Catalytic Linear Oligomerization of Ethylene to Higher α-Olefins: Insight into the Origin of the Selective Generation of 1-Hexene Promoted by a Cationic Cyclopentadienyl-Arene Titanium Active Catalyst

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A detailed theoretical investigation is presented of crucial elementary steps of the selective linear ethylene oligomerization to 1-hexene by the cationic $[(\eta^5\text{-}C_5H_4\text{-}(CMe_2)\text{-bridge})\text{-}C_6H_5)\text{-}Ti^{IV}(CH_3)_2]^+$ precatalyst, employing a gradient-corrected DFT method. The essential aspects of the originally proposed mechanism have been confirmed and supplemented by novel insights into how the selective ethylene oligomerization operates. This includes the examination of the ability of titana(IV)cycle intermediates to grow and/or to decompose affording α-olefins as a function of their size, the prediction of the favorable route for precatalyst activation, and the exploration of the cycloalkane production as a possible side process. After the $Ti^{IV}-Me_2$ precatalyst is smoothly converted into the active $Ti^{II}-(ethylene)_2$ catalyst complex, the two ethylene moieties readily undergo oxidative coupling to afford first the titana(IV)cyclopentane species. Metallacycle growth through bimolecular ethylene uptake and subsequent insertion displays very similar structural and energetic characteristics for five- and seven-membered titana(IV)cycles. Decomposition of titana(IV)cycles to α-olefins preferably takes place via a concerted transition-metal-assisted β-H transfer for conformationally flexible metallacycles beginning with the titana(IV)cycloheptane, with very similar barriers having to be overcome. This decomposition path, however, is kinetically inaccessible for the rigid five-membered titana(IV)cyclopentane. Instead, the stepwise mechanism via a metastable $Ti^{IV}-$alkenyl-hydride species is found to be operative in this case. A significantly raised activation barrier is connected with the stepwise path, which makes the growth of the titana(IV)cyclopentane to the seven-membered cycle the more favorable process than its decomposition to 1-butene. Cycloalkanes are less likely to be formed, due to a kinetically handicapped reductive CC elimination. On the basis of the detailed insights into the ability of titana(IV)cycles to undergo either growth or decomposition to α-olefins, the thermodynamic and kinetic aspects for the selectivity control of the linear ethylene oligomerization have been rationalized. The crucial role played by the hemilabile arene ligand for the selective oligomerization process has also been analyzed.

Introduction

Higher (C_4-C_{20}) linear α-olefins are versatile intermediates and building blocks for the chemical industry.[1] They have become increasingly interesting as monomers (for production of poly-α-olefins) and as comonomers (C_4-C_8 to generate linear low-density LLDPE[3] polyeth-

ylene) in catalytic olefin polymerization.[1,2] Apart from their use as polyolefin building blocks, higher linear α-olefins find their main application as starting material for plasticizers (C_6-C_{10}) and surfactants ($C_{12}-C_{20}$). The inexpensive availability of ethylene together with the high quality of the α-olefin products makes oligomerization of ethylene nowadays the predominant route to α-olefins.[1d,4]

Several catalysts are known that actively assist the oligomerization of ethylene. Most of them afford a mixture of linear α-olefins having different chain lengths, which usually obey a Schulz−Flory[5] distribution. It is

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generally agreed that, in this case, chain propagation proceeds via ethylene insertion into the alkyl−transition-metal bond (with the transition metal in a high formal oxidation state), i.e., according to the classical coordination−migratory insertion mechanism proposed by Cossee and Arlman.[6] Chain transfer, on the other hand, takes place by β-hydrogen elimination or alternatively (and more probably for early as well as late transition metal complexes) by β-hydrogen transfer directly to the monomer.[7] Each of these elementary processes can be envisioned to have rates that are nearly independent of the oligomer's chain length, in the absence of unfavorable steric interactions between the oligomer chain and the surrounding ligand sphere. As a consequence, oligomerization catalysts with comparable rates for chain propagation and chain transfer (i.e., $k_{CP} \sim k_{CT}$) are likely to generate a statistical distribution of oligomers having different chain lengths.

In contrast to the abundance of known catalysts capable of oligomerizing ethylene and other short-length olefins to a Schulz−Flory distribution of higher linear α-olefins, there are only a few catalysts based on chromium,[8−10] tantalum,[11] and titanium[12,13] that oligomerize ethylene selectively to a certain linear α-olefin, with 1-hexene as the most common product. For the selective olefin oligomerization to afford a specific linear higher α-olefin, clearly a mechanism other than migratory insertion and chain transfer must be operative. Metallacycles are hypothesized to be involved in the alternative mechanism, an assumption that has been supported by X-ray characterization of chromacyclic structures for a class of chromium-based compounds that display a tendency for selective trimerization of ethylene.[9,14] The ability of the metallacycle to enlarge, as well as decompose, to afford the respective α-olefin

can be envisioned as being nonuniform for different metallacycle sizes. Additionally, distinct relative rates are likely for these two processes for different metallacycles, which may rationalize the generation of a specific higher α-olefin. Furthermore, the oligomerization via metallacycle intermediates is accompanied by a repeated change in the formal oxidation number of the transition metal by two (for instance $M^{II} \rightleftharpoons M^{IV}$). Accordingly, a well-balanced oxidation−reduction potential of the transition metal represents a prerequisite for an efficient catalyst.

The mono(cyclopentadienylarene)titanium [$(\eta^5\text{-}C_5H_3R\text{-}$(bridge)-Ar)Ti^{IV}Cl$_3$]/MAO (Ar = Ph, 4-MeC$_6H_4$, 3,5-Me$_2C_6H_3$; R = H, CMe$_3$, SiMe$_3$) systems have been reported recently as generators for a class of highly active catalysts for the selective trimerization of ethylene to 1-hexene.[13] The hemilabile ancillary arene ligand is indicated to decisively influence the product composition as well as the catalyst's activity. For an arene ligand that is able to coordinate efficiently to the titanium atom, 1-hexene (as well as products of 1-hexene/ethylene co-trimerization) is almost exclusively formed. In the absence of the arene ligand (i.e., Ar = Me), however, the catalyst switches from oligomerization to polymerization activity. Metallacycle intermediates have been assumed to be involved in the catalytic reaction course for ethylene oligomerization (vide infra). Although these catalyst systems are one of the very few examples where the nature of the catalytically active species could be clearly imagined, neither the precise nature of the active catalyst nor the possible intermediates have been conclusively elucidated.

This leads us to scrutinize theoretically all critical elementary reaction steps of the proposed catalytic cycle for the cationic [$(\eta^5\text{-}C_5H_4\text{-}(CMe_2\text{-bridge})\text{-}C_6H_5)Ti^{IV}(CH_3)_2$]$^+$ precatalyst (vide infra),[13c] which has been demonstrated to generate 1-hexene with high selectivity.[13d] Theoretical studies at the B3LYP level of approximation have been reported recently for the same catalyst[15a] as well as for a different catalyst (i.e., with a CH$_2$-bridge)[15b] of the class of titanium-based catalysts investigated here, which provided a basic insight into the catalytic process. The present theoretical examination of critical elementary steps for metallacycle intermediates up to titana(IV)cyclononane, however, is aimed at extending the mechanistic understanding into the process of selective oligomerization of ethylene by clarifying the following intriguing mechanistic aspects. (1) What is the preferred route for precatalyst activation? (2) Does the titana(IV)-cycle's decomposition, affording linear α-olefins, take place preferably via a concerted or a stepwise pathway? (3) Does the rate for the overall process of metallacycle enlargement, as well as for the metallacycle's decomposition, appear as being nearly identical among the variation of the titana(IV)cycle's size or do they display a nonuniform behavior? (4) What are the critical thermodynamic and kinetic factors that regulate the selectivity of the linear oligomerization of ethylene to predominantly afford 1-hexene?

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Scheme 1.   Proposed Catalytic Cycle for Selective Linear Oligomerization of Ethylene to 1-Hexene with a Cationic Cyclopentadienyl-Arene Titanium Precatalyst[13a,b,16]
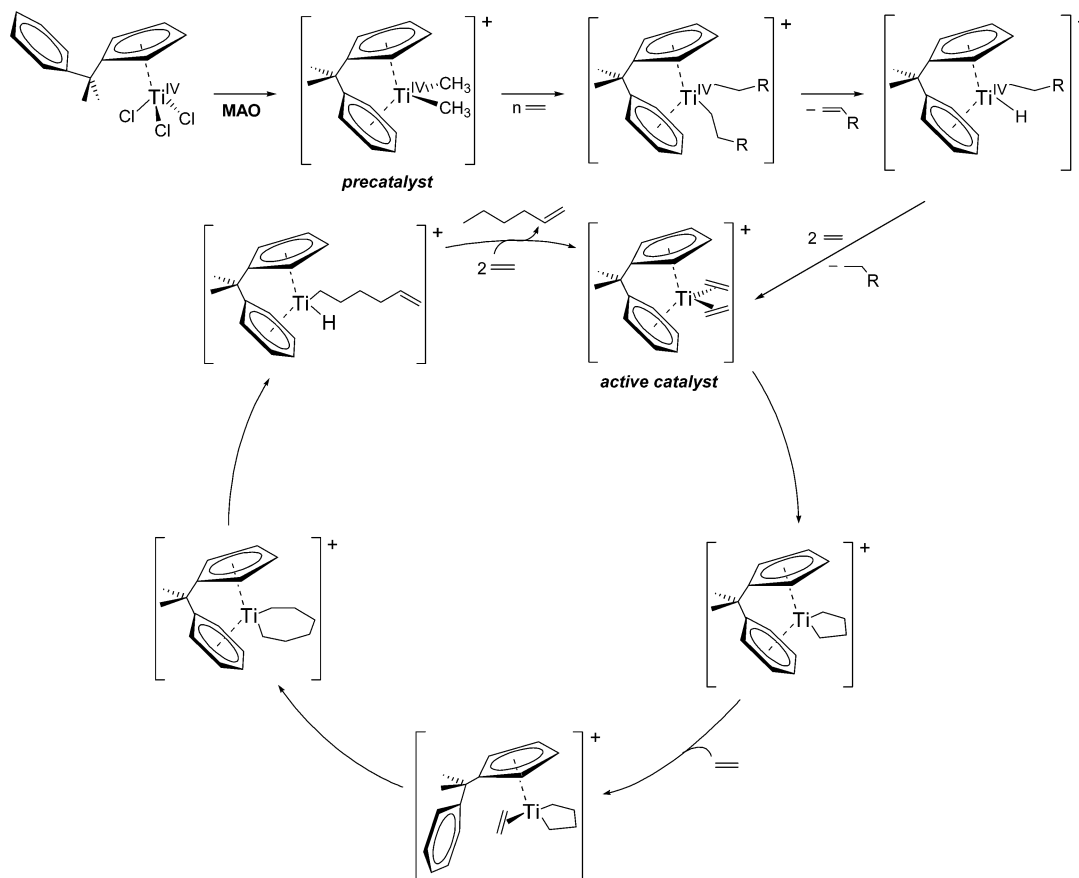
Proposed Catalytic Reaction Cycle

For the linear oligomerization of ethylene by the class of cationic $[(\eta^5\text{-}C_5H_3R\text{-}(bridge)\text{-}Ar)Ti^{IV}R_2]^+$ precatalyst the catalytic cycle displayed in Scheme 1 has been proposed.[13a,b] The reaction course involves metallacycle intermediates in order to account for the selective 1-hexene generation. Commencing from the $[(\eta^5\text{-}C_5H_3R\text{-}(bridge)\text{-}Ar)Ti^{IV}Cl_3]$/MAO starting material, activation with MAO probably leads first to the cationic $[(\eta^5\text{-}C_5H_3R\text{-}(bridge)\text{-}Ar)Ti^{IV}Me_2]^+$ precatalyst, via MAO-triggered alkylation and methyl/chlorine anion abstraction. The precise sequence of steps involved subsequently, however, is not known for this initial stage, where the precatalyst calls for activation while undergoing transformation into the bis(ethylene)–Ti^{II} active catalyst species. Once precatalyst activation succeeds, oxidative coupling of the two ethylene moieties leads first to the titana(IV)cyclopentane species. Subsequent ethylene uptake under formation of the π-complex and insertion into the Ti^{IV}–C bond gives the titana(IV)cycloheptane. This intermediate is assumed to readily undergo decomposition under reduction of the titanium atom (Ti^{IV} → Ti^{II}) to yield 1-hexene. This can be accomplished either in a stepwise fashion by β-H abstraction and consecutive reductive CH elimination or alternatively by a concerted transition-metal-assisted β-H transfer.[16] The catalytic cycle is closed via the facile 1-hexene displacement by new ethylene monomers, which regenerates the active catalyst complex.

Computational Model and Method

Model. All critical elementary reaction steps for linear oligomerization of ethylene, viz., oxidative coupling, ethylene insertion into titana(IV)cycles, β-H abstraction and reductive CH elimination, concerted β-H transfer, as well as possible side reactions, like cyclization via reductive CC elimination, have been scrutinized theoretically for the real cationic $[(\eta^5\text{-}C_5H_4\text{-}(CMe_2\text{-}bridge)\text{-}C_6H_5)Ti^{IV}(CH_3)_2]^+$ precatalyst. Metallacycle intermediates up to titana(IV)cyclononane were considered in the present investigation. Furthermore, the favorable route for precatalyst activation has been clarified by exploring several conceivable pathways.

The effect of the solvent and the counterion was neglected in the present study, which is aimed at the elucidation of principal mechanistic aspects of the ethylene oligomerization reaction. For the actual catalyst investigated here, the hemilabile ancillary arene ligand acts to saturate efficiently the coordination sphere around the titanium atom (vide infra). Accordingly, the catalyst–counterion interaction and specific solvent (toluene) influence can be assumed to be of minor importance.[13c] The mechanistic conclusions drawn in the present study, therefore, are in a strict sense valid for oligomerization occurring in noncoordinating solvents with weakly interacting counterions involved.

Method. All reported DFT calculations were performed by using the TURBOMOLE program package developed by Häser and Ahlrichs.[17] The local exchange–correlation potential by Slater[18a,b] and Vosko et al.[18c] was augmented with gradient-corrected functionals for electron exchange according to Becke[18d]

(16) According to the mechanistic proposal (refs 13a,b), Scheme 1 contains only the Ti^{IV}-hydride intermediate, which is envisioned to be involved along the stepwise process.

and correlation according to Perdew[18e] in a self-consistent fashion. This gradient-corrected density functional is usually termed BP86 in the literature. In recent benchmark computational studies it was shown that the BP86 functional gives results in excellent agreement with the best wave function-based methods available today, for the class of reactions investigated here.[19]

For all atoms a standard all-electron basis set of triple-ζ quality for the valence electrons augmented with polarization functions was employed for the geometry optimization and the saddle-point search. The Wachters 14s/9p/5d set[20a] supplemented by two diffuse p[20a] and one diffuse d function[20b] contracted to (62111111/5111111/3111) was used for titanium, and standard TZVP basis sets[20c] were used for carbon (a 10s/6p/1d set contracted to (7111/411/1)) and for hydrogen (a 5s/1p set contracted to (311/1)). The frequency calculations were done by using standard DZVP basis sets,[20c] which consist of a 15s/9p/5d set contracted to (63321/531/41) for titanium, a 9s/5p/1d set contracted to (621/41/1) for carbon, and a 5s set contracted to (41) for hydrogen, for DZVP-optimized structures, which differ in marginal extent from the triple-ζ-optimized ones. The corresponding auxiliary basis sets were used for fitting the charge density.[20c,d]

Stationary Points. The geometry optimization and the saddle-point search were carried out at the BP86 level of approximation by utilizing analytical/numerical gradients/ Hessians according to standard algorithms. No symmetry constraints were imposed in any case. The stationary points were identified exactly by the curvature of the potential-energy surface at these points corresponding to the eigenvalues of the Hessian. All reported transition states possess exactly one negative Hessian eigenvalue, while all other stationary points exhibit exclusively positive eigenvalues. The many isomers that are possible for each of the investigated species were carefully explored, with particular attention being given to the different conformers of the metallacycle intermediates. Only the most stable isomers of each of the key species were reported, for which the reaction and activation free energies (ΔG, $\Delta G^{\ddagger}$ at 298 K and 1 atm) were evaluated according to standard textbook procedures[21] using computed harmonic frequencies.

Labeling of the Molecules. Roman numerals were used for species that participate along possible paths leading to precatalyst activation (except the Ti^{IV}–Me$_2$ precatalyst **1**), while crucial species of the catalytic ethylene oligomerization cycle were labeled with the following specific notation: the active catalyst complex **2**; the transition state for oxidative coupling **3**; the titana(IV)cycloalkanes **XC**; the key species encountered during the enlargement of the metallacycle, viz., the ethylene π-complex **XC-E** and the transition states for ethylene uptake **TXC-U** and for ethylene insertion **TXC-I**; the transition state for β-H abstraction **TXC-HA** and for reductive CH elimination **TXC-HRE**, and the Ti^{IV}–alkenyl-hydride intermediate **XC-H**, involved along the stepwise path of titana-(IV)cycle's degradation to α-olefins, the transition state for β-H transfer **TXC-HT** for the concerted process; the olefin–Ti^{II} complex **XC-O**; the transition state for reductive CC elimina-

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tion **TXC-CC**. The notation **X** = **5**, **7**, **9** was used to indicate whether five-, seven-, or nine-membered titana(IV)cycle intermediates, i.e., titana(IV)cyclopentane, titana(IV)cycloheptane, and titana(IV)cyclononane, respectively, were involved.

Results and Discussion

We shall start our investigation by exploring conceivable competing pathways for precatalyst activation. This is followed by the examination of crucial elementary steps of the oligomerization cycle, for which the overall free-energy profile is collected in Table 1. Here, special attention has been given to how the rate for individual steps is influenced by the size of the involved titana-(IV)cycles. On the basis of the achieved insights, the mechanistic implications for the selectivity control of the linear ethylene oligomerization process will be analyzed.

As a general feature, the pendant arene ligand displays a highly hemilabile character, as revealed from the ready change of the phenyl–Ti coordination mode, which depends on both the formal oxidation state of titanium and on the surrounding ligand sphere (vide infra). On the other hand, the cyclopentadienyl ligand always keeps the η^5-coordination in the most stable isomers for each of the investigated key species.[22]

I. Exploration of Conceivable Routes for Precatalyst Activation. Several conceivable paths for the transformation of the Ti^{IV}–Me$_2$ precatalyst **1** into the active bis(ethylene)–Ti^{II} catalyst complex **2** are shown in Figure 1 together with the respective reaction and activation free energies and involved key species.

One path for precatalyst activation starts from **1** with the reductive CC elimination under liberation of ethane to yield the Ti^{II} species **I**, which readily gets converted into **2** through ethylene uptake. The reductive CC elimination is an exergonic process ($\Delta G = -12.5$ kcal mol^{-1}, **1** → **I** + C$_2$H$_6$) that requires an activation free energy of 28.8 kcal mol^{-1}. The alternative path that starts with ethylene insertion into the Ti^{IV}–Me bond of **1** to give the Ti^{IV}–Me/Pr species **II** is predicted to be more facile ($\Delta G = 21.4$ kcal mol^{-1}, $\Delta G = -8.1$ kcal mol^{-1}, **1** + C$_2$H$_4$ → **II**), as indicated by a barrier that is 7.4 kcal mol^{-1} lower ($\Delta\Delta G^{\ddagger}$, relative to the **1** → **I** + C$_2$H$_6$ step). Very similar activation barriers of ~21 kcal mol^{-1} can reasonably be assumed for the insertion of further ethylene into the Ti^{IV}–Me or the Ti^{IV}–Pr bonds of **II**, although we did not examine these processes explicitly.

Among the many examined elementary steps that commence from **II**, the reductive β-CH elimination under liberation of methane is indicated as being the favorable process, on both kinetic and thermodynamic grounds. This process preferably takes place through the concerted β-H transfer, with a Ti^{IV}–H intermediate not found to participate along the most feasible pathway. The Ti^{IV}–H/Me species **V**, which is likely to be involved along a stepwise pathway after expulsion of propylene, is seen to play no role along any viable path for precatalyst activation, as it represents a energetically high-lying species (only 3.2 kcal mol^{-1} below the favorable transition state for the concerted process). The reductive β-CH elimination leads to the formation of the Ti^{II}–propylene species **III** in an exergonic process ($\Delta G = -14.1$ kcal mol^{-1}) that has a moderate barrier of 14.3 kcal mol^{-1} ($\Delta G^{\ddagger}$, **II** → **III** + CH$_4$). The substitution of propylene by an additional ethylene monomer is driven

Table 1. Calculated Gibbs Free-Energy Profile (in kcal mol^{-1}) of Crucial Elementary Steps and Possible Side Reactions of the Selective Linear Oligomerization of Ethylene for the Cationic [(η^5-C$_5$H$_4$-(CMe$_2$)-bridge)-C$_6$H$_5$)Ti^{II}(C$_2$H$_4$)$_2$]$^+$ Active Catalyst Complex^a

complex description	species	ΔG	$\Delta G^{\ddagger}_{rel}$
Ti^{II}−(ethylene)$_2$ active catalyst	**2**	0.0	
TS for oxidative coupling	**3**	5.2	5.2
titana(IV)cyclopentane	**5C**	−7.6	
key species for competing steps commencing from **5C**			
TS for ethylene uptake	**T5C-U**	8.1	15.7
ethylene π-complex	**5C-E**	6.5	
TS for ethylene insertion	**T5C-I**	11.9	19.5
TS for β-H abstraction	**T5C-HA**	15.1	22.7
Ti^{IV}−alkenyl-hydrido intermediate	**5C-H**	13.5	
TS for reductive CH elimination	**T5C-HRE**	15.0	22.6
Ti^{II}−η^6-ϕ + 1-butene	**4** + 1-butene	−10.7	
TS for concerted β-H transfer	**T5C-HT**	18.3	25.9
Ti^{II}−1−butene	**5C-O**	−17.2	
TS for reductive CC elimination	**T5C-CC**	22.0	29.6
Ti^{II}−η^6-ϕ + cyclobutane	**4** + cyclobutane	−3.9	
titana(IV)cycloheptane	**7C**	−14.0	
key species for competing steps commencing from **7C**			
TS for ethylene uptake	**T7C-U**	3.7	17.7
ethylene π-complex	**7C-E**	0.5	
TS for ethylene insertion	**T7C-I**	6.5	20.5
TS for β-H abstraction	**T7C-HA**	8.5	22.5
Ti^{IV}−alkenyl-hydrido intermediate	**7C-H**	6.8	
TS for reductive CH elimination	**T7C-HRE**	8.2	22.2
Ti^{II}−η^6-ϕ + 1-hexene	**4** + 1-hexene	−16.8	
TS for concerted β-H transfer	**T7C-HT**	−3.8	10.2
Ti^{II}-1−hexene	**7C-O**	−26.3	
TS for reductive CC elimination	**T7C-CC**	10.9	24.9
Ti^{II}−η^6-ϕ + cyclohexane	**4** + cyclohexane	−33.2	
titana(IV)cyclononane	**9C**	−15.0	
key species for competing steps commencing from **9C**			
TS for concerted β-H transfer	**T9C-HT**	−4.0	11.0
Ti^{II}-1-octene	**9C-O**	−34.5	
TS for reductive CC elimination	**T9C-CC**	12.4	27.4
Ti^{II}−η^6-ϕ + cyclooctane	**4** + cyclooctane	−29.1	

^{a} Free energies are given relative to **2** corrected by the respective number of ethylene molecules.

by a thermodynamic force of −3.4 kcal mol^{-1} (ΔG, **III** + C$_2$H$_4$ → **IV** + C$_3$H$_6$) in a smooth process that should not be accompanied with a significant kinetic barrier. Uptake of a further ethylene to **IV** yields the active catalyst complex **2** in a process that is slightly endergonic (ΔG = 5.5 kcal mol^{-1}), due to the entropy cost associated with this bimolecular step.

On the other hand, neither the insertion of ethylene into the alkyl−Ti^{IV} bonds of **II** ($\Delta G^{\ddagger} \approx 21$ kcal mol^{-1}, vide supra) nor the generation of **I** (and **2**, subsequently) through reductive CC elimination ($\Delta G^{\ddagger}$ = 29.5 kcal mol^{-1}, **II** → **I** + C$_4$H$_{10}$) is indicated to be likely steps in the course of precatalyst activation, due to unfavorable kinetics ($\Delta \Delta G^{\ddagger}$ = 6.7 and 15.2 kcal mol^{-1}, respectively, relative to the **II** → **III** + CH$_4$ process). Furthermore, the alternative path for reductive α-CH elimination under CH$_4$ liberation, which is thermodynamically less favorable (ΔG = 5.3 kcal mol^{-1}, **II** → **VI** + CH$_4$), is indicated to be almost precluded, kinetically, as well ($\Delta G^{\ddagger}$ = 20.9 kcal mol^{-1}). Therefore, the Ti^{II}−carbene species **VI** should occur in negligible concentrations, which prevents this species from undergoing further coupling and metathesis steps with ethylene.

After inspecting several competing pathways, we suggest the following sequence of elementary steps as being involved along the favorable route for precatalyst activation (cf. Figure 1): Ti^{IV}−Me$_2$, **1** → Ti^{IV}−Me/Pr, **II** → Ti^{II}−propylene, **III** → Ti^{II}−ethylene, **IV** → bis-(ethylene)−Ti^{II}, **2**. The entire process is exergonic (ΔG = −20.0 kcal mol^{-1}, **1** + 3C$_2$H$_4$ → **2** + CH$_4$ + C$_3$H$_6$) and

involves a largest overall barrier of 21.4 kcal mol^{-1} ($\Delta G^{\ddagger}$, **1** + C$_2$H$_4$ → **II**). This indicates that the transformation of the precatalyst **1** into the active catalyst **2** is a feasible process, with **2** expected to occur in appreciable concentrations.[23] Accordingly, the initial precatalyst activation should not discriminate the overall catalytic activity.

II. Exploration of Crucial Elementary Steps in the Linear Oligomerization Mechanism. A. Oxidative Coupling to Generate the Titana(IV)cyclopentane. After the active catalyst complex **2** is formed, the two coordinated ethylene moieties undergo oxidative addition under CC-bond formation with leads to the titana(IV)cyclopentane **5C**. The key species for the step together with the reaction and activation free energies are part of Figure 2.

The favorable isomer of **2** is characterized by an unsymmetrical phenyl ring coordination, with the two ethylene moieties oriented in-plane. Both the ethylene moieties and the phenyl ring contribute to the coordinative stabilization of the low-valent titanium atom through a significant π-back-donation interaction. This

(22) (a) Although ring slippage is known as a facile process in several Cp-based complexes, isomers that are characterized by a reduced hapticity of the Cp−Ti interaction were generally found to be energetically less favorable. Therefore, only species with a η^5-Cp−Ti moiety will be discussed in the following sections. (b) For facile ring slippage processes, see for instance: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(23) Under actual reaction conditions, the ethylene pressure (5 bar, ref 13c) acts to shift the **1** + 3C$_2$H$_4$ → **2** + CH$_4$ + C$_3$H$_6$ process to the right.
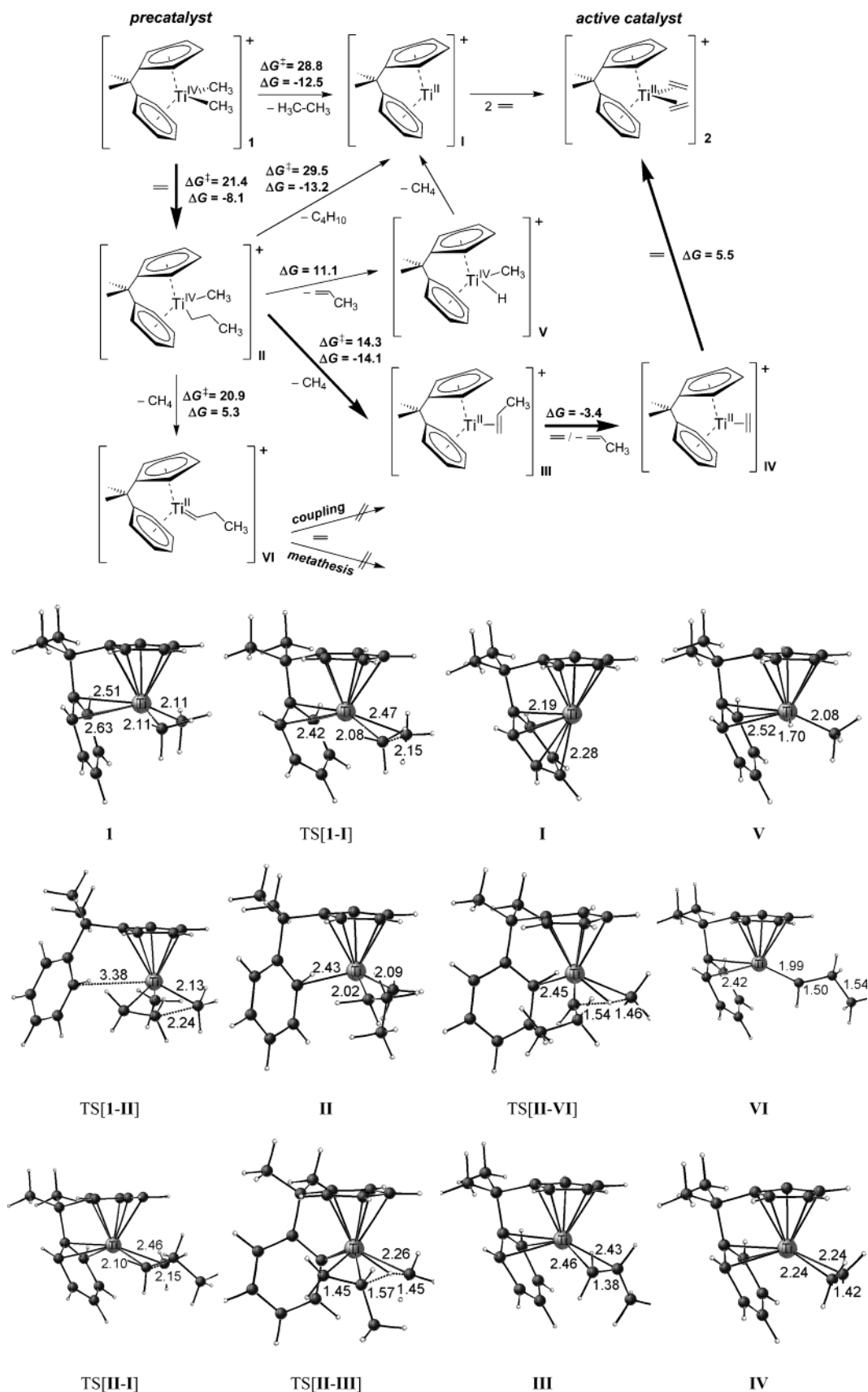
Figure 1. (Top) Condensed Gibbs free-energy profile (ΔG, $\Delta G^{\ddagger}$ in kcal mol^{-1}) of competing reaction routes for precatalyst activation. (Bottom) Optimized structures of involved key species. The reaction and activation free energies for individual steps are given relative to the respective precursor. The favorable route is indicated by bold reaction arrows.

is revealed, in the case of ethylene for example, by the elongation of the olefinic double bond (1.40 Å, cf. Figure

2). Commencing from the nearly coplanar arrangement of the two reactive ethylene moieties in **2**, no further
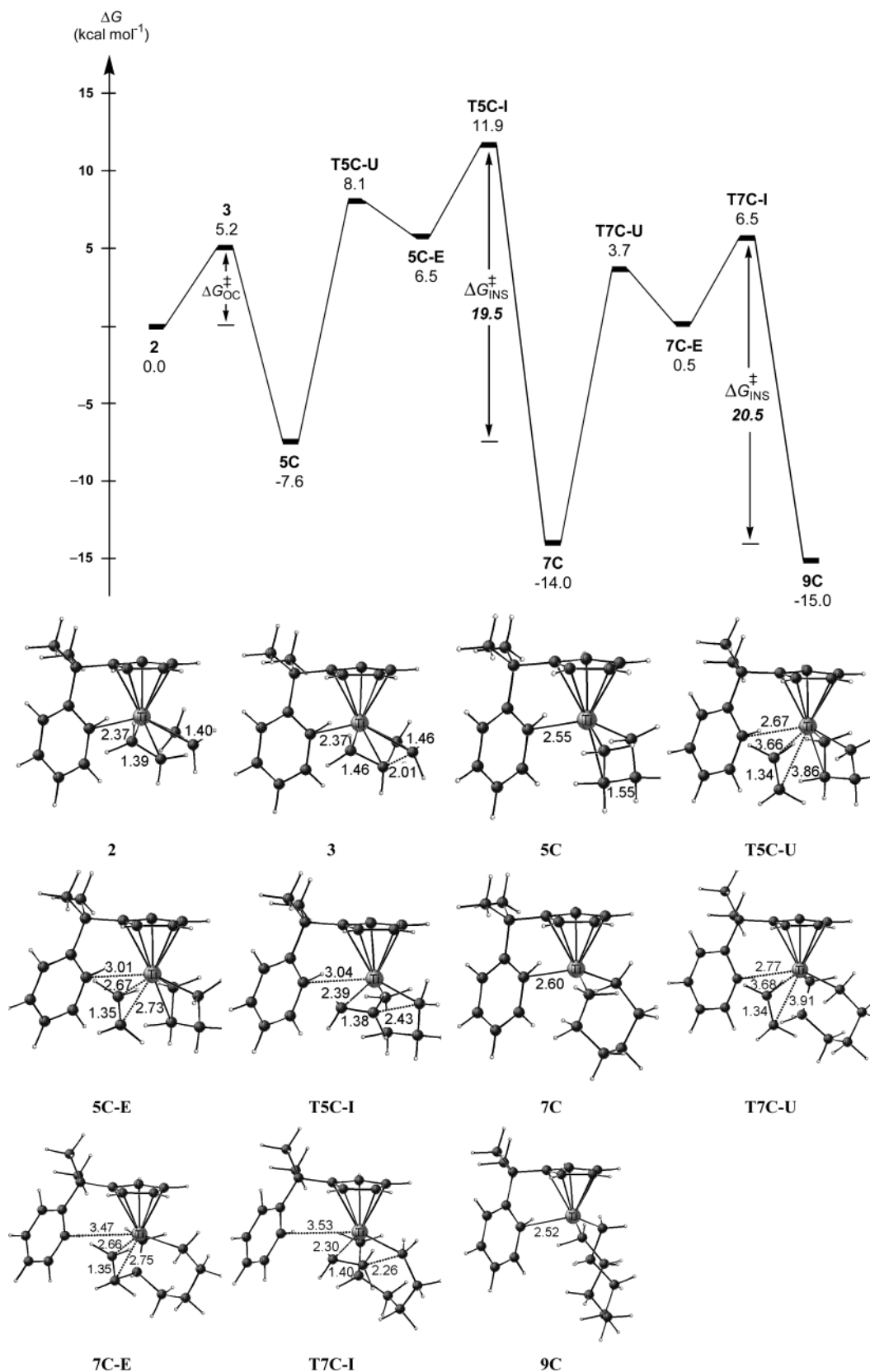
Figure 2. (Top) Gibbs free-energy profile (ΔG, $\Delta G^{\ddagger}$ in kcal mol^{-1}) of the reaction cascade for generation of titana(IV)cycle intermediates. Free energies are given relative to **2** corrected by the respective number of ethylene molecules. (Bottom) Optimized structures of involved key species.

reorientation is required along the favorable pathway for oxidative coupling. The transition state **3** is reached when the two moieties approach each other at a distance of ~2.01 Å. At this stage, the phenyl−Ti coordination

does not undergo any significant rearrangement; overall **3** appears educt-like. For the product **5C** of the oxidative coupling, however, distinct larger phenyl−Ti distances are found (cf. Figure 2), which indicates a much weaker

interaction in this case. This is understandable from the fact that the titanium atom undergoes an increase of its formal oxidation number by two ($Ti^{II} \rightarrow Ti^{IV}$) along the process. Accordingly, the stabilizing π-back-donation is significantly less pronounced, if not almost disrupted, in **5C**, giving rise to a weaker phenyl−Ti interaction when compared with **2**. The change in the coordination behavior of the phenyl group occurring along the **2** → **5C** oxidative coupling clearly illustrates the hemilabile character of its interaction with the titanium atom. This elucidates the role played by the ancillary arene ligand for stabilization of reaction intermediates, with the titanium in a low formal oxidation state.

The oxidative coupling is seen to be highly facile kinetically and accompanied by a free-energy barrier of 5.2 kcal mol^{-1} (**2** → **5C**, cf. Figure 2). The active catalyst species **2**, which is generated during the initial precatalyst activation (cf. Figure 1), is therefore likely to become readily transformed into **5C** by a process that is driven by a thermodynamic force of −7.6 kcal mol^{-1} (ΔG).

B. Increase of the Titana(IV)cycle's Size. Commencing from the titana(IV)cyclopentane **5C**, the generation of larger metallacycle intermediates occurs via a repeated sequence of consecutive elementary steps of ethylene uptake and insertion into the Ti^{IV}−C bond of the last generated titana(IV)cycle, with the Ti^{IV} formal oxidation state being preserved through the overall process. The free-energy profile of the reaction cascade for metallacycle generation up to the titana(IV)cyclononane **9C** is shown in Figure 2, together with a pictorial representation of important key species.

As evident from Figure 2, the key species for the uptake, as well as for the insertion process, display a structural characteristic that does not change remarkably with variation of the metallacycle's size. Ethylene uptake, in general, goes along with a displacement of the pendant phenyl ring from the immediate proximity of the titanium atom, to accommodate the incoming ethylene. Along the most feasible pathway, the ethylene preferably approaches perpendicular with respect to the terminal Ti−C bond of the titana(IV)cycle. The transition states for ethylene uptake, **T5C-U** and **T7C-U**, occur at a large distance between the incoming monomer and Ti^{IV}, with the phenyl ring indicated as still having a weak interaction with the titanium atom. Following the reaction path, next the ethylene π-complexes, **5C-E** and **7C-E**, are encountered, where the phenyl group is almost entirely displaced from the immediate coordination sphere of Ti^{IV}. The rather large ethylene−Ti^{IV} distance of ∼2.6−2.7 Å points to a weakly stabilized π-complex that may represent a transient intermediate along the overall process for increasing the size of the titana(IV)cycle.

For insertion to occur along the most feasible pathway, the ethylene moiety has to undergo rotation from a perpendicular to an in-plane orientation with respect to the terminal Ti^{IV}−C bond, into which insertion will take place. Insertion preferably proceeds through a transition state structure that is characterized by a quasi-planar four-membered cis arrangement of ethylene, the metallacycle's terminal Ti^{IV}−C bond, and the titanium atom, which occurs at a distance of ∼2.3−2.4 Å of the emerging C−C σ-bond for **T5C-I** and **T7C-I**, respectively. The pendant phenyl ring resides outside

the immediate coordination sphere of the titanium atom during the insertion process, but it becomes attached more closely to Ti^{IV} after the process has concluded with the formation of a new titana(IV)cycle intermediate.

The general trends analyzed so far on the basis of the structural characteristics of the involved key species are reflected in the energy profile (cf. Figure 2). The calculated reaction and activation free energies for individual elementary steps display an overall uniform behavior and are found to be mostly independent of the actual titana(IV)cycle intermediate involved. Ethylene uptake is accompanied with an activation free energy of 15.7−17.7 kcal mol^{-1} ($\Delta G^{\ddagger}$ for the **XC** + C_2H_4 → **XC-E** process, with **X** = **5**, **7**). The barrier originates to a large extent from the loss of translational and rotational degrees of freedom associated with olefin complexation (∼11 kcal mol^{-1}). The reorganization of the ancillary phenyl group, which is already weakly bound to Ti^{IV} in **5C** and **7C**, and of the metallacycle moiety due to the approaching olefin causes, however, an enthalpic barrier of only 4.8−6.8 kcal mol^{-1} ($\Delta H^{\ddagger}$ for the **XC** + C_2H_4 → **XC-E** process, with **X** = **5**, **7**). The ethylene π-complex is encountered next along the reaction path, which is only 1.6−3.2 kcal mol^{-1} lower in free energy than the corresponding transition state for uptake. Thus, the π-complex is likely to be formed in a reversible, endergonic process, which is found to be energetically unfavorable by 0.3−1.6 kcal mol^{-1} (ΔH for the **XC** + C_2H_4 → **XC-E** process, with **X** = **5**, **7**) at the enthalpic surface as well. This, together with the above analyzed structural properties, indicates the π-complex as a transient species, which is not likely to occur in an appreciable thermodynamic population under catalytic reaction conditions. Commencing from the π-complexes, **5C-E** and **7C-E**, a free-energy barrier of 5.4−6.0 kcal mol^{-1} has to be overcome for the final insertion step, which leads to **7C** and **9C**, respectively, in an exergonic step.

Considering the overall process to increase the size of the metallacycle, the generation of **7C** and **9C** gives rise to similar total barriers of 19.5 and 20.5 kcal mol^{-1} ($\Delta G^{\ddagger}$, relative to **5C** + C_2H_4 and **7C** + C_2H_4), respectively, for the final insertion step. The barrier can be attributed for the major part to the entropy contribution from the bimolecular ethylene uptake step. The formation of **7C** and **9C** also have similar thermodynamic driving forces with heat of reactions given by −6.4 and −1.0 kcal mol^{-1} (ΔG, relative to **5C** + C_2H_4 and **7C** + C_2H_4), respectively.[24] Accordingly, our investigation reveals a very similar energy profile for the successive enlargement of the titana(IV)cycle's size through ethylene uptake and insertion (cf. Figure 2). Almost independent of the actual titana(IV)cycle intermediate involved, the total free-energy barrier for this process is predicted to be ∼20.0 kcal mol^{-1}. This uniform behavior led us to conclude that five- and seven-membered titana(IV)cycles display similar abilities for increasing the metallacycle, in the absence of unfavorable steric interactions.

(24) (a) The smaller thermodynamic force connected with the formation of **9C** can be rationalized from the fact that the nine-membered ring represents the least favorable medium-sized ring. (b) See for instance: Allinger, N. L.; Cava, M. P.; de Jongh, D. C.; Johnson, C. R.; Lebel, N. A.; Stevens, C. L. *Organic Chemistry*; Worth: New York, 1976; p 40.

Scheme 2. Stepwise (top) and Concerted (bottom) Reaction Paths for Decomposition of Titana(IV)cycle Intermediates Affording α-Olefins, Exemplified for the Five-Membered Cycle
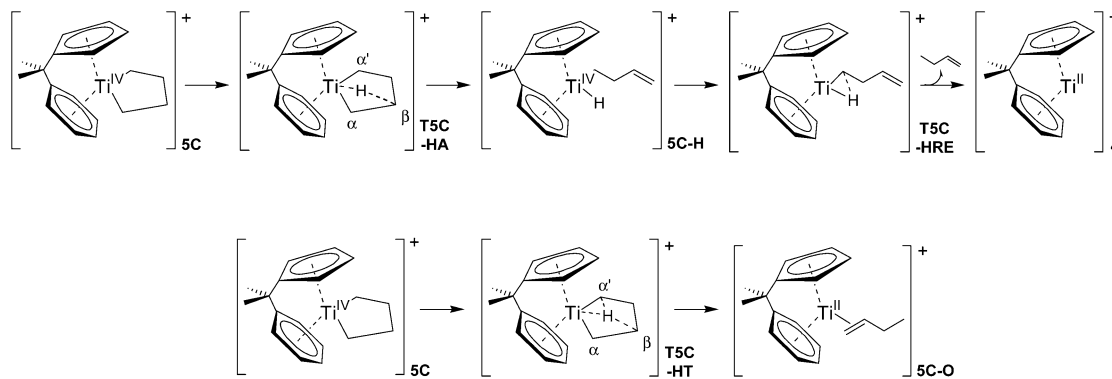
C. Decomposition of Titana(IV)cycle Intermediates under Ti^{IV} → Ti^{II} Reduction Affording α-Olefins. As already outlined in the Introduction, this reaction step can proceed according to two distinct mechanisms. The first mechanism involves β-H abstraction and subsequent reductive CH elimination along a stepwise reaction path, with an Ti^{IV}−alkenyl-hydride intermediate participating. The concerted transition-metal-assisted β-H transfer represents the second mechanistic alternative (cf. Scheme 2). Previous theoretical studies[15] did not entirely succeed in the attempt to localize the key species for the different reaction paths.[25] In this section, however, we report on the completely characterized minimum energy pathways for the two mechanisms for five- and seven-membered titana(IV)-cycles, while for the nine-membered intermediate we are entirely focusing on the kinetically favorable (vide infra) concerted path (cf. Figure 3).

Starting with the stepwise mechanism, the localized key species are found to be very similar in crucial structural aspects for the process to commence from different titana(IV)cycle intermediates. The transition state for β-H abstraction exhibits a hydrido−titanium bond that seems to be almost fully established already, together with an emerging olefinic subunit that is moving out of the coordination sphere of Ti^{IV}. Thus, **T5C-HA** and **T7C-HA** appear product-like. The transition state decays into a stable Ti^{IV}−alkenyl-hydride intermediate, where in the initially formed species, **5C-H** and **7C-H**, the alkenyl moiety is η^1-coordinated to Ti^{IV} by its alkyl terminus. These species can readily rearrange into thermodynamically more favorable isomers, e.g., into a Ti^{IV}−η^2-alkenyl-hydride species that is ∼7.0 kcal mol^{-1} (ΔG) more stable, which, however, are not encountered along the minimum energy pathway (vide infra). The relief of the steric pressure in the coordination sphere around the titanium atom in **5C-H** and **7C-H** is compensated for by the closer approaching phenyl ring, which here functions to saturate the coordination sphere around Ti^{IV}. An exploration of several pathways revealed **5C-H** and **7C-H** as the precursor for the subsequent reductive CH elimination to occur along the most feasible pathway. Following the reaction path the transition states **T5C-HRE** and **T7C-HRE** are reached at a distance of ∼1.81 Å of the emerging CH bond, giving rise to the [(η^5-C$_5$H$_4$-(CMe$_2$-bridge)-η^6-C$_6$H$_5$)Ti^{II}]$^+$ complex **4** under liberation of 1-butene and 1-hexene, respectively. For the second reductive elimination step, both the diminishing coor-

dination sphere around the titanium atom and the increasing Ti^{II}−phenyl back-donation interaction cause the closer approach of the pendant phenyl group.

The similarity in structural aspects, observed so far for the stepwise mechanism, is paralleled in the energetics of the process (cf. Figure 3). Accordingly, the predicted free-energy profile for five- and seven-membered titana(IV)cycle intermediates can reasonably be extrapolated to larger metallacycles, which led us to characterize the stepwise mechanism in a general way. The decomposition of titana(IV)cycloalkanes to afford α-olefins, which occurs in two consecutive steps, exhibits a double-valley profile, where almost identical activation barriers have to be overcome for the β-H abstraction (Δ$G^{\ddagger}$ 22.5−22.7 kcal mol^{-1}, for **TXC-HA** − **XC**, relative to **XC**, with **X** = **5**, **7**) and for reductive CH elimination (Δ$G^{\ddagger}$ 22.2−22.6 kcal mol^{-1}, for **TXC-HRE** − **XC**, relative to **XC**, with **X** = **5**, **7**). The intervening Ti^{IV}−alkenyl-hydrido species is separated by a free-energy barrier of only ∼1.5 kcal mol^{-1} from the educt and product sides. Accordingly, this intermediate is indicated as being highly active with a negligible stationary concentration. Furthermore, its rearrangement to more stable isomeric forms (vide supra) is less likely to take place for this short-lived species. The overall stepwise process, which includes the bimolecular liberation of the α-olefin, is calculated to be slightly exergonic (ΔG ≈ −3.0 kcal mol^{-1}).[26]

In a second instance, α-olefins are formed by titana-(IV)cycle decomposition occurring through a concerted β-H transfer (C$^{\beta}$ → C$^{\alpha'}$ hydrogen transfer), without a stable hydride intermediate involved. The corresponding transition state constitutes the synchronous hydrogen shift between the C$^{\beta}$ and C$^{\alpha'}$ carbons of the metallacycle taking place in close proximity to the titanium center (Ti−H distance of ∼1.7 Å, cf. Figure 3). As revealed for **T7C-HT** and **T9C-HT**, the favorable transition state

(25) For the process to commence from different titana(IV)cycle precursors, only one of the two alternative reaction paths has been able to be characterized computationally (cf. ref 15).

(26) It should be noted that a reaction path, different from the one reported in the present study, has been suggested by previous theoretical investigations (ref 15). The first β-H abstraction step bears resemblance in both structural and energetic aspects to our results, while a different pathway with a significantly higher barrier (Δ$G^{\ddagger}$ >31.0 kcal mol^{-1}, e.g., relative to **5C**) has been located for the reductive CH elimination. From this, it was concluded that the Ti^{IV}−alkenyl-hydrido intermediate should be present in an appreciable concentration and may play an important role in the catalytic reaction course. The reaction path presented in the present study, however, is indicated as being a more feasible alternative, with a short-lived Ti^{IV}−alkenyl-hydrido intermediate.
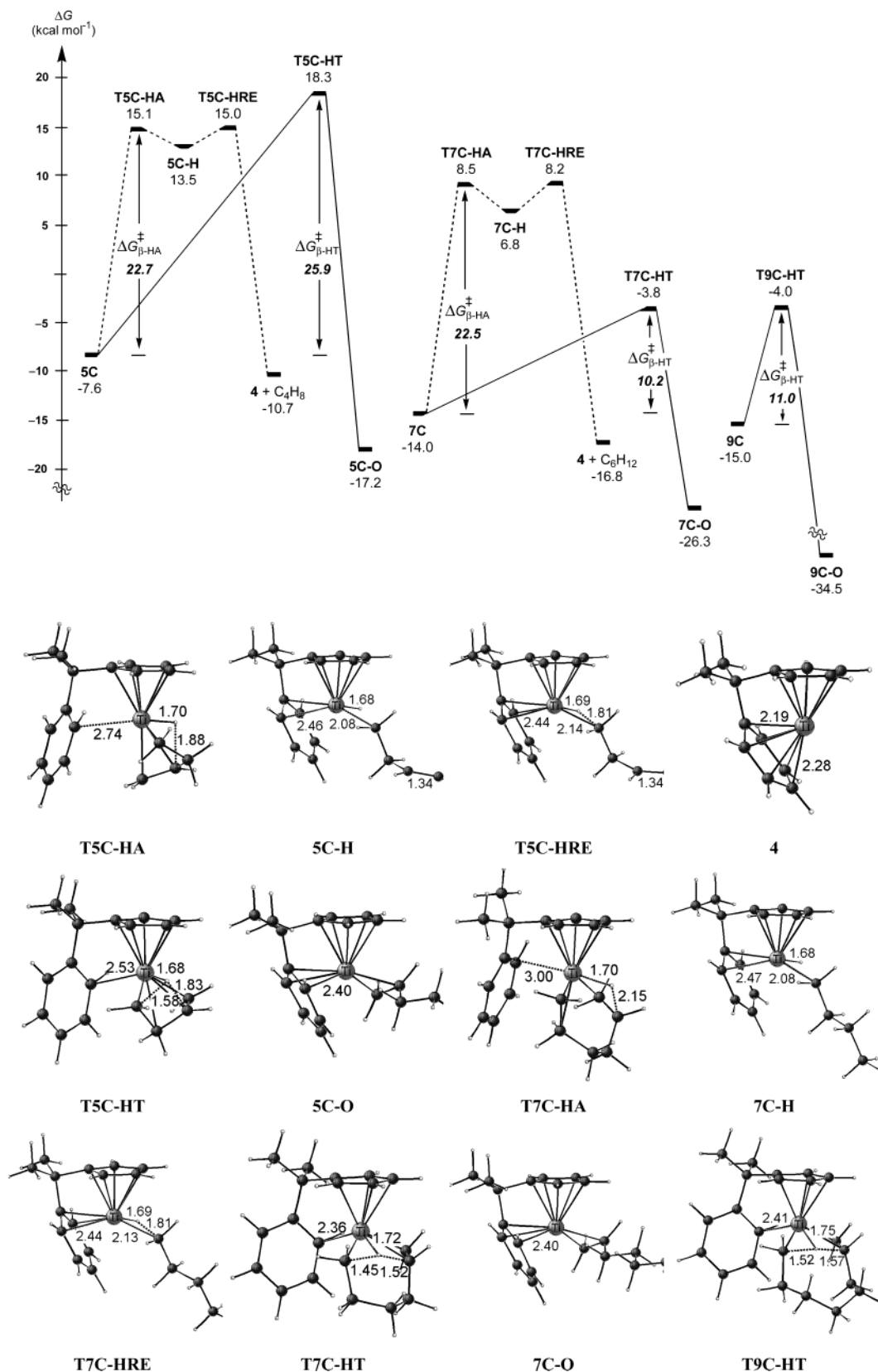
Figure 3. (Top) Gibbs free-energy profile (ΔG, $\Delta G^{\ddagger}$ in kcal mol^{-1}) for the generation of α-olefins through degradation of titana(IV)cycle intermediates, occurring via a concerted (—) and a stepwise (- - -) pathway (see the text). The relative energetics for the titana(IV)cycloalkane precursor species, viz., **5C**, **7C**, and **9C**, respectively, are taken from Table 1. (Bottom) Optimized structures of involved key species. Please note that the carbon chain is displayed in a truncated fashion for several of the nonmetallacyclic species.

structure is characterized by a quasi-planar arrangement of the TiC$^{\beta}$HC$^{\alpha\prime}$ fragment, where the transferring

hydrogen atom is at roughly equal distances from C$^{\beta}$ and C$^{\alpha\prime}$. This energetically preferred transition state

structure, however, cannot be accomplished for the structurally rigid five-membered titana(IV)cycle. **T5C-HT** exhibits a strong nonplanarity of the TiC$^\beta$HC$^{\alpha\prime}$ fragment and different C$^\beta$−H and C$^{\alpha\prime}$−H distances, which points to a high barrier connected with 1-butene formation along the concerted decomposition pathway. The synchronous β-H transfer is completed after crossing **T5C-HT**, **T7C-HT**, and **T9C-HT** with the formation of the Ti^{II}−1-butene, **5C-O**, Ti^{II}−1-hexene, **7C-O**, and Ti^{II}−1-octene, **9C-O**, product complexes, respectively, where the olefin is η^2-coordinated by its double bond to Ti^{II}. As this elementary step is accompanied with a decrease in the coordination sphere around the titanium, as well as with a reduction of the formal oxidation state of titanium by two (Ti^{IV} → Ti^{II}), the pendant phenyl group approaches at closer distances to the titanium atom in the Ti^{II}−olefin products.

As far as energetic aspects are concerned, very similar free-energy barriers of 10.2 and 11.0 kcal mol^{-1} have to be overcome along the concerted β-H transfer occurring in seven- and nine-membered titana(IV)-cycles, respectively. Similar barriers can be reasonably assumed for larger metallacycles. This lets us predict a barrier of ∼10.5 kcal mol^{-1} ($\Delta G^\ddagger$) for the step taking place via conformationally flexible metallacycles, starting with the titana(IV)cycloheptane. As already indicated by the unfavorable transition state structure, a significantly higher barrier of 25.9 kcal mol^{-1} ($\Delta G^\ddagger$) is connected with the rigid five-membered metallacycle. The Ti^{II}−olefin products are formed in an exergonic process, driven by a thermodynamic force of ca. −(10−20) kcal mol^{-1} (ΔG), from which the α-olefins are readily displaced by an incoming ethylene under recreation of **2**.

To summarize, the decomposition of titana(IV)cycloalkanes following the alternative reaction paths for generation of α-olefins is seen to exhibit different characteristics with the variation of the metallacycle's size. On one hand, an almost uniform behavior of both structural and energetic aspects is revealed for the process occurring in a stepwise fashion, while the ability to undergo the concerted β-H transfer is found to be strongly dependent on the conformational flexibility of the involved titana(IV)cycle. The concerted β-H transfer is predicted to be the operative mechanism for seven-membered and larger titana(IV)cycle intermediates, which is connected with a free-energy barrier of 10.2−11.0 kcal mol^{-1}. Similar barriers are suggested for larger titana(IV)cycles, which points to nearly uniform rates for decomposition of titana(IV)cycles starting with **7C**. The stepwise mechanism, which requires significantly higher barriers ($\Delta\Delta G^\ddagger$ > 12.0 kcal mol^{-1}), is clearly seen to be kinetically unfavorable in these cases. For the rigid five-membered titana(IV)cycle to decompose, however, the stepwise mechanism, with a largest overall activation free energy of 22.7 kcal mol^{-1}, is indicated to be slightly preferred over the concerted path.

D. Decomposition of Titana(IV)cycle Intermediates under Ti^{IV} → Ti^{II} Reduction Affording Cycloalkanes. Formation of cycloalkanes, taking place via reductive CC elimination under ring closure commencing from the metallacycle intermediates, is a possible side process that competes with α-olefin generation (cf. section II.C). The free-energy profiles, as well as the pictorial representations of the key species, for the process to commence from **5C**, **7C**, and **9C**, respectively, are shown in Figure 4.

The cycloalkanes are generated by the formation of a C−C σ-bond between the terminal C$^\alpha$ and C$^{\alpha\prime}$ carbons of the titana(IV)cycle intermediates. The transition states **T5C-CC**, **T7C-CC**, and **T9C-CC**, which are quite similar in critical structural features, appear at a distance of ∼2.1−2.2 Å for the newly formed bond. The product-like transition states, with an essentially completed cycloalkane that is already slightly displaced from the titanium, decay into **4** with the liberation of the respective cycloalkane.

The reductive CC elimination is seen to be a kinetically difficult process that requires an activation free energy of 29.6, 24.9, and 27.4 kcal mol^{-1} for five-, seven-, and nine-membered titana(IV)cycloalkanes. This points to the reductive CC elimination as an unfeasible side process, which is kinetically disfavored relative to the hydrogen shift, occurring in either a concerted or stepwise fashion. As a consequence, the favorable route for titana(IV)cycle decomposition leads predominantly to α-olefins.[27] The formation of cycloalkanes, however, should be almost entirely precluded due to kinetic considerations, even in the case of the thermodynamically favorable cyclohexane. Our findings are consistent with the experimental observation[13] that the product mixture does not contain any detectable amount of cycloalkanes.

III. The Entire Catalytic Reaction Course. A. Free-Energy Profile. On the basis of the careful theoretical exploration of crucial elementary steps, reported in previous sections, we are now able to present the free-energy profile of the catalytic reaction course (cf. Scheme 3). It consists of the most feasible pathways for each of the crucial elementary steps for the selective linear oligomerization of ethylene to 1-hexene. The ethylene insertion into the titana(IV)cyclopentane is connected with the overall highest activation barrier of all crucial elementary steps and is therefore predicted as being rate-controlling. The originally proposed mechanism[13a,b] is confirmed in essential details, but supplemented by novel insights into the selectivity control of the oligomerization process (based on the analysis presented in sections II.B and II.C, respectively) as well as into the role played by the pendant arene ligand. This will be the issue addressed in the following section.

B. Interrelation between Titana(IV)cycle's Growth and Decomposition: Implications for the Selectivity of the Linear Ethylene Oligomerization. The thermodynamically determined abundance of the titana(IV)cycle intermediates and their ability (1st) to increase their size by ethylene uptake and insertion and (2nd) to decompose affording α-olefins are the crucial aspects that require investigation, for the elucidation of the selectivity of the ethylene oligomerization process.

5C is readily accessible after precatalyst activation through the facile oxidative coupling. Decomposition of **5C** to yield 1-butene, which is most likely to occur in a stepwise fashion, is indicated as a slow, kinetically

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(27) Ethylene/1-hexene C$_{10}$-co-trimer products, with 5-methylnon-1-ene in particular, are formed as minor products as well, which, however, are not considered in the present study (cf. ref 13d).
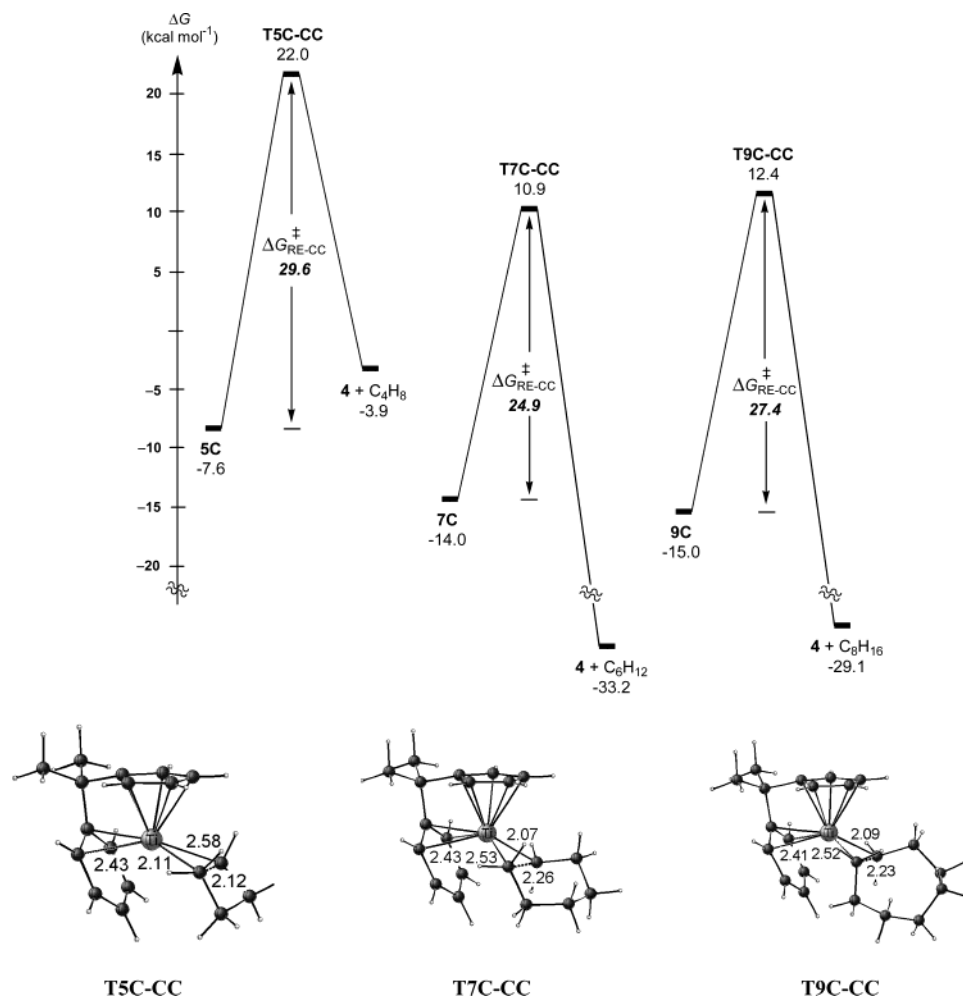
Figure 4. (Top) Gibbs free-energy profile (ΔG, $\Delta G^{\ddagger}$ in kcal mol^{-1}) for the generation of cycloalkanes through degradation of titana(IV)cycle intermediates. The relative energetics for the titana(IV)cycloalkane precursor species, viz., **5C**, **7C**, and **9C**, respectively, are taken from Table 1. (Bottom) Optimized transition state structures.

unfavorable step that requires a significant barrier ($\Delta G^{\ddagger}$ = 22.7 kcal mol^{-1}). Accordingly, the ethylene uptake and insertion, although they suffer from additional entropy costs, are predicted to be kinetically preferred by 3.2 kcal mol^{-1} ($\Delta\Delta G^{\ddagger}$) over the metallacycle decomposition for the five-membered titana(IV)cycle. Therefore, the production of 1-butene is kinetically almost precluded, which agrees with experimental findings.

For **7C**, however, the decomposition to 1-hexene becomes significantly accelerated along the now accessible concerted β-H transfer path ($\Delta G^{\ddagger}$ = 10.2 kcal mol^{-1}). The increase of the metallacycle via **7C** + C$_2$H$_4$ → **9C** requires a barrier very similar to the **5C** + C$_2$H$_4$ → **7C** process ($\Delta G^{\ddagger}$ = 20.5 kcal mol^{-1}). This indicates that further metallacycle growth is unlikely. As a consequence, (1st) **7C** is the largest titana(IV)cycle occurring in appreciable concentrations during the reaction course, while the appearance of larger cycles should be almost kinetically prevented, and (2nd) among the several ethylene oligomers, 1-hexene is the α-olefin that is almost exclusively produced. Additional support for these conclusions comes from the experimental observation of C$_{10}$-olefins as minor products.[27]

The competition between the unimolecular decomposition and the bimolecular growth of the titana(IV)cycles is clearly seen as the discriminating factor for the selec-

tivity of the ethylene oligomerization. The difference in the respective activation barriers is predicted to 10.4 kcal mol^{-1} ($\Delta\Delta G^{\ddagger}$) for the seven-membered cycle, an estimate based on gas-phase entropies. The entropies in solution are likely to decrease to approximately half of the gas-phase value, as reported in a recent theoretical study.[28] Taking this into account for the bimolecular growth step, the gap would then become reduced to ~3.0 kcal mol^{-1} ($\Delta\Delta G^{\ddagger}$), with formation of 1-hexene still being preferred.

The nearly uniform rates for growth (r_{MG}) and decomposition (r_{MD}) of seven-membered and larger titana(IV)cycles (cf. sections II.B and II.C) led us to suggest the following conclusion. Provided that $r_{MG} \sim r_{MD}$ could be realized for the seven-membered and larger cycles,[29] the formation of titana(IV)cycle intermediates would not stop after **7C**, but the selectivity would decrease significantly, if not become almost fully lost, as a statistical distribution of linear α-olefins starting with 1-hexene would be expected.

The hemilabile phenyl ring is clearly indicated to play a critical role for the oligomerization process. It serves

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(28) Cooper, J.; Ziegler, T. *Inorg. Chem.* **2002**, *41*, 6614.
(29) This could be accomplished by the retardation of the β-H transfer and/or acceleration of the metallacycle growth, e.g., by increasing the ethylene pressure.

Scheme 3. Gibbs Free-Energy Profile (ΔG, $\Delta G^{\ddagger}$ in kcal mol^{-1}) of Crucial Elementary Steps of the Selective Linear Oligomerization of Ethylene to 1-Hexene by the Cationic [(η^5-C$_5$H$_4$-(CMe$_2$)-bridge)-C$_6$H$_5$)Ti^{II}-(ethylene)$_2$]$^+$ Active Catalyst[a]
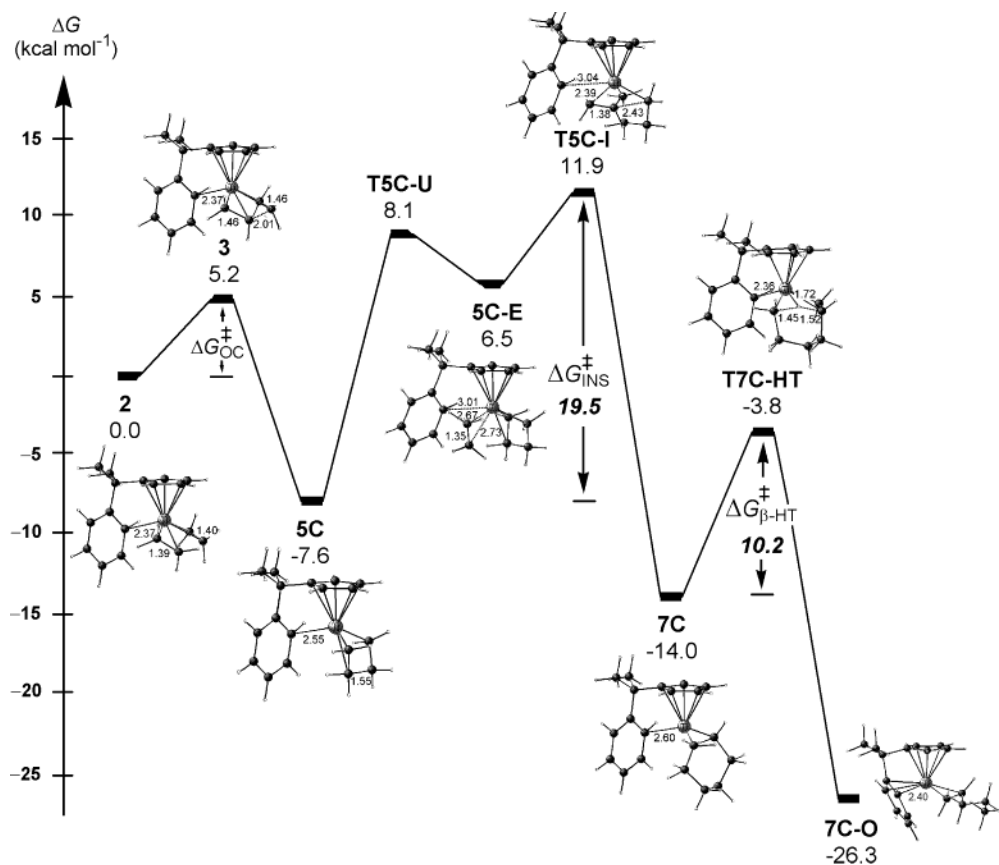
[a] Free energies are given relative to **2** corrected by the respective number of ethylene molecules.

to stabilize the low formal Ti^{II} oxidation state through a significant back-bonding interaction, thus making the oligomerization route via titana(IV)cycle intermediates, involving a repeated Ti^{II} ⇌ Ti^{IV} change, operable. In the absence of the pendant phenyl group, however, this route should be almost entirely inaccessible, since the Ti^{IV} state is likely to be kept during the overall process. Instead the Cossee−Arlman mechanism is operative in this case, with the Ti^{IV}−alkyl bond being involved in chain propagation and termination. As outlined in the Introduction, this gives rise to a statistical distribution of α-olefins and/or to polymers, which rationalizes the experimental findings for the catalyst with a methyl group instead of the phenyl ring (cf. the Introduction). Accordingly, different species, i.e., Ti^{II}−(ethylene)$_2$ and Ti^{IV}−(alkyl)$_x$, respectively, are proposed as the active catalyst complexes, responsible for the switch between ethylene oligomerization and polymerization activity in these two cases. This will be the subject of forthcoming investigations.

Concluding Remarks

We have presented a detailed theoretical investigation of crucial elementary steps of the selective linear oligomerization of ethylene to 1-hexene by the cationic [(η^5-C$_5$H$_4$-(CMe$_2$)-bridge)-C$_6$H$_5$)Ti^{IV}(CH$_3$)$_2$]$^+$ precatalyst, employing a gradient-corrected DFT method. The originally proposed mechanism[13a,b] has been confirmed in essential details, but supplemented by novel insights

into how the selective ethylene oligomerization operates. This includes the examination of the ability of titana-(IV)cycle intermediates to grow and/or to decompose affording α-olefins as a function of their size, the prediction of the favorable route for precatalyst activation, and the exploration of the cycloalkane production as a possible side process. Our present study therefore extends the mechanistic understanding gained from previous theoretical investigations.[15]

Precatalyst activation to afford the Ti^{II}−(ethylene)$_2$ active catalyst complex, which involves the following sequence of elementary steps—viz., ethylene insertion into the Ti^{IV}−Me bond, the concerted reductive β-H transfer under liberation of methane, and subsequent propylene displacement by ethylene together with uptake of a second ethylene moiety—along the most feasible route, is seen to be a smooth process with the largest overall barrier being lower than the discriminating barrier during the oligomerization reaction course. Accordingly, the initial Ti^{IV}−Me$_2$ precatalyst to active Ti^{II}−(ethylene)$_2$ catalyst complex conversion should not affect the overall catalytic activity.

The first titana(IV)cyclopentane species is generated by a highly facile ($\Delta G^{\ddagger}$ = 5.2 kcal mol^{-1}) exergonic oxidative coupling of the two coordinated ethylene moieties. For small to medium titana(IV)cycle intermediates their growth is indicated to be taking place at nearly uniform rates requiring an activation free energy of 19.5−20.5 kcal mol^{-1}. The barrier is seen to be mainly attributed to the entropy costs for the bimolecular uptake step.

The decomposition of titana(IV)cycle intermediates to α-olefins, however, displays a different trend as a function of the metallacycle's size. The concerted transition-metal-assisted β-H transfer is the operative mechanism for conformationally flexible metallacycles starting from the seven-membered cycle. Nearly identical barriers ($\Delta G^{\ddagger} = 10.1-11.0$ kcal mol^{-1}) for decomposition of seven- and nine-membered titana(IV)cycles, which can reasonably be extrapolated to larger ones, point to comparable rates in these cases. For the rigid titana(IV)cyclopentane the concerted pathway is kinetically disabled. Instead, the stepwise mechanism via a meta-stable Ti^{IV}−alkenyl-hydride intermediate becomes prevalent, which is shown not to be operative for larger metallacycles. The stepwise path is accompanied with a significantly higher barrier ($\Delta G^{\ddagger} = 22.7$ kcal mol^{-1}), such that the bimolecular increase to the titana(IV)cycloheptane is kinetically superior to the competitive 1-butene formation.

On the basis of these general insights into the ability of titana(IV)cycles either to grow or to decompose into α-olefins, the thermodynamic and kinetic aspects that decisively control the selectivity of the linear oligomerization of ethylene have been rationalized.

The formation of cycloalkanes, via the competing reductive CC elimination under ring closure occurring from the titana(IV)cycle intermediates, should be almost entirely precluded due to kinetic considerations, which agrees with experiment findings.

The experimentally suggested hemilabile character of the pendant arene group is confirmed by our investigations. Its role for the selective oligomerization process has been elucidated. Two important aspects are revealed from the present investigation. The phenyl group acts (1st) as a counterbalance for the reduction and the increase of the coordination sphere around the titanium atom that accompanies the several elementary steps and (2nd) to stabilize the low formal Ti^{II} oxidation state through a significant back-bonding interaction, thus making the oligomerization occurring via metallacycle intermediates operable. Furthermore, the switch from the selective ethylene trimerization to the statistical oligomerization and/or polymerization activity, which is observed experimentally for the class of catalysts investigated here that lack the coordinating arene functionality, has been rationalized.

Supporting Information Available: Full descriptions of the geometry of all reported species (Cartesian coordinates in Å). This material is available free of charge via the Internet at http://pubs.acs.org.

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