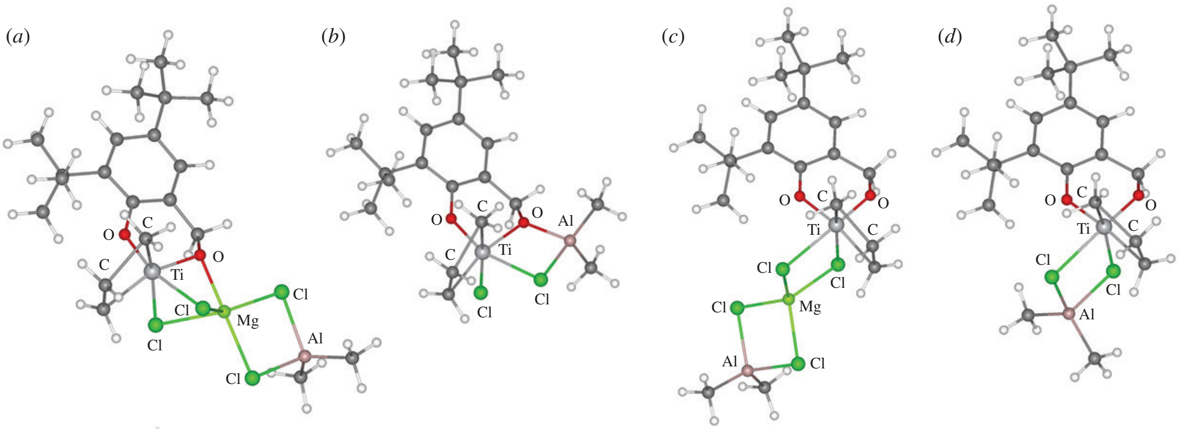


Figure 2 Optimized structures of the transition states (*a*) **TS2(4a)**, (*b*) **TS2(6a)**, (*c*) **TS2(5a)** and (*d*) **TS2(7a)**.

atoms is terminal, but when the ethylene molecule coordinates, it displaces to the Mg atom, providing space in the coordination sphere of the Ti atom for the ethylene molecule and forming the extra Ti–Cl–Mg bridge bond.

In all the cases (**a**–**d**), transition states **TS2**(**4**) have lower total energies than transition states **TS2**(**5**) formed by isomers **5** (Table 1). Free energies of **TS2**(**4**) and **TS2**(**5**) have the same regularity, but their values are much closer to each other than the total energies due to greater entropy losses in the former case, as compared to the latter case. Total and free energies of **TS2**(**4**) are close for four ligands L (**a**–**d**), the same conclusion can be inferred for **TS2**(**5**). Thus, quantum chemical calculations predict that, within the framework of the mechanism proposed for ethylene polymerization, the catalytic activity should not be sensitive to the structure of the substituent X. This conclusion is in a good agreement with recently published experimental results.[3]

On the contrary, the substituent X strongly affects the relative energies of **TS2**(**6**) and **TS2**(**7**). In the cases **c** and **d**, the energies of **TS2**(**6**) are even higher than that for **TS2**(**7**).

Mg-free binuclear compound **6** has the structure similar to **4**, but it does not form an extra bridge bond Ti–Cl–Al in the course of its reaction with ethylene. In **TS2**(**6**), one chlorine atom remains terminal and the ligand surrounding of the Ti atom has a distorted octahedral configuration [Figure 2(*b*)]. Substantial changes in the system geometry result in higher total and free energies of the transition states **TS2**(**6**), as compared to **TS2**(**4**).

We did not find visible distinctions in the structures of Mg-free compounds **7** and corresponding transition states **TS2**(**7**) [Figure 2(*d*)], as compared with Mg-containing system **5** and **TS2**(**5**) [Figure 2(*c*)], respectively. Nevertheless, the total and free energies of **TS2**(**7**) are always higher than the energies of **TS2**(**5**).

In Table 1, the minimal values of ΔE(**TS2**) and ΔG(**TS2**) for Mg-containing (**4** and **5**) and Mg-free (**6** and **7**) systems are boldfaced. A comparison of the minimal energies of **TS2** for each system shows that the activation barrier of the C–C bond formation decreases in Mg-containing systems with respect to Mg-free systems by 3.6–7.7 [ΔE(**TS2**)] and 2.4–4.4 [ΔG(**TS2**)] kcal mol^{-1}.

For all transition states **TS2**, the nearest energy minima on a potential energy surface of the system, which correspond to intermediate **C** and primary product **P** (Scheme 1), were determined. Geometry parameters of **C** and **P** were optimized and their energy characteristics were calculated. Intrinsic reaction coordinate was located to ensure that transition state **TS2** connects the energy minima corresponding to **C** and **P**. For compounds **6**, no intermediates were found on the reaction path, and transition states **TS2**(**6**) are the only energy barriers, which lie between reagents **6** + C_2H_4 and products **P**.

Thus, from the energy characteristics of the transition states **TS2** (Table 1), one can conclude that model particles **4** and **5** formed with one $MgCl_2$ molecule should always have higher reactivity toward ethylene than compounds **6** and **7** formed without the participation of $MgCl_2$. As we noted above, compounds **4** and **5** are also more thermodynamically stable than **6** and **7**. Therefore, the catalytic activity of the Mg-free system $LTiCl_2$–AlR_2Cl should be essentially lower than that for the Mg-containing systems $LTiCl_2$–R'_2Mg–AlR_2Cl. This conclusion is in a good agreement with the experimental data.[2,3]

According to our data, the reason for $MgCl_2$ influence on the catalytic activity of the test systems in ethylene polymerization is the formation of the secondary complexes of Ti, Mg and Al, which are catalytic particles. The formation of the extra bridge bond Ti–Cl–Mg decreases the maximal energy barrier on the pathway of the reaction of these particles with ethylene.

However, another reason can be proposed for the effect of Mg compounds on the catalytic activity of the above Ti complexes. Recently,[8] we proposed and confirmed by quantum chemical calculations that Mg compounds participate in the pre-catalyst $LTiCl_2$ alkylation reaction. We found that this process was thermodynamically unfavorable without Mg-containing compounds.

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