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Ti–C bond formation reactions in post-titanocene catalytic systems for alkene polymerization: a DFT study

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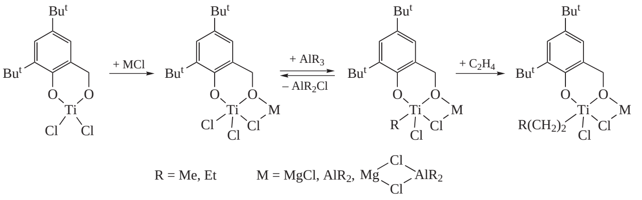
The quantum-chemical modeling of post-titanocene catalytic systems for alkene polymerization suggests that the activation effect of Mg-containing compounds in alkene polymerization can be caused by a greater exothermicity of Cl ligand exchange in bi- and trinuclear heterocomplexes of Ti, Mg and Al for the alkyl group of AlR_3 with respect to a Ti complex and their higher stability and reactivity toward alkenes, as compared to Ti and Al compounds formed in the Mg-free system.

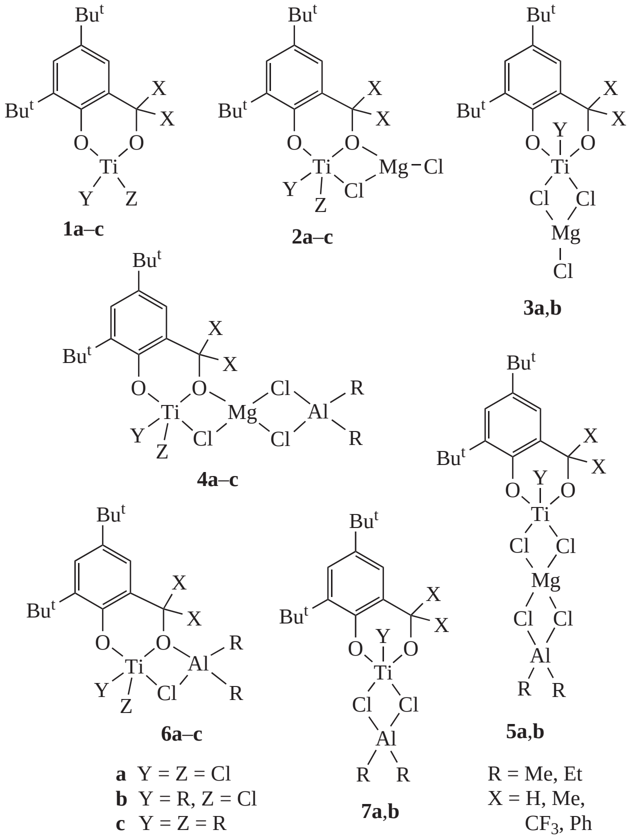


Numerous activation effects caused by non-transition metal compounds in catalytic systems for alkene polymerization based on transition metal complexes are well known. In particular, complexes of the composition $LTiCl_2$ (**1a**, Figure 1), where L is a saligenin type ligand[1,2] or other ligand,[3] were synthesized and studied as catalysts for ethylene, propylene and hexene polymerization. These complexes showed a relatively high catalytic activity when a Mg-containing compound was added into the system as a component of the binary activator $MgBu_2/AlEt_2Cl$ or introduced at the stage of pre-catalyst synthesis. High molecular weight polymer formation[1–3] was consistent with the Ti^{IV} nature of the active centers for alkene polymerization. These centers were modeled using a DFT method.[4–6] It has been shown that Mg-containing compounds (as well as Li or other non-transition metal containing compounds) activate pre-catalyst **1** by the formation of bi- and trinuclear heterocomplexes of Ti, Mg and Al (structures **2**–**5** in Figure 1). The bridge bonds Ti–O–Mg and Ti–Cl–Mg connect the Ti and Mg atoms in **2** and **4**. There are only the Ti–Cl–Mg bridge bonds in **3** and **5**. Complexes of types **2** and **4** are more thermodynamically stable and more reactive species with respect to ethylene than **3** and **5**. In suggested models of catalytic particles **2b**–**5b**,[4–6] the alkyl group R substitutes the growing polymer chain. The Mg-free model centers **6b** and **7b** are less reactive with respect to ethylene than Mg-containing compounds with a similar structure, *i.e.* **2b**, **4b** for **6b** or **3b**, **5b** for **7b**.

According to previously published data,[4] the formation of the Ti–C bond in pre-catalyst **1a** is thermodynamically unfavorable. Non-transition metal compounds could promote this reaction by the transformation of **1a** into **2a**. We suggest that the formation of bi- and trinuclear heterocomplexes **3a**–**7a** can also affect the thermodynamic characteristics of the Ti–C bond formation reactions. Therefore, in order to elucidate the reason for the activation effect of Mg-containing compounds in alkene polymerization, we have calculated the energy characteristics of the stepwise exchanges of the first and the second Cl ligands in **1a**–**7a** for the alkyl groups of AlR_3 (R = Me, Et).

Calculations were carried out using the PRIRODA program,[7] the PBE functional,[8] and TZ2P Gaussian-type basis sets. The contraction schemes for orbital basis sets used in this work were described previously.[4–6] Complete geometry optimization was performed for all stable and transition states without imposing symmetry or other restrictions and followed by vibrational frequencies analysis. Free energies G_{298} were calculated at 298.15 K using ideal gas, rigid rotator and harmonic oscillator approximations.

Reaction (1) between the components of the binary co-catalyst, $MgBu_2$ and $AlEt_2Cl$, was studied experimentally.[9,10] The finely



a Y = Z = Cl
b Y = R, Z = Cl
c Y = Z = R

R = Me, Et
X = H, Me, CF_3, Ph

Figure 1 Pre-catalyst **1** and model centers **2**–**7**.

Table 1 Total (ΔE) and free (ΔG_{298}, in italics) energies (kcal mol^{-1}) of reactions (4)–(8) and transition states of C–C bond formation in reactions (9).

Compound	R = Me, $AlMe_3$				R = Et, $AlEt_3$		
	1st Cl exchange (4)	2nd Cl exchange (5)	***na*** formation (6)–(8)	TS^{CC}(***nb***) ***nb*** + C_2H_4 (9)	1st Cl exchange (4)	2nd Cl exchange (5)	***na*** formation (6)–(8)
1	3.7[a]	7.9[a]	–	–	0.8	6.7	–
	1.4	*5.2*	–	–	*–0.2*	*5.5*	–
2	0.6[a]	4.6[a]	–23.8	6.0[a]	–2.9	2.6	–23.8
	–1.1	*2.6*	*–11.8*	*21.6*	*–2.7*	*2.0*	*–11.8*
3	1.0	–	–19.6	16.7[a]	–2.3	–	–19.6
	–1.1	–	*–8.5*	*31.3*	*–2.7*	–	*–8.5*
4	0.5	4.8	–23.3	11.0[a]	–3.0	2.7	–23.4
	–0.9	*3.0*	*–10.5*	*27.6*[a]	*–2.7*	*1.6*	*–9.1*
5	1.0	–	–19.5	17.6[a]	–2.3	–	–19.5
	–0.8	–	*–7.0*	*31.7*[a]	*–2.8*	–	*–6.5*
6	0.4	4.6	–20.4	15.5[a]	–2.7	2.6	–20.7
	–0.8	*2.6*	*–6.3*	*30.0*[a]	*–2.4*	*1.8*	*–5.8*
7	1.1	–	–14.2	22.1[a]	–2.2	–	–14.6
	–0.8	–	*–1.0*	*35.7*[a]	*–1.8*	–	*–1.8*

[a] Data were obtained using the same calculation method as in this work and published in refs. 4–6. The energies of TS^{CC}(***nb***) were calculated with respect to the sum of energies of the most stable isomer of two (**2b**, or **4b**, or **6b**) and ethylene molecule.

dispersed $MgCl_2$ slowly precipitated from an aromatic solvent (toluene).

$$\mathrm{Bu_2Mg + 2AlEt_2Cl \rightarrow MgCl_2 + AlEt_2Bu.} \tag{1}$$

In this work, the Bu fragment of $AlEt_2Bu$ was replaced by the shorter Et fragment. Trimethylaluminum was used[1] to activate pre-catalyst **1a** with a Mg-containing compound implemented at the stage of pre-catalyst synthesis. Here, we consider complex **1a** with a saligenin type ligand without substituent X (X = H), which was previously studied experimentally.[2]

Table 1 summarizes the calculated thermodynamic characteristics of reactions (2) and (3) of the first and the second Cl atoms exchanges for alkyl groups R = Me, Et between **1a** and AlR_3.

$$\mathrm{LTiCl_2\ (\mathbf{1a}) + AlR_3 \rightarrow LTi(R)Cl\ (\mathbf{1b}) + AlR_2Cl,} \tag{2}$$

$$\mathrm{LTi(R)Cl\ (\mathbf{1b}) + AlR_3 \rightarrow LTiR_2\ (\mathbf{1c}) + AlR_2Cl.} \tag{3}$$

In the case of R = Me, reactions (2) and (3) are accompanied by an increase in the total energy (E) and free energy (G_{298}) of the system. In the case of R = Et, the exchange of the first Cl atom is almost free of energy charge, whereas the exchange of the second Cl atom is an endergonic process. In both cases (R = Me or Et), the exchange of the first Cl atom is more favorable thermodynamically than the exchange of the second Cl atom. The same energy characteristics were calculated for reactions (4) and (5), where ***n*** = **2**–**7** (Table 1).

$$\boldsymbol{n}\mathbf{a} + \mathrm{AlR_3} \rightarrow \boldsymbol{n}\mathbf{b} + \mathrm{AlR_2Cl,} \tag{4}$$

$$\boldsymbol{n}\mathbf{b} + \mathrm{AlR_3} \rightarrow \boldsymbol{n}\mathbf{c} + \mathrm{AlR_2Cl.} \tag{5}$$

In all the cases, the addition of a $MgCl_2$ or AlR_2Cl molecule or their complex $ClMg(\mu\text{-}Cl)_2AlR_2$ to **1a** results in the formation of compounds ***na***. This causes a decrease in ΔE and ΔG_{298} of reactions (4) and (5), thereby promoting the Cl ligand exchange reactions. The energy effects are close in the lines of compounds with the similar structure, *i.e.* **2**, **4** and **6**, in which the oxygen bridge bond connects the Ti and Mg/Al atoms, and **3**, **5** and **7** without such a bond. The differences in ΔE and ΔG_{298} values for the compounds denoted by even and odd numbers are also insignificant. On the contrary, there are significant differences in the values of energies in the columns R = Me and R = Et in Table 1. In the latter case, reactions (4) and (5) proceed with more energy gain; therefore, these reactions are more favorable thermodynamically. This can be explained by higher electron charge delocalization in the Et fragment, as compared to Me. The reactions of the second Cl atom exchange always result in an increase in E and G_{298} energies of the system. This is in an agreement with the mechanism for ethylene polymerization on the model centers of **2**–**7** proposed previously,[4–6] which implies that the alkyl group R replaces only one Cl ligand.

The surprising result of our work concerns the ΔE and ΔG_{298} energies of reactions (4) and (5) of Mg-free compounds **6** and **7**. They are close to the same energies calculated for Mg-containing compounds **2**, **4** and **3**, **5**, respectively. However, the energies of the model particles ***na*** formation in reactions (6)–(8) should be taken into account since they characterize the thermodynamic stability and, as a consequence, the number of ***na*** particles formed in the system. The ΔE and ΔG_{298} energies of reactions (6)–(8) are presented in Table 1 for R = Me, Et.

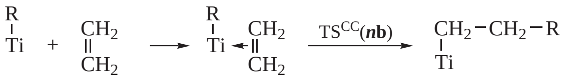
$$\mathbf{1a} + \mathrm{MgCl_2} \rightarrow \mathbf{2a},\ \mathbf{3a}, \tag{6}$$

$$\mathbf{1a} + \mathrm{ClMg(\mu\text{-}Cl)_2AlR_2} \rightarrow \mathbf{4a},\ \mathbf{5a}, \tag{7}$$

$$\mathbf{1a} + \mathrm{AlR_2Cl} \rightarrow \mathbf{6a},\ \mathbf{7a}. \tag{8}$$

The absolute values of reaction energies are close for compounds **2a** and **4a**, but substantially lower for compound **6a** with a similar structure. They are also close for compounds **3a** and **5a**, but lower for their structural analogue **7a**. At the same time, the calculated energy effects are nearly the same for R = Me and R = Et for each compound ***na***. Thus, the reactions of the Mg-containing compounds with **1a** lead to the formation of more stable bi- and trinuclear compounds **2a**–**5a** as compared to their analogues **6a** and **7a** in Mg-free systems. Reactions (4) of complexes **2a**–**5a** with AlR_3 result in the formation of compounds **2b**–**7b**, which are probable catalytic centers for alkene polymerization. This is the first reason of the higher activity of the Mg-containing system in ethylene polymerization as compared to the Mg-free system.

Reactions of **2b**–**7b** with ethylene were modeled[4–6] using the same calculation method as in this work. The total and free energies of the transition state TS^{CC}(***nb***) of C–C bond formation in reaction (9) are given in Table 1 for R = Me. According to ref. 4, TS^{CC}(***nb***) corresponds to the highest energy point on the path of reaction (9). Thus, the energy of TS^{CC}(***nb***), calculated with respect to the sum of reagent energies (***nb*** + C_2H_4), can be considered as a quantitative characteristic of ***nb*** reactivity toward ethylene.



$$\mathrm{R{-}Ti} + \mathrm{CH_2{=}CH_2} \longrightarrow \mathrm{R{-}Ti{\leftarrow}(CH_2{=}CH_2)} \xrightarrow{\mathrm{TS^{CC}}(\boldsymbol{n}\mathbf{b})} \mathrm{Ti{-}CH_2{-}CH_2{-}R} \qquad (9)$$

The lowest energy barrier $\mathrm{TS^{CC}}$(**2b**) has been found for the **2b** + C_2H_4 system with the three-coordinated Mg atom, which can complete its coordination sphere due to the binding of activator, solvent or other molecules. The energies of **2b** transformation into **4b** (R = Me) were calculated recently[5] using the same calculation method.

$$\mathbf{2b} + \mathrm{AlMe_2Cl} \rightarrow \mathbf{4b}. \qquad (10)$$

The energy values $\Delta E(10) = -32.0$ kcal mol^{-1} and $\Delta G_{298}(10) = -19.5$ kcal mol^{-1} suggest that the formation of the particles of type **2b** in the presence of AlR_2Cl is improbable.

The energy barriers $\mathrm{TS^{CC}}$(**4b**) are markedly lower than $\mathrm{TS^{CC}}$(**6b**), suggesting a higher reactivity of **4b** toward ethylene, as compared to **6b**. This is the second reason of the higher activity of the Mg-containing system in ethylene polymerization, as compared to the Mg-free system.

Thus, the activation effect of Mg-containing compounds in post-titanocene catalytic systems for alkene polymerization can be caused by a higher stability of complexes **2a**–**5a** and a greater exothermicity of Cl ligand exchange in their reactions with AlR_3, as compared to pre-catalyst **1a**.

However, there may be another reason for this effect in the test system. The ‘kinetic’ explanation is based on a comparison of the highest energy barriers of the model active center reaction with ethylene. In particular, the energy barrier of the C–C bond formation step of reaction (9) for **4b** is lower than that for **6b** due to the ability of **4b** to form the extra Ti–Cl–Mg bridge bonds stabilizing the system on the reaction path.[6]

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