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DFT modeling of the effect of magnesium dichloride on the catalytic activity of post-titanocene complexes in ethylene polymerization

Leila Yu. Ustynyuk* and Boris M. Bulychev

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
Fax: +7 495 932 8846; e-mail: leila_ust@mail.ru

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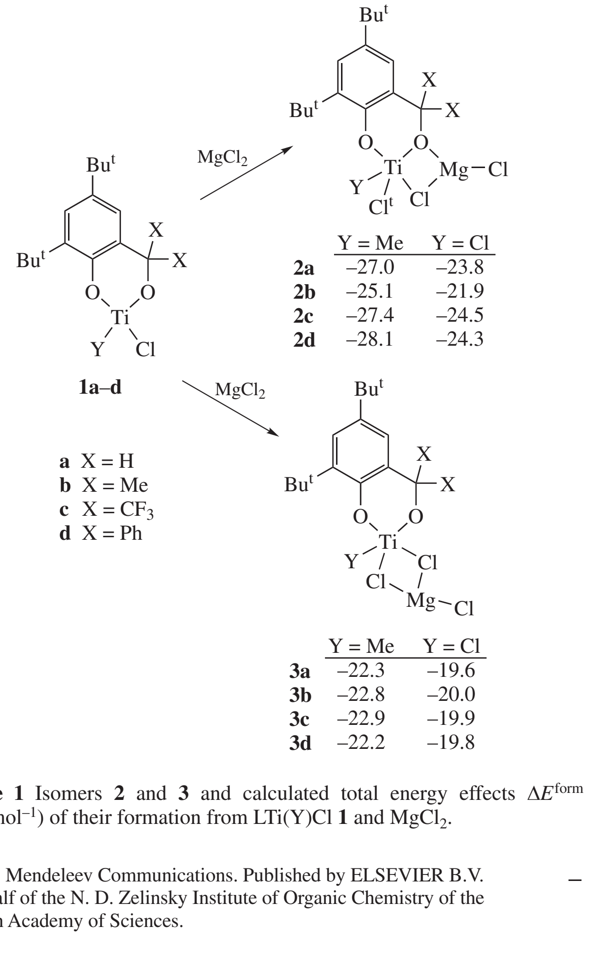
The DFT study of magnesium dichloride effect on the catalytic activity of titanium complexes LTi(Y)Cl (where L is a saligenin-type ligand, and Y is Cl or Me) in olefin polymerization has demonstrated that heterobinuclear titanium–magnesium complex with –O– and –Cl– bridging bonds is the most stable product of the reaction between $MgCl_2$ and LTi(Y)Cl and the most probable catalytic particle for ethylene polymerization.

Magnesium compounds are known to promote olefin polymerization.[1] For instance, the titanium complex $LTiCl_2$ **1** with one saligenin-type ligand (X = CF_3, Y = Cl) (Figure 1) was synthesized.[2] This complex was inactive in ethylene polymerization with methylaluminoxane (MAO) or aluminum alkyls as activators. However, in the presence of the binary co-catalyst $MgBu_2/3AlEt_2Cl$ in toluene, this complex demonstrated high catalytic activity in the synthesis of high-molecular-weight linear polyethylene. According to published data,[3] $MgCl_2$ appears in the system due to reaction (1), and it rapidly or slowly precipitates as finely dispersed solid in aliphatic or aromatic solvents, respectively.

$$\mathrm{MgBu_2 + 2AlEt_2Cl \rightarrow MgCl_2 + 2AlEt_2Bu.} \qquad (1)$$

Our DFT calculations showed that reaction (1) is an exergonic process with a total energy effect of about –11.1 kcal mol^{-1}.



1a–d

a X = H
b X = Me
c X = CF_3
d X = Ph

	Y = Me	Y = Cl
2a	–27.0	–23.8
2b	–25.1	–21.9
2c	–27.4	–24.5
2d	–28.1	–24.3

	Y = Me	Y = Cl
3a	–22.3	–19.6
3b	–22.8	–20.0
3c	–22.9	–19.9
3d	–22.2	–19.8

Figure 1 Isomers **2** and **3** and calculated total energy effects ΔE^{form} (kcal mol^{-1}) of their formation from LTi(Y)Cl **1** and $MgCl_2$.

Previously[2] it was proposed that secondary complexation reactions between $MgCl_2$ and complex **1** yield the products $LTiCl_2{\cdot}nMgCl_2$ (n = 1, 2) with enhanced electrophilic reactivity of the titanium center, as compared to that of **1**.

Trialkylaluminum is the second product of reaction (1). It can participate in alkyl exchange reactions with $LTiCl_2$ to form monoalkyl- [LTi(R)Cl, R = Et, Bu] and dialkyltitanium ($LTiR_2$) derivatives. Here, using the density functional theory (DFT) method, we studied the secondary complexation and alkyl exchange reactions of $MgCl_2$ and AlR_3 (for R = Me) with LTi(Y)Cl **1** with the following substituents in the ligand L: X = H, Me, CF_3 and Ph[†] and Y = Cl, Me (Figure 1). Calculations were carried out using the functional PBE[4] and the PRIRODA program.[5] The TZ2p 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 have the following contraction schemes: $(5s\,1p)/[3s\,1p]$ for H, $(11s\,6p\,2d)/[6s\,3p\,2d]$ for C, O and F, $(14s\,10p)/[9s\,5p]$ for Mg, $(15s\,11p\,2d)/[10s\,6p\,2d]$ for Cl, and $(17s\,13p\,8d)/[12s\,9p\,4d]$ for Ti. The auxiliary basis sets represent the following uncontracted sets of Gaussian functions: $(5s\,2p)$ for H, $(10s\,3p\,3d\,1f)$ for C, O, and F, $(14s\,3p\,2d)$ for Mg, $(14s\,3p\,3d\,1f\,1g)$ for Cl, $(18s\,6p\,6d\,5f\,5g)$ for Ti. The complete geometry optimization was performed for all stable and transition states beside **TS1** without imposing symmetry or other restrictions. Vibrational frequencies and thermodynamic characteristics were calculated using the ideal gas, rigid rotator and harmonic oscillator approximations. The energies of transition states **TS1** were estimated by scanning the energy profile of the systems with a step of 0.05 Å along two fixed distances, Ti–C^1/Ti–C^2, from the Ti atom to the C^1 and C^2 atoms of the ethylene molecule, which were taken equal to each other. Other geometrical parameters varied arbitrarily during the geometry optimization procedure. The vibrational spectra of transition states **TS1** and **TS2** revealed only one imaginary mode corresponding to the reaction coordinate. No imaginary modes were found in the vibrational spectra of stable states. Solvent effects were not considered.

We considered two potential ways of $MgCl_2$ complexation with LTi(Y)Cl **1a–d** (Figure 1). First, we optimized the structures with one or two short contacts of the magnesium atom with ligand oxygen atoms, Mg–O(Ti). Second, we searched for the structures only with Mg–Cl–Ti bridging bonds. We obtained from

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[†] Compound **1c** (X = CF_3) was obtained previously.[2] The structures of modified compounds **1a**,**b**,**d** were suggested by S. Ch. Gagieva and V. A. Tuskaev, whose experimental data will be published elsewhere.

Table 1 Total energy effects ΔE^{meth} (kcal mol^{-1}) for the first and second chlorine–methyl exchange in the reactions of **1** and **2** (Y = Cl) with $AlMe_2Cl$, $AlMe_3$ and $MgMe_2$.

X		1st Cl Y = Cl $AlMe_2Cl$ ($Al_2Me_4Cl_2$)	1st Cl Y = Cl $AlMe_3$ (Al_2Me_6)	2nd Cl Y = Me $AlMe_2Cl$ ($Al_2Me_4Cl_2$)	2nd Cl Y = Me $AlMe_3$ (Al_2Me_6)	1st Cl Y = Cl $MgMe_2$	2nd Cl Y = Me $MgMe_2$
H	**1**	8.2 (7.9)	3.7 (4.6)	12.5 (12.1)	7.9 (8.8)	–4.5	–0.3
	2	5.1 (4.8)	0.6 (1.5)	9.2 (8.9)	4.6 (5.6)	–7.7	–3.6
Me	**1**	8.7 (8.4)	4.2 (5.1)	12.8 (12.5)	8.2 (9.1)	–4.1	0
	2	5.6 (5.3)	1.0 (2.0)	9.4 (9.2)	4.9 (5.8)	–7.2	–3.3
CF_3	**1**	6.8 (6.5)	2.3 (3.2)	11.0 (10.7)	6.5 (7.4)	–5.9	–1.8
	2	3.9 (3.6)	–0.6 (0.3)	8.4 (8.1)	3.9 (4.8)	–8.9	–4.4
Ph	**1**	8.7 (8.4)	4.2 (5.1)	12.3 (12.0)	7.8 (8.7)	–4.1	–0.5
	2	4.9 (4.6)	0.4 (1.3)	10.1 (9.8)	5.6 (6.5)	–7.8	–2.7

one to four structures of each type depending on the fragment Y. Among them, isomers **2** and **3** have the lowest energies. They are the most probable products of the secondary complexation reactions.

We assume that alkylation is the second step of the formation of an active site for ethylene polymerization in the test system. Table 1 presents the total energy effects (ΔE^{meth}) of alkylation reactions (2) and (3) for complex **1** with $AlMe_2Z$ (Z = Me, Cl),

$$LTiCl_2 + AlMe_2Z \rightarrow LTi(Cl)Me + Al(Me)(Cl)Z, \qquad (2)$$

$$LTi(Cl)Me + AlMe_2Z \rightarrow LTiMe_2 + Al(Me)(Cl)Z \qquad (3)$$

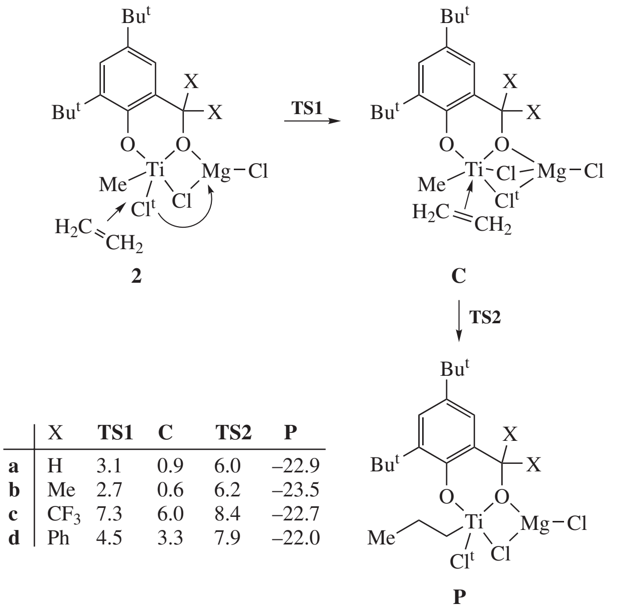
and similar reactions of complex **2** with $AlMe_2Z$. Almost all of these alkylation reactions are endothermic. The only exception is the reaction of the first chlorine atom exchange with $AlMe_3$ in **2**. In this case, ΔE^{meth} energies are close to zero for all of the ligands.

The following conclusions can be made from the data presented in Table 1. First, trialkylaluminum is the most probable alkylation agent for a chlorine atom exchange reaction. Second, the formation of heterobinuclear compound **2** facilitates the alkylation reaction. Third, only one of two chlorine atoms is replaced with an alkyl group. The third conclusion is consistent with data on the selective alkylation reactions of dichloride titanium or zirconium complexes with trialkylaluminum.[6,7] The enthalpies ΔH_{298} for the above methylation reactions at 298 K were estimated. The total energy effects ΔE^{meth} were analogously calculated for methylation reactions with dimers $Al_2Me_4Cl_2$ and Al_2Me_6 (Table 1). The results of DFT calculations are in a good agreement with experimental data on the activity of the catalyst prepared *in situ* by the treatment of $TiCl_4$ with magnesium salt of the ligand (*i.e.*, without the removal of by-product $MgCl_2$ from the catalyst).[2] The highest activity in ethylene polymerization was found[2] for the activator Al_2Me_6, whereas no activity was observed for $Al_2Me_4Cl_2$ as an activator.

Thus, we conclude that AlR_3 (or its dimer) serves as an alkylation agent. In the case of AlR_2Cl (or its dimer), alkylation is a thermodynamically unfavorable process, and the catalytically active particles do not appear in noticeable amounts.

In accordance with the generally accepted Cossee mechanism,[8] the interaction of a catalytic particle with an olefin molecule involves the following two main stages: (i) the olefin molecule binding to the catalytic site yields a π-complex; (ii) the insertion of the coordinated olefin molecule into the M–C bond results in the formation of a C–C bond and the growth of a polymer chain.

We studied the dependence of the geometrical parameters and energy of the **2** + C_2H_4 system on the distances Ti–C^1/Ti–C^2 (C^1 and C^2 are ethylene carbon atoms) and found that, when the ethylene molecule approaches the Ti atom of complex **2**, the terminal atom Cl^t is displaced to the Mg atom and forms one additional bridging bond Ti–Cl^t–Mg (Figure 2). After the insertion of the ethylene molecule into the Ti–C bond, the 'temporary' bridging bond Ti–Cl^t–Mg breaks and the Cl^t atom becomes terminal again. Figure 3 shows the structures of complex **2** for X = CF_3 and corresponding transitional state **TS2**. The ethylene molecule in **TS2** takes the place of the Cl^t ligand in complex **2**. The short intramolecular contact Mg–F, which is characteristic of complex **2** (X = CF_3), breaks in **TS2** when the Cl^t ligand approaches the Mg atom.



	X	**TS1**	**C**	**TS2**	**P**
a	H	3.1	0.9	6.0	–22.9
b	Me	2.7	0.6	6.2	–23.5
c	CF_3	7.3	6.0	8.4	–22.7
d	Ph	4.5	3.3	7.9	–22.0

Figure 2 Reaction of isomer **2** with the ethylene molecule and total energies (kcal mol^{-1}) of stable and transition states on the reaction pathway calculated with respect to the sum of reagent energies.

We also calculated the energies of intermediates, transition states and products formed in the reaction between complexes **2a–d** and C_2H_4. Transition state **TS2** of the step of C–C bond formation corresponds to the global energy maximum on the reaction pathway (Figure 2). Therefore, the difference between the energies of **TS2** and non-interacting reagents (**2** + C_2H_4), ΔE(**TS2**), can be considered as a measure of the reactivity of complex **2** with respect to ethylene. Transition states **TS1** of ethylene coordination have lower energies than that of **TS2** in all the cases. The values of ΔE(**TS2**) increase in the order **2a** ≈ **2b** < **2d** ⩽ **2c**. In this order, steric hindrances produced by the substituent X increase to result in **TS2** destabilization by bulky CF_3 and Ph groups. The reactivity of complexes **2** with respect to ethylene should decrease in the same order.

The formation of intermediate complex **C** with two Ti–Cl–Mg bridging bonds is the energetically unfavorable step of the reaction. For **2a** and **2b**, the energy effects ΔE(**C**) for the ethylene

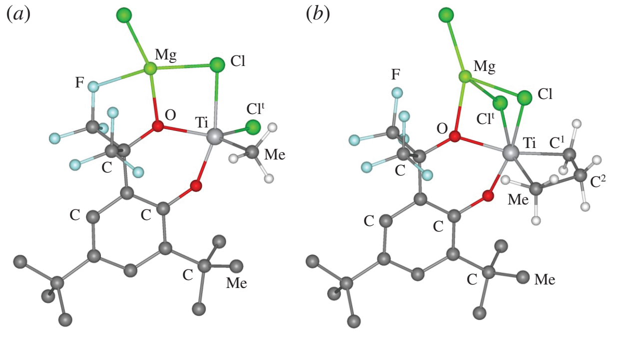


Figure 3 Optimized structures of (*a*) complex **2** for X = CF_3, Y = Me and (*b*) corresponding transitional state **TS2**. Hydrogen atoms of the ligand are not shown.

coordination step are close to zero. For **2d** and, to a greater extent, **2c**, these effects are virtually positive.

Less stable isomer **3** can also react with ethylene. Modeling of this interaction (data not shown) revealed that new Mg–Cl or Mg–O bonds did not appear, and the energy barrier of C–C bond formation was substantially higher than the energy of **TS2**. Thus, the reactivity of **3** with respect to ethylene is lower than the reactivity of **2**.

Here we suggest the mechanism of the activation effect of $MgCl_2$ in ethylene polymerization on post-metallocene complexes $LTiCl_2$ with one ligand of saligenin type. The key point of this mechanism is the formation of the heterobimetallic cycle **2** and its transformation into intermediate **C** with two chlorine bridges in the course of the reaction with ethylene. The Cl^t ligand displacement to the Mg atom provides a space in the coordination sphere of the Ti atom required for ethylene molecule coordination.

Dialkylmagnesium compounds are efficient alkylation reagents, which readily form dialkyl derivatives reacting with Ti and Zr dichloride complexes. The results of DFT calculations (Table 1) show that both steps of $LTiCl_2$ **1** methylation with $MgMe_2$ are exothermic. Therefore, an excess of dialkylmagnesium should lead to the formation of a dialkyltitanium complex. At the same time, according to our DFT calculations (data not shown), the complexes $LTiMe_2$ with the same set of ligands and heterobinuclear compounds formed in the $\{LTiMe_2 + MgCl_2\}$ system are less active in ethylene polymerization than their alkyl chloride analogues formed in the $\{LTi(Me)Cl + MgCl_2\}$ system. Thus, the terminal chlorine atom is important for catalytic activity.

The inactivity of the post-metallocene catalysts without magnesium compounds can be explained by the endothermic character of pre-catalyst alkylation reaction which prevents the formation of active particles. Reaction (1) yields magnesium dichloride and trialkylaluminum as products.[3] As follows from our results, the first product ($MgCl_2$) binds to pre-catalyst $LTiCl_2$ to form heterobinuclear complex **2** (Y = Cl). The second product ($AlEt_2Bu$) is a selective alkylation agent for one chloride ligand exchange in this secondary complex, which is necessary for the generation of the active particle in olefin polymerization reaction of the type **2** (Y = Et or Bu).

The role of magnesium dichloride in Ziegler catalysis is still a matter of discussions.[9] The above results of quantum-chemical modeling led us to the assumption that the high activities of industrial heterogeneous titanium–magnesium catalysts can be associated with the formation of heterobinuclear Ti compounds with individual $MgCl_2$ molecules, which escape a crystalline solid under treatment with internal and external donors.

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