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On the mechanism of olefin polymerisation with titanium β-diketonato complexes. A model density functional study

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Abstract

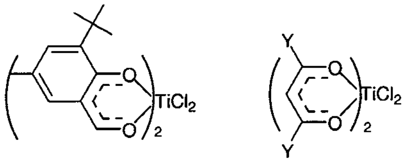
According to density functional calculations (BP86/AE1 + ZPE level) for a model system with L = HC(O)CHC(O)H, cationic titanium complexes of the type L_2TiR^+ (R = growing alkyl chain) can be viable intermediates in the homogeneous olefin polymerisation catalysed by titanium β-diketonato complexes. As with the related cationic metallocenes, olefin insertion in β- and α-agostic intermediates is a facile process. Little activation for chain propagation is computed on the potential energy surface, 2.9 kcal mol^{-1} (incl. ZPE), but this value is raised to 15.8 kcal mol^{-1} on the free energy surface at 298 K. The main portion of this total barrier stems from the entropic destabilisation of the intermediate olefin π-complexes. Chain termination via β-H transfer requires significantly higher activation, consistent with the observation of olefin polymerisation, rather than oligomerisation. Electron-withdrawing substituents at the diketonate ligand are predicted to lower the barrier for chain propagation by as much as 4.5 or 5.4 kcal mol^{-1} for L = $F_3CC(O)CHC(O)CF_3$ (hfac) or NCC(O)CHC(O)CN, respectively. Thus, hfac complexes should produce highly active catalysts.

Keywords: Olefin polymerisation; Titanium β-diketonato complexes; Density functional study

1. Introduction

In homogeneous olefin polymerisation, the search for "life beyond metallocenes" [1] is being actively pursued. Several transition-metal complexes have recently been shown to match, or even surpass, the well-established Kaminski-type zirconocenes [2] in catalytic activity. While impressive progress has been made with complexes containing middle or late transition metals [3], much of the research efforts are still concentrated on the development of catalysts based on early transition metals, in particular Ti and Zr. One example is the phenoxy-derived titanium complex **1**, which—after activation with excess methylaluminoxane (MAO)—is a moderately active catalyst for homogeneous ethylene polymerisation (Scheme 1) [4]. Related bis(β-diketonato)titanium species **2**–**5** have subsequently been used successfully, either in homogeneous solution [5,6] or, in heterogeneous fashion, supported on $MgCl_2$ [7]. In both system types, the Ti complexes have displayed higher catalytic activity than their Zr congeners.

Detailed mechanistic information, much of it from density functional computations [8], is available for the titanocene- and zirconocene-catalysed olefin polymerisation. It is generally accepted that cationic agostic alkyl complexes are the key intermediates. In contrast, little is known about the mechanism operative for the β-diketonato species **1**–**4**. For instance, are similar intermediates involved, and if so, what is the rate-determining step? How should the ligands be modified in order to lower the corresponding activation barrier? To



1

2 (Y = Me)
3 (Y = Ph)
4 (Y = *t*Bu)
5 (Y = CF_3 / Ph)

Scheme 1.

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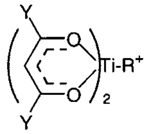


6 (Y = H, R = Et)

Scheme 2.

address these questions, we performed calculations for model system **6** + ethylene at an appropriate level of density functional theory (DFT) (Scheme 2). Special attention is called to the possible occurrence of agostic alkyl complexes and to the mechanisms of ethylene uptake, chain propagation, and termination. Our results extend earlier data on a related model with one propanediketonato ligand, which was part of a systematic study of elementary processes pertinent to olefin polymerisation [9].

2. Computational details

Geometries were fully optimised at the BP86/AE1 level, i.e. employing the exchange and correlation functionals of Becke [10] and Perdew [11], respectively, together with a fine integration grid (75 radial shells with 302 angular points per shell), the augmented Wachters' basis [12] on Ti (8s7p4d), and 6-31G* [13] basis on all other elements. This and comparable DFT levels have proven quite successful for transition-metal compounds and are well suited for the description of structures, energies, barriers, etc. [14]. The nature of the stationary points was verified by computations of the harmonic frequencies at that level. Transition states were characterised by a single imaginary frequency, and visual inspection of the corresponding vibrational modes ensured that the desired minima are connected. In cases of doubt, the key parts of the intrinsic reaction coordinate were followed. The computed harmonic frequencies were used to evaluate zero-point energies (ZPEs) and enthalpic and entropic corrections. Unless otherwise noted, energies are reported at the BP86/AE1 + ZPE level.

In addition, single-point energy calculations were performed for the BP86/AE1 geometries employing basis II′, that is, the augmented Wachters' basis on Ti, double-zeta basis on H [15], and the IGLO-basis II [15] (which is of polarised triple-zeta quality)on the remaining ligands, together with the BP86 and B3LYP functional, the latter according to Becke (hybrid) [16] and Lee et al. [17]. All computations employed the Gaussian 98 program package [18], except for the topological analyses (Bader analyses) [19], which were performed using the Morphy program [20].

3. Results and discussion

3.1. Chain propagation

Activation by MAO of $(C_5H_5)_2MCl_2$ (M = Ti, Zr, Hf) and derivatives thereof produces cationic complexes of the type $(C_5H_5)_2MR^+$ (R = Me) believed to be the active polymerisation catalysts. Chain propagation is realised by insertion of the olefin into the M–C(alkyl) bond. It is reasonable to assume that MAO and other suitable cocatalysts will have a similar alkylating and ionising effect on the titanium diketonate complexes **1**–**5**. Thus, complex **6** with an ethyl moiety as the smallest possible model for the growing alkyl chain was chosen as starting point for the exploration of the potential energy surface (PES). Starting from several initial configurations for **5** with and without agostic Ti···H(alkyl) interactions, optimisations always converged to the structure displayed in Fig. 1. This structure is devoid of such agostic interactions and is

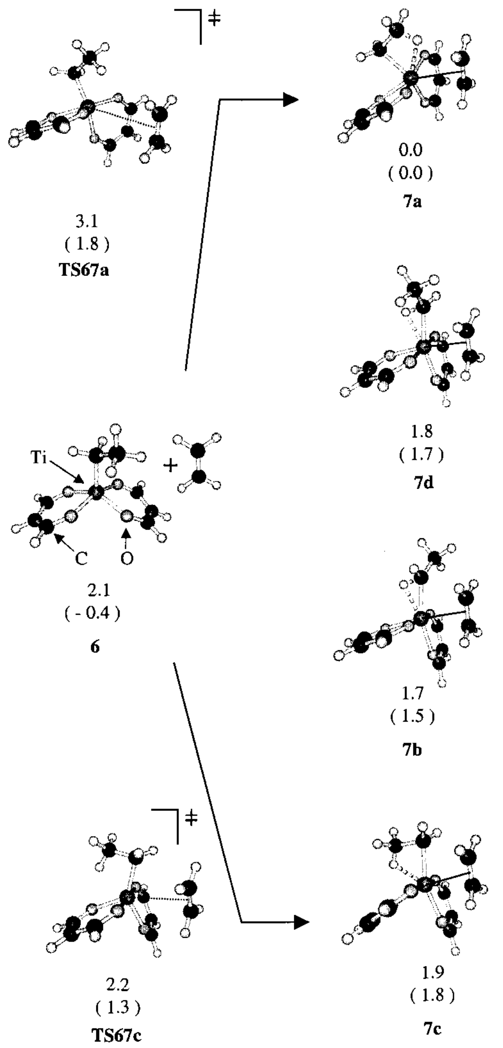


Fig. 1. Ethylene uptake by model catalyst **6**. Relative energies in kcal mol^{-1} are included (BP86/AE1 level; in parentheses: including zero-point energies).

characterised by a tetragonal pyramidal coordination sphere about Ti. In contrast, only α- or β-agostic minima can be located for the related $(C_5H_5)_2MEt^+$ systems or in the dicationic Ti and Zr alkyl complexes with one propanedionato ligand [9a].

The search for π-complexes resulting from ethylene addition to **6** afforded four minima **7a**–**7d**. In contrast to reactant **6**, noticeable Ti···H(alkyl) contacts are present in all of these π-complexes (Fig. 1). There are two diastereomeric pairs of α- and β-agostic species, **7b**,**d** and **7a**,**c**, respectively, of which the β-complex **7a** is the most stable. This situation is reminiscent of that in $TiCl_3Et$, where no Ti···H contact is found in the free molecule, but occurs upon increase of the Ti coordination number by complex formation with a chelating ligand [21,22]. In order to estimate the strength of the Ti···H agostic interaction, a partial optimisation was performed for **7a** with the Ti–C(α)–C(β) angle fixed to 109.47°. The resulting structure is found 3.5 kcal mol^{-1} above **7a**, the product of the unconstrained optimisation. Topological analysis of the BP86/AE1 total electron density in **7a** reveals a bond path between Ti and the β-H atom in question [23], which is not present in **6**. Removal of ethylene from **7a** and partial optimisation with the Ti–Et moiety fixed in the β-agostic conformation affords a structure 2.3 kcal mol^{-1} above **6**, which also shows no bond path between Ti and H, despite the short spatial contact. Hence, the agostic interaction is weak and is easily superseded by other electronic or steric effects.

As a consequence, only moderate stabilisation of the π-complexes by agostic interactions is to be expected. The computed binding energies of the olefin in **7a**–**7d** are indeed quite low, between -2.1 and -0.2 kcal mol^{-1} on the PES, and are even slightly unfavourable upon inclusion of zero-point corrections, between $+0.4$ and $+2.2$ kcal mol^{-1} (see respective differences of the relative energies in Fig. 1). However, little or no extra activation is required for ethylene uptake by **6**, as the computation of two representative transition structures **TS67a** and **TS67c** afforded total barriers of only 2.2 kcal mol^{-1} (corresponding barriers are to be expected for **TS67b** and **TS67d** which have not been located). Similarly small ethylene-uptake energies around -2 kcal mol^{-1} have been computed for $(C_5H_5)_2TiEt^+$ [9a,24].

The reaction can proceed with insertion of ethylene into the Ti–C(α) bonds of the π-complexes **7**. In the most stable form, **7a**, the mutual arrangement of the ligands is unfavourable for this insertion, since the Ti–C(α) bond is blocked by the agostic Ti···H moiety (a possible reaction for **7a** is H-transfer, see below). Thus, when **7a** is formed it must rearrange to one of the isomeric species **7b**–**7d** before insertion can take place. It is such a rearrangement from a β- to an α-agostic complex which is computed to be the rate-determining step in the zirconocene-catalysed olefin polymerisation [8].

The reaction coordinate connecting **7a**–**7d** can be described as a rotation of the ethyl unit about the Ti–C(α) bond. The relevant stationary points are shown in Fig. 2. In the relevant transition structures **TS7xy**, the agostic Ti···H interactions are noticeably weakened compared to the corresponding minima, as judged from geometric criteria (C–H bond lengths or C–C–H angles). As a consequence, notable barriers are obtained, between 5.1 and 7.8 kcal mol^{-1} relative to **7a**. Despite considerable efforts we were not able to locate a transition state between **7a** and **7d**. If such a saddle point exists, its energy is probably in the same range as those of the other **TS7xy**.

The barriers for direct rearrangements between **7a**–**7d** (Fig. 2) are significantly higher than those for decomposition into **6** and ethylene (Fig. 1). Thus, the preferred pathway for interconversion between any two π-complexes would be dissociation of the olefin and appropriate re-coordination. Given the low barriers for olefin dissociation and uptake, the distribution of the π-complexes could well be thermodynamically, rather than kinetically controlled (see however the discussion of free energies below).

The transition states for ethylene insertion starting from the π-complexes **7b**–**7d** are displayed in Fig. 3. Only minute barriers are computed for insertion within

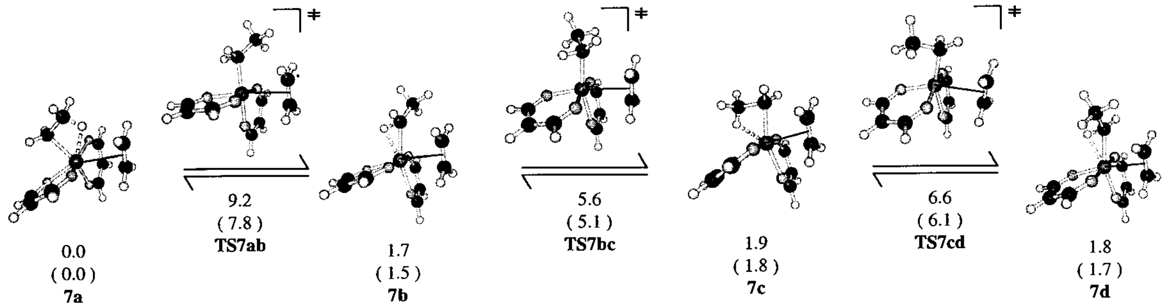


Fig. 2. Interconversion of π-complexes **7a**–**7d**. Relative energies in kcal mol^{-1} are included (BP86/AE1 level; in parentheses: including zero-point energies).

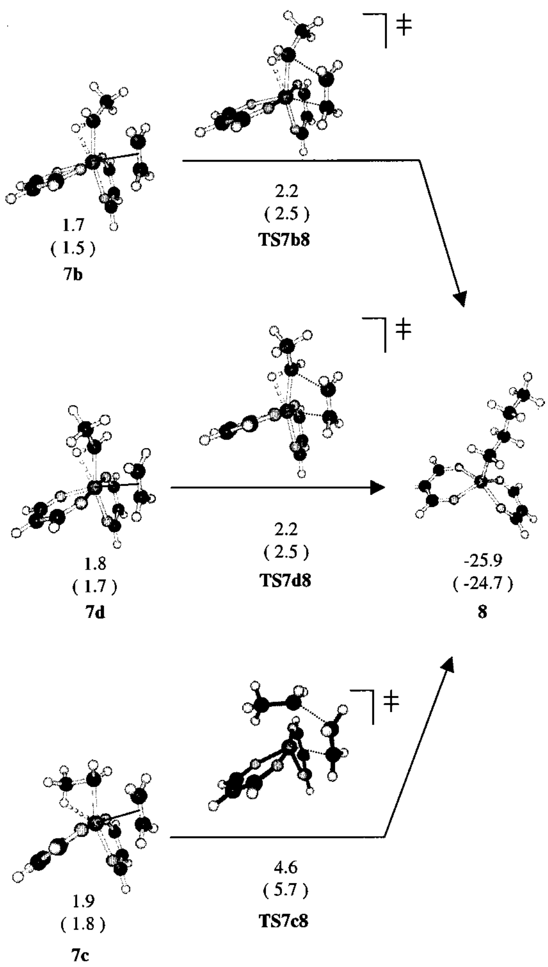


Fig. 3. Chain propagation by ethylene insertion. Energies are given in kcal mol^{-1} relative to **7a** (BP86/AE1 level; in parentheses: including zero-point energies).

the α-agostic reactants **7b** and **7d**. The corresponding transition states **TS7b8** and **TS7d8** are only 1.0–0.7 kcal mol^{-1} above the respective minima. Similarly low (or even vanishing) olefin insertion barriers have been computed for $(C_5H_5)_2MR^+$ species (M = Ti and Zr). The saddle points **TS7b8** and **TS7d8** differ in the stereochemistry of the olefin with respect to the growing polymer chain, and are virtually isoenergetic. A larger energetic discrimination between the corresponding insertion modes is observed (and computed) in the zirconocene systems, which has important consequences for the tacticity of polymers built from substituted olefins [2,25].

Compared with the barriers for insertion in the α-agostic complexes, the computations predict a noticeably higher activation barrier for backside insertion in the β-agostic species, as the corresponding transition state **TS7c8** is 3.9 kcal mol^{-1} above **7c** (Fig. 3). Olefin insertion should thus proceed preferably via α-agostic complexes, as is the case for the zirconocene systems.

The common, eventual product of the transition structures **TS7x8** is the butyl complex **8** (Fig. 3). The primary insertion products are *gauche* isomers, which are slightly less stable than the all-*trans* form **8** and which can easily convert into the latter by simple rotations about C–C single bonds. As with the ethyl analogue **6**, no agostic interactions are present in **8**, and the coordination geometry about Ti is tetragonal pyramidal. Due to the considerable exothermicity of the insertion process, which is rooted in the driving force for polymerisation, **TS7a8**–**TS7c8** are early transition states. Thus, very low barriers are to be expected.

3.2. Chain transfer

Chain termination is the undesired reaction competing with chain propagation. For a number of cationic d^0 complexes, DFT computations have indicated that intramolecular H-transfer from the growing alkyl chain to a coordinated olefin is, in general, the preferred termination mechanism (via chain transfer) [9c]. Another possible mechanism, β-H-elimination via a free metal hydride, is usually much less favourable. The same is found for our model system **8**, namely that the latter process is highly endothermic, by more than 37 kcal mol^{-1} (Fig. 4, top). We have not attempted to locate the transition state for this process, since it is clear that the actual barrier must be even higher.

Ethylene complex **7a** is an excellent candidate for intramolecular H-transfer: one β-H atom of the ethyl group is activated by an agostic interaction with Ti and is in close proximity to the coordinated ethylene moiety. It is therefore not surprising that a relatively low

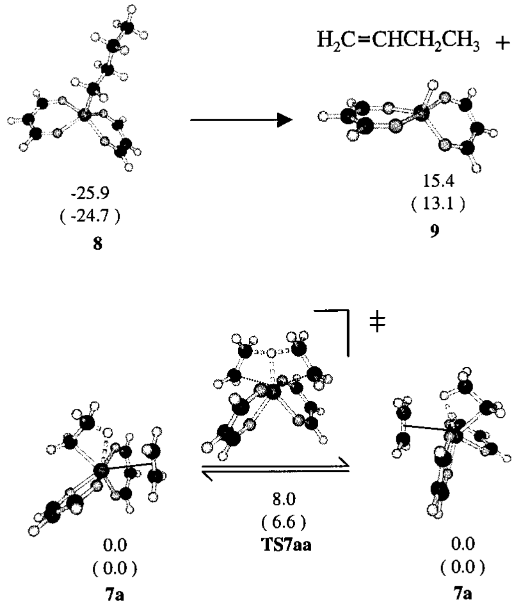


Fig. 4. Possible mechanisms for chain termination: β-H-elimination (top) and chain transfer via intramolecular H migration (bottom) Energies are given in kcal mol^{-1} relative to **7a** (BP86/AE1 level; in parentheses: including zero-point energies).

barrier, 6.6 kcal mol^{-1}, is computed for this process (Fig. 4, bottom), similar to corresponding values in related systems [9c]. In our model system, reactant and product of this H-transfer are identical and the corresponding transition state (**TS7aa** in Fig. 4) has C_2 symmetry. In the real system, the growing alkyl chain attached to C(β) of the ethyl group in **7a** would end up on the coordinated olefin, from where dissociation of this substituted olefin, according to the data in Fig. 1, can take place easily and the remaining ethyl complex can start a new chain. The barrier for this termination mechanism via **TS7aa** is low, as just mentioned, but is still significantly higher than that for chain propagation via **TS7b8** or **TS7d8**. This result is consistent with the observed high molecular weights of the polymers produced in the experiments [5,7]. For the corresponding dicationic model with only one propanedionato ligand, in contrast, the transition state for β-H transfer was computed below that of olefin insertion [9b,9c], which would imply olefin oligomerisation rather than polymerisation.

On the zero-point corrected PES, that is, at zero K, the whole polymerisation sequence starting from **6** would require very little activation. The highest point in sequence (1),

$$\mathbf{6} + C_2H_4 \xrightarrow{\mathbf{TS67b}} \mathbf{7b} \xrightarrow{\mathbf{TS7b8}} \mathbf{8} \qquad (1)$$

is just 2.9 kcal mol^{-1} above the reactants. However, inclusion of thermal and, in particular, entropic contributions estimated from the harmonic vibrational frequencies results in a strong stabilisation of the reactants over the other stationary points (see ΔG^{298} values in Table 1). On the free energy surface, **TS7b8** is still the highest, rate-determining point on this path, but is 15.8 kcal mol^{-1} higher in energy than the reactants.

The free activation energy for H-transfer via **TS7aa** is 21.2 kcal mol^{-1} with respect to $\mathbf{6} + C_2H_4$, suggesting that chain propagation should be faster than termination by several orders of magnitude.

It should be kept in mind that entropic corrections from statistical thermodynamics can be associated with noticeable errors, that only a model system lacking the bulkier substituents of **1**–**5** has been studied so far, and that effects of counterions [26] and solvents are neglected. Nevertheless, the ΔG^{298} values in Table 1 should be in the correct order of magnitude. An overall activation barrier around 16 kcal mol^{-1} can still be overcome under normal conditions, but is much higher than the propagation barrier of ca. 7 kcal mol^{-1} estimated for zirconocene-based systems [27]. This result is thus in complete accord with the observation that catalysts derived from **1** are only moderately active. According to the model calculations, the reason for this reduced activity compared to zirconocenes is rooted in the small olefin binding energy of the bis(β-diketonato)alkyltitanium cations. With the practically vanishing binding enthalpy in model compound **5** [28], the principal part of the overall propagation barrier is entropic in nature, arising from the decrease in particle numbers upon formation of the olefin π-complex.

To what extent do these conclusions depend on computational details such as basis set and density functional employed? In a model study of ethylene insertion into TiH_2Me^+, small such effects were noted [29]. To address this question, single point energy evaluations have been carried out at the BP86/II′ and B3LYP/II′ levels, that is, using a somewhat larger basis set and a popular hybrid density functional. Compari-

Table 1
Relative energies (kcal mol^{-1}) of minima and transition states (BP86/AE1 level except where otherwise noted)

Complex	ΔE	ΔE (BP86/II)	ΔE (B3LYP/II′)	ΔE+ZPE [a]	ΔH^{298} [b]	ΔG^{298} [b]
6+C_2H_4	2.1	0.1	−4.1	−0.4	0.4	−13.2
7a	0.0	0.0	0.0	0.0	0.0	0.0
7b	1.7	2.7	2.7	1.5	1.7	0.5
7d	1.8	2.8	3.0	1.7	1.9	0.9
7c	1.9	2.5	2.1	1.8	2.2	0.5
8	−25.9	−23.8	−26.2	−24.7	−24.7	−27.4
9	15.4	13.0	8.5	13.1	12.9	−0.1
TS67a	3.1	2.1	−0.4	1.8	2.2	−0.6
TS67c	2.2	2.1	0.2	1.3	1.4	−0.1
TS7ab	9.2	10.0	7.3	7.8	8.1	6.8
TS7bc	5.6	6.3	5.3	5.1	5.0	4.8
TS7cd	6.6	7.3	5.9	6.1	6.1	5.2
TS7b8	2.2	3.6	5.7	2.5	1.9	2.6
TS7d8	2.2	3.6	5.6	2.5	1.9	2.9
TS7c8	4.6	6.3	9.4	5.7	4.9	6.5
TS7aa	8.0	7.4	12.9	6.6	5.7	8.0

Energies are reported relative to the most stable π-complex, **7a**.

[a] BP86/AE1 including zero-point energies.

[b] At 298 K, estimated from BP86/AE1 energies and corrections from the harmonic frequencies obtained at that level.

son of the corresponding relative energies in Table 1 (first three columns) reveals noticeable variations with the theoretical level, up to several kcal mol^{-1}. However, the qualitative conclusions are not affected: Ethylene binding is weak throughout, and is indicated to be even less favourable with the larger basis set (attributable to a reduced basis-set superposition error) and with the hybrid functional (probably related to the destabilisation of agostic complexes at the B3LYP level noticed earlier [30]). At all levels, the β-agostic isomer **7a** is the most stable among the ethylene complexes, and ethylene insertion into an α-agostic complex is the highest point on the reaction path (Eq. (1)), with significantly higher barriers for the termination processes.

3.3. Substituent effects

As noted above, the main part of the chain-propagation barrier on the free energy surface arises from the small olefin binding energy of cationic alkyl complexes such as **6**. In order to enhance the catalytic activity of titanium diketonato complexes, the reduction of ligand basicity would appear to be a promising strategy as this should lead to increased olefin binding energies in the presumed active, cationic catalysts. For a first estimate of substituent effects, we have located the transition structures corresponding to **TS7b8** with modified diketonate ligands (see Table 2). Assuming that the nature of the rate-determining step does not change upon this type of substitution, the energy differences with respect to the corresponding reactants (**6**, or derivatives thereof, and ethylene) amounts to the rate-limiting barrier, reflecting the trends in the expected catalyst activity. The resulting barriers are given in Table 2, together with the change relative to that of the parent system (R = H, values in parentheses).

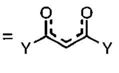
Changing the substituent from Y = H to Y = Me, i.e. on going to the acetylacetonato (acac) ligand, affords an increase of the barrier, as expected from the increased ligand basicity. In contrast, switching from Y = H to the electron-withdrawing Y = CF_3, i.e. on going to the hexafluoroacetylacetonato (hfac) ligand, results in a barrier reduction. In both cases, the magnitude of the barrier change is quite large, well above 4 kcal mol^{-1} (Table 2) [31].

An even larger barrier reduction, by more than 5 kcal mol^{-1} is computed on going to X = CN, i.e. using another strong σ-acceptor. Intermediate values are obtained for X = F, Cl, or Br, ca. 2–3 kcal mol^{-1} (Table 2), probably due to attenuation of the acceptor capabilities by π-donation. We have not explicitly computed the olefin binding energies, but it is quite likely that they would follow the same trend as that emerging from the data in Table 2. The same trend should transpire to the free energy surface, by way of enthalpy-modulation of the essentially entropic barrier (see above). Indeed, very similar entropic corrections to the barriers are computed from the harmonic frequencies (compare relative ΔE_a and ΔG_a data in Table 2).

Experimentally it has been noted that the nature of alkyl or aryl side chains at the ligands can affect the catalytic activity [5], and that introduction of a CF_3 group makes the $MgCl_2$-supported heterogeneous catalyst more reactive [7b]. Likewise, partial fluorination of the acac ligand in $Zr(acac)_2Cl_2$ increases its activity in ethylene oligomerisation [32]. Our computations predict a significant increase of catalyst activity when the hfac ligand is employed instead of acac [33].

Searching for a new NMR/reactivity correlation [34] we have also investigated the effect of the same substituents on the ^{49}Ti chemical shifts [35] of the potential catalyst precursors L_2TiCl_2. A number of correlations between rate constants or catalytic activities and transition-metal chemical shifts have been observed empirically [34,36] or predicted computationally [37]. However, no such correlation is apparent in the present case: Only minor variations are computed for the $\delta(^{49}Ti)$ values, on the order of a few dozen ppm, and no trend parallel to that in the barriers is found. Thus, no possible screening of prospective catalysts by their NMR spectra [38] can be predicted.

Table 2
Substituent effects on the insertion barrier (kcal mol^{-1}), taken as difference between **TS7b8** and **6**$+C_2H_4$ (BP86/AE1 level); in parentheses: changes relative to the parent system with

L =  (Y = H)

Y	ΔE_a	(rel.)	ΔE_a+ZPE	(rel.)	ΔH_a^{298}	(rel.)	ΔG_a^{298}	(rel.)
H	0.1	(0.0)	2.9	(0.0)	1.5	(0.0)	15.8	(0.0)
Me	4.9	(4.8)	7.6	(4.7)	6.4	(4.9)	19.9	(4.1)
CF_3	−4.5	(−4.4)	−1.6	(−4.5)	−2.9	(−4.4)	11.6	(−4.2)
CN	−5.3	(−5.2)	−2.5	(−5.4)	−3.8	(−5.3)	10.2	(−5.6)
F	−2.8	(−2.7)	0.0	(−2.9)	−1.3	(−2.8)	12.4	(−3.4)
Cl	−1.6	(−1.5)	1.2	(−1.7)	−0.1	(−1.6)	13.6	(−2.2)
Br	−1.5	(−1.4)	1.3	(−1.6)	0.0	(−1.5)	14.2	(−1.6)

4. Conclusions

Model DFT computations suggest that cationic alkyl titanium β-diketonato complexes of the type L_2TiR^+, once formed by activation of suitable precursors, can be viable intermediates in catalytic olefin polymerisation. For the free model system L_2TiEt^+ (L = 1,3-propanedionato), olefin uptake under formation of any of several π-complexes is energetically and, in particular, entropically unfavourable. Agostic interactions between Ti and aliphatic H atoms of the alkyl chain occur only in the π-complexes, not in the resting state, L_2TiR^+. The highest and therefore rate-limiting point on the whole polymerisation path is the transition state for olefin insertion into the Ti–C(alkyl) bond. Electron-withdrawing substituents at the diketonato ligand are computed to stabilise the transition state for insertion with respect to the reactant resting state. This reduction of the insertion barrier is more pronounced for pure σ-acceptors than for π-donors. Thus, using the well-known hfac or related ligands instead of alkylated acac derivatives should result in an increase of the catalytic activity.

5. Supplementary material

Optimised cartesian coordinates for complexes and transition states in xyz format are available upon request from the authors, or can be downloaded from http://www.mpi-muelhim.mpg.de/kofu/institut/arbeitsbereiche/buehl/pubti-supp.htm.

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