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Strength of the Metal–Olefin Bond in Titanium Complexes Related to Ziegler–Natta Catalysis. A Theoretical Model Study of a Square-Pyramidal Active Center Postulated To Be Found in Titanium Halide Based Catalysts

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Calculations, generally including correlation effects of all valence electrons and using extended atomic basis sets, were performed on square-pyramidal (SP) models of the active center in a heterogeneous titanium halide based Ziegler–Natta catalyst. All our calculations reveal a weak complexation between ethylene and titanium. Coordinating ethylene to the SP active center, TiX_5^{n-} (X = Cl, F, H; $n = 1, 2$), gives binding energies between 7 and 11 kcal/mol and a titanium–ethylene bond distance of 2.80 Å at the MCPF level. Allowing for relaxation of the SP active center to a trigonal-bipyramidal geometry makes ethylene coordination unfavorable. Only minor differences were found when comparing the ethylene binding energies in Ti(IV) and Ti(III) model complexes. Formaldehyde, included to represent carbonyl-type moderators, has 15–20 kcal/mol higher binding energy than ethylene in complexes such as $TiF_2H_2(CH_2O)(C_2H_4)$. Our results are compared to recent calculations on various model homogeneous catalysts, and special attention is paid to the charge and rigidity of the active centers.

1. Introduction

Polymerizations of olefins by Ziegler–Natta catalysts are unusual reactions for several reasons. They are extremely fast,[1–4] yield long molecular chains, and may proceed with a stereospecificity that is higher than any other nonenzymatic reaction.[5] It is therefore natural that the mechanisms of Ziegler–Natta polymerization have been subjected to numerous studies. Several reasonable mechanistic schemes have been suggested,[6–9] but even basic parts of the process, such as the olefin coordination strength and the action of moderators, need further investigation. In the present paper, we will mainly discuss the Cossee mechanism,[6] which is the most widely accepted. In this mechanism, the active transition-metal complex has a square-pyramidal structure (SP, an octahedron with a vacant site) and one alkyl group (the growing polymer chain) as a ligand. The remaining ligands may be halide ions. The first step of the propagation, which is the scope of the present study, is, according to the Cossee mechanism, the coordination of the monomer to the vacant site on the octahedral metal complex. Cossee assumed that π back-donation from the metal is important for the bond formation. In the second step, the monomer inserts into the metal–alkyl bond, presumably via a four-center transition state involving the alkyl group, the alkene, and the transition metal. The Cossee mechanism was postulated to be valid for both homogeneous and heterogeneous halide-based catalysts,[6] but the assumed structure of the active center has been used mainly for heterogeneous $TiCl_3$-based or $MgCl_2$-supported catalysts. Corradini et al.[10] have described how five-coordinate SP active centers, as found in the Cossee model, may be formed and bridged to lateral cuts on the support.

Because titanium catalysts have been widely used in Ziegler–Natta polymerization, and because intermediate complexes are difficult to observe experimentally, a large number of quantum chemical calculations on titanium–alkene systems have been performed. In early CNDO[11,12] and SCF-Xα-SW calculations,[13] the importance of π back-

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donation was questioned. Ab initio calculations on $TiCl_2(CH_3)(C_2H_4)(\mu\text{-}Cl)_2Al(CH_3)_2$[14,15] also suggest that back donation is unimportant and that the titanium–ethylene bond is weak (3–4 kcal/mol). A similar result was obtained for the anionic $[TiCl_4(CH_3)(C_2H_4)]^-$ with the paired interacting orbital (PIO) method.[16]

The development of very active homogeneous titanocene and zirconocene Ziegler–Natta catalysts has been the background for several quantum chemical studies during the last years. Calculations on the cationic complexes $[MCl_2(CH_3)(C_2H_4)]^+$ (M = Ti, Zr) indicate a much stronger interaction between the metal and the olefin than the earlier calculations mentioned above. Ethylene coordination energies of 33–49 kcal/mol are reported for these cationic models.[17–20] Recently, a calculated ethylene coordination energy of 33 kcal/mol has also been reported for the very realistic model catalyst $[Zr(SiH_2Cp_2)CH_3(C_2H_4)]^+$.[21] Positively charged centers are generally seen to have a larger attraction on the olefin. Recent calculations[22] have shown that the positive charge reduces the amount of repulsive s,p-electrons on the metal and also exerts a charge-induced dipole force on the olefin. The importance of reducing the amount of repulsive s,p-electrons is also seen in calculations on Ziegler–Natta olefin insertion for second-row transition metals.[23,24]

In addition to the charge of the complex and the nature of the auxiliary ligands, the oxidation state of titanium should be of importance. In a PIO study of $[TiCl_4(CH_3)(C_2H_4)]^{n-}$, where $n = 1$ (Ti(IV)) and 3 (Ti(II)),[16] the calculated ethylene bond strength is larger for the Ti(II) complex due to π back-donation, which was found to be small in the Ti(IV) complex. The strength of the metal–alkene bond in Ti(II) complexes is demonstrated by the fact that the only stable titanium–ethylene complex isolated so far is a Ti(II) complex.[25] Ti(II) intermediates, however, are unlikely in Ziegler–Natta catalysis. In contrast, there is considerable experimental evidence (e.g., EPR measurements[26]) that active centers may contain Ti(III). Titanium(III) complexes would be expected to be intermediate between Ti(II) and Ti(IV) with regards to bond strength and the amount of π back-donation. This assumption is supported by extended Hückel,[27] HF-Slater,[28] and SCF-Xα-SW[29] calculations. In order to check if this difference between Ti(III) and Ti(IV) is real, we performed ab initio calculations at the correlation level of the binding energy and π back-donation in octahedral complexes $[TiX_5(C_2H_4)]^{n-}$, where $n = 1$ (Ti(IV)) and 2 (Ti(III)) and X = Cl, F, and H. This work is the most advanced quantum chemical study of any six-coordinate Ti(III) or Ti(IV) ethylene complex presented so far.

Another important aspect is whether the complexation of ethylene on the active centers can compete with the complexation of Lewis bases present in the reaction medium. For example, $MgCl_2$-supported catalysts for polymerization of propylene to isotactic polymer generally include Lewis bases as promoters and moderators. Bases are partly included in the solid catalysts themselves, but Lewis bases are also added to the liquid phase to improve stereoregularity of the polymer.[30] A common Lewis base is ethyl benzoate,[31,32] but other aromatic esters[33] and silanes[34] are also used. Although experimental evidence[31,35] shows that, in the final catalyst, the Lewis bases tend to coordinate to Mg and not to $TiCl_4$, it is very likely that there may be Lewis bases available to compete for the acidic sites at the catalytic centers.[9] In fact, these bases may form stable complexes with $TiCl_4$.[31] With this in mind, it is of interest to study the relative stability of Lewis base complexes and monomer complexes. It also seems plausible that such modifiers may increase the reactivity of the catalysts by inducing formation of cationic species by displacement of chloride. In this paper, we present the first ab initio calculations dealing with the role of Lewis bases in the Ziegler–Natta process. In this work, we have chosen CH_2O as a model for the η^1-bonding ester ligands.[36] By employing model complexes of the type $[TiF_xH_2(CH_2O)_y(C_2H_4)_z]^{2-x}$ $(x + y + z = 4)$ (**1**–**5**) and SP $TiF_2H_2(CH_2O)$ (**6**), we can compare the binding energy of a model carbonyl Lewis base (formaldehyde) with halide ions (fluoride) and the monomer (ethylene).

All the model active centers used in the present work are SP, and are close to what is postulated to be the case in titanium halide based catalysts. Our results from the calculations on ethylene coordination to the model compounds described above are compared to recent calculations on various model homogeneous catalysts.[17–20] Such comparisons should be of interest since the construction of model homogeneous active centers is based on far more precise structural information than what is possible for model heterogeneous active centers as the ones used used in the present study. Special attention in these comparisons is paid to the charge and to the rigidity of the model active centers.

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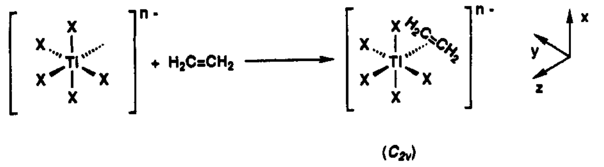

Figure 1. Ethylene coordination to the square-pyramidal model active center TiX_5^{n-} (X = F, Cl, H; n = 1, 2 (Ti(IV) and Ti(III), respectively)).

Table 1. Bond Distance Ti–X,[a] Reaction Energies for the Reaction $TiX_5^{n-} + C_2H_4 \rightarrow [TiX_5(C_2H_4)]^{n-}$, Net Metal Charge, q_M, and Mulliken 3d Populations of $[TiX_5(C_2H_4)]^{n-}$ [b,c]

X	n	ox. state	symmetry	Ti–X	ΔE_{SCF}	ΔE_{MCPF}	q_M	3d population
F	1	IV	$^1A_1$	1.84	–9.4	–9.1	1.2	–2.1
F	2	III	$^2B_1$	1.98	–3.7	–6.9	1.4	–2.0
Cl	1	IV	$^1A_1$	2.35	–8.2	–10.7	–0.1	–2.8
Cl	2	III	$^2B_1$	2.49	–4.5	–10.2	0.5	–2.4
H	1	IV	$^1A_1$	1.78	–4.9	–8.2	0.0	–2.0
H	2	III	$^2B_1$	1.95	–5.2	–8.1	–0.1	–2.1

[a] Partially optimized. [b] From MCPF calculations. [c] The distance Ti-BMP was set to 2.80 Å. BMP denotes the C–C bond midpoint. The value 2.80 Å is in accordance with reaction coordinate calculations (Figure 2). Units: energies, kcal/mol; distances, Å; populations, e.

2. Results and Discussion

The computational details can be found in the Appendix.

2.1. Ethylene Coordination to Model Complexes TiX_5^{n-}. In the calculations, SP complexes TiX_5^{n-}, where X = F, Cl, and H and n = 1 and 2 (Figure 1), were used as models for the active center. The bond lengths were partially optimized (see the Appendix for details) at the SCF level, with all Ti–X bonds being equal to reduce the complexity of the calculations. All angles were fixed at 90°, which is rationalized by considering formation of chloride bridges to the support surface in a heterogeneous catalyst. In a real catalytic center, one of the ligands must be an alkyl or a hydride, but it is unlikely that this will have a large influence on the binding of ethylene. Another deviation from a real catalyst system is that the support itself is not modeled, giving rise to negatively charged complexes. The total charge of the complex determines the oxidation state of titanium, n = 1 giving Ti(IV) and n = 2 giving Ti(III).

In order to study the potential surface of ethylene coordination and to determine the equilibrium titanium–ethylene bond length, we first performed calculations on $[TiF_5(C_2H_4)]^{n-}$ by varying the Ti-BMP (BMP denotes the ethylene C–C bond midpoint) distance, keeping constant the partially optimized SP TiF_5^{n-} geometries given in Table 1. The SCF approximation is known not to provide a satisfactory description of the metal–olefin bond,[24] and thus the potential surface of ethylene coordination was determined at the MCPF level. We used a planar ethylene geometry with a C–C bond of 1.35 Å, equivalent to that in free ethylene. The results are presented in Figure 2 as the energy relative to infinite Ti–ethylene separation. In the next step the equilibrium titanium–ethylene bond length calculated for $[TiF_5(C_2H_4)]^{n-}$ (2.80 Å) was used in the calculations on $[TiX_5(C_2H_4)]^{n-}$, where X = Cl and H and n = 1 and 2. The calculated reaction energies, net metal charge, and 3d populations are shown in Table 1.

The potential surface of ethylene coordination in Figure 2 is quite flat for both oxidation states, and there is no barrier to coordination. There is an energy minimum at about 2.80 Å for both oxidation states (with the complexation energies 6.9 and 9.1 kcal/mol for Ti(III) and Ti(IV), respectively), although the bond distance is not very definite. This is a much longer titanium–ethylene bond length than the 2.04 Å found by X-ray diffraction studies of $Ti^{II}(C_5(CH_3)_5)_2(C_2H_4)$,[25] suggesting a significant difference between Ti(II) and the two higher oxidation states. It is also much longer than the bond length suggested by Corradini et al.[37,38] for heterogeneous catalysts promoting stereoregular polymerization of propylene, using models quite similar to the ones in the present study. With the weak metal–olefin interaction, coordinated ethylene should have a relaxed geometry very close to the geometry of free, unperturbed ethylene. For the shortest complexation distance investigated (2.30 Å), the binding energy, assuming a longer C–C bond length (1.40 Å) and a back-bending of the hydrogens (12.9°), was also calculated. This gave 2 kcal/mol higher energy for both Ti(III) and Ti(IV) compared to calculation with planar unperturbed ethylene, thus demonstrating that ethylene is close to unperturbed upon coordination to titanium. With an exception for the shortest bond length investigated (2.30 Å), the complexation is stronger for the Ti(IV) complex than for the Ti(III) complex. Close to the equilibrium bond distance 2.80 Å, the difference in stability is 2.2 kcal/mol in favor of Ti(IV).

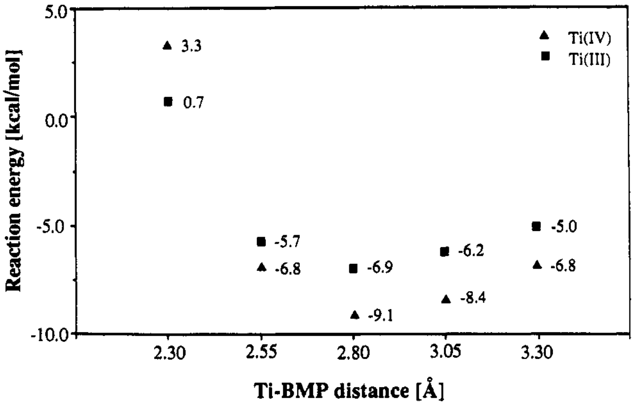

Figure 2. Reaction coordinate diagram of ethylene coordination to square-pyramidal TiF_5^{n-} (n = 1, 2 (Ti(IV) and Ti(III), respectively)). The reaction energies (kcal/mol) are at the MCPF level, and are given relative to infinite titanium–ethylene separation.

Ethylene complexation to the model active centers TiX_5^{n-} is generally found to be rather weak. All the coordination energies in Table 1 fall between 7 and 11 kcal/mol. The same difference between the two oxidation states seen in $[TiF_5(C_2H_4)]^{n-}$ is, although of varying size, also seen for the other complexes. Calculations on neutral complexes of the two oxidation states confirm the difference: the coordination energies of ethylene to SP $TiFH_2(CH_2O)_2$ (Ti(III)) and $TiF_2H_2(CH_2O)$ (Ti(IV)) are 9.8 and 14.2 kcal/mol, respectively.[39] Including more correlation energy through augmentation of the basis set with polarization functions on all atoms in the hydride complexes $[TiH_5(C_2H_4)]^{n-}$, the binding energy was found to be slightly higher for the Ti(III) (10.8 kcal/mol) than for

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(39) The Ti(IV) complex is identical to structure **3** in Figure 3. The construction of both complexes was based upon the gradient-optimized structure **3′** (Table 3).

the Ti(IV) complex (10.1 kcal/mol). Thus, the ultimate conclusion to draw from the results in Table 1 seems to be that Ti(IV) and Ti(III) have an almost equal ability to bind ethylene.

It should be noted that the reported populations and charges of the Ti–ethylene complexes in Table 1 are close to those calculated for the SP reactant fragments TiX_5^{n-}, thus indicating that only small electronic rearrangements are involved in the reactions. A small σ donation (0.1–0.2 electron) from the ethylene π orbital to the metal is, however, observed. There is almost no π back-donation in the Ti(IV) complexes, whereas the back-donation amounts to 0.1 electron at 2.30 Å for $[TiF_5(C_2H_4)]^{2-}$. This effect probably explains why the Ti(III) complex is more stable than the Ti(IV) complex at 2.30 Å. At longer Ti–BMP distances there is almost no interaction between d_{yz} on Ti and π^* on ethylene. Thus, at the longer binding distances, the ethylene coordination strength seems to be governed by the Lewis acid strength of the respective titanium complex.

It is interesting to compare these results with the experimental observation that the IR carbonyl stretching frequencies of η^1-coordinate esters are lower for $TiCl_4$ than for $TiCl_3$,[40–42] indicating a stronger ester coordination to the Ti(IV) complex. In the present results, ethylene coordinates almost equally strongly to Ti(IV) and Ti(III). η^1-bonded carbonyl is a quite pure σ donor,[36] and it seems as if the somewhat weaker ethylene σ donation toward Ti(III) is compensated for by a larger π back-donation from the metal, thus resulting in the almost similar binding energies for the two oxidation states.

A few words should be mentioned about the populations reported in Table 1. As can be seen, the net metal charge is higher on Ti(III) than on Ti(IV), which seems puzzling. This is mainly an artifact from the Mulliken population analysis, which is not always completely reliable. A small part of the effect could also be caused by the longer Ti–X distances in the Ti(III) complexes. Adopting the $TiCl_5^{2-}$ bonding distances to $TiCl_5^-$ increases the net metal charge by an amount of 0.2. However, careful analysis of our calculations also shows that changes in the formal charge on the metal atom may, at least for the complexes studied, be compensated for by changes in the π donation from the ligands.

Looking at the relatively small ethylene coordination energies in Table 1, it is evident that another problem must be considered, and that is how rigid the active center should be for the complexation to take place. The coordination energies are considerably lower than the energy (23.1 kcal/mol[43]) required to force a totally relaxed five-coordinate reactant, which has a trigonal-bipyramidal (TBP, D_{3h}) configuration, into a SP (C_{4v}) structure. This makes ethylene coordination to TBP titanium seem unfavorable, and in fact, no bonding between this totally relaxed TBP fluoride complex and ethylene was found at the SCF level of theory. However, this may be counteracted by the presence of chloride bridges to the support, preserving the SP structure of the active center.

Several simplifications regarding the geometries are made, and it is necessary to check the geometries and how the simplifications influence the energy evaluations. The experimentally determined Ti–Cl bond lengths in the titanium tetrachloride–ester complexes are slightly shorter, 2.22–2.25 Å,[31] than that calculated for the Ti(IV) complex $TiCl_5^-$ (2.35 Å). For the Ti(III) complex, the deviation is larger, calculated 2.49 Å versus experimental 2.33 Å.[44] The larger deviation for the latter is attributed to the higher overall charge on the complex, which indicates that the charge is a part of the explanation for the deviation. Including *d* functions on chlorine reduces the deviation significantly: to 2.30 Å (*trans* to the vacancy) and 2.24 Å calculated for $TiCl_5^-$, and 2.46 Å (*trans*), 2.42 Å, and 2.49 Å (in-plane with the singly occupied B_1 orbital) calculated for $TiCl_5^{2-}$, respectively (gradient-optimized, C_{2v} symmetry, fixed 90° angles).

Contrary to what one might expect, the relaxation of the different Ti–Cl bonds together with relaxation of the corresponding ethylene complex (the product) does not influence the ethylene complexation energy significantly. Gradient optimization of $[TiCl_5(C_2H_4)]^{2-}$ (C_{2v}, fixed 90° angles) resulted in small differences in Ti–Cl bond lengths compared to the reactant, but the Ti–BMP distance became longer (2.95 Å compared to 2.80 Å when partially optimized at the MCPF level). However, these effects did not seem to alter the final coordination energy notably. The ethylene coordination energy was calculated to be 10.8 kcal/mol (compared to 10.2 with the partially optimized geometry) at the MCPF level. Including *d* functions in the chlorine basis set resulted in an increase in the ethylene coordination energy of only 0.2 kcal/mol. We therefore conclude that the geometries used in the energy evaluations are adequate for our rather qualitative purpose. Augmentation of the basis sets in the final energy evaluations is also seen to have only a minor influence on the results.

2.2. Ethylene Coordination to Octahedral and SP Formaldehyde-Titanium Complexes. In the octahedral model complexes $[TiF_xH_2(CH_2O)_y(C_2H_4)_z]^{2-x}$ ($x + y + z = 4$) (**1**–**5**) and in the SP model complex $TiF_2H_2(CH_2O)$ (**6**) (Figure 3), the hydride ligands in the complexes act as models for alkyl groups. η^1-bonding formaldehyde is a model for the esters which are often used as moderators in heterogeneous catalysts.[36] By replacing the fluoride ligands with formaldehyde, we can adjust the charge on the complex without changing the formal oxidation state of the metal atom. The calculated relative stabilities of the six different formaldehyde titanium complexes (**1**–**6**) are given in Figure 3, and the most important Mulliken populations calculated for these complexes are listed in Table 2. The geometries of the complexes **1**–**6** are all based upon[45] the gradient geometry optimizations of $TiF_2H_2(CH_2O)_2$ (**2′**) and $TiF_2H_2(CH_2O)(C_2H_4)$ (**3′**), which are reported in Table 3.

The Ti–O distances 2.20 and 2.18 Å and the TiOC angles 133° and 132° for **2′** and **3′**, respectively, are in excellent agreement with experimental data for octahedral $TiCl_4$

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(43) Both the SP and the TBP structures were gradient-optimized at the SCF level (see the Appendix for details). The reported energy difference (23.1 kcal/mol) was obtained at the MCPF level.

(44) Sobota, P.; Ejfler, J.; Utko, J.; Lis, T. *J. Organomet. Chem.* **1991**, *149*, 410. This is to our knowledge the only existing X-ray crystallography study of a Ti(III)–ester complex ($[TiCl_3(DEP)]_2$ where DEP is diethyl phtalate).

(45) The bond distances in **1**–**6** are all taken from gradient-optimized geometries (see the Appendix for details) of $TiF_2H_2(CH_2O)_2$ (**2′**) and $TiF_2H_2(CH_2O)(C_2H_4)$ (**3′**) (Table 3). The internal formaldehyde geometry (including the TiOC angle) was also taken from **2′** and **3′**. The construction of **1**, **2**, and **4** (aldehyde complexes) is based upon **2′** and that of **3**, **5** (corresponding ethene complexes), and **6** (SP intermediate) upon **3′**. The models in Figure 3, however, are somewhat adjusted compared to **2′** and **3′**. The angles between the ligands are all set to 90° to increase the symmetry and thereby reduce the complexity of the calculations.

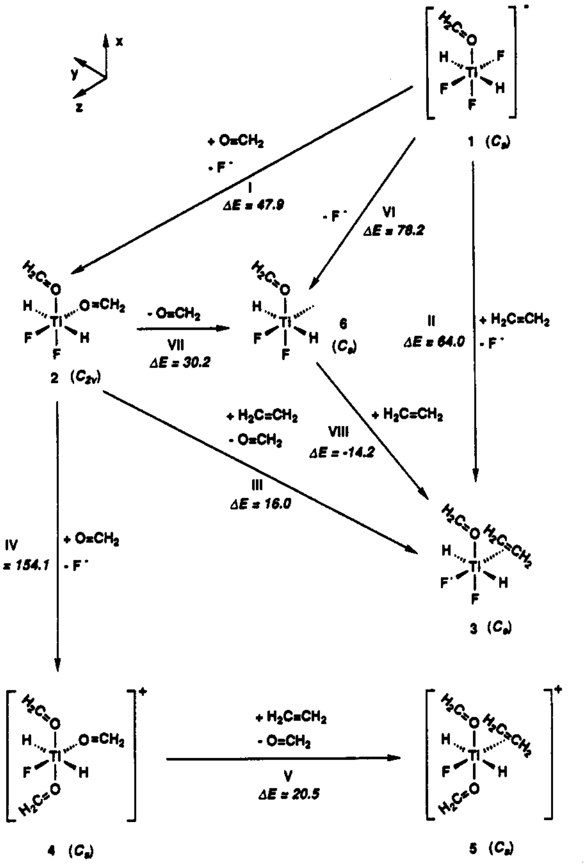

Figure 3. Relative MCPF level stabilities (kcal/mol) of octahedral titanium(IV) complexes of the type $[TiF_xH_2(CH_2O)_y(C_2H_4)_z]^{2-x}$ ($x + y + z = 4$) (1–5). A square-pyramidal complex (6) is also given. The point groups of the complexes are shown in brackets. The figure shows various reaction routes for forming titanium–ethylene complexes when Lewis bases are present.

Table 2. Mulliken Populations and Net Charges[a] (e) of Compounds in Figure 3

complex	symmetry	q_M	3d population	$q_{ethylene}$	C–C π	$q_{formaldehyde}$
1	$^1A'$	0.5	2.1			0.2
2	$^1A_1$	0.7	2.0			0.2
3	$^1A'$	0.7	2.1	0.1	1.8	0.2
4	$^1A'$	0.9	1.9			0.2
5	$^1A'$	0.8	1.9	0.2	1.7	0.3
6	$^1A'$	0.7	2.1			0.1
ethylene	A_g			0.0	1.9	
formaldehyde	$^1A_1$					0.0

[a] From MCPF calculations.

complexes of carbonyl compounds.[46] Some of the angles in 2′ and 3′ deviate substantially from the 90° angles expected for an octahedral arrangement (upon which the structures 1–6 are based). The largest deviation from an octahedral configuration is found for the HTiH angle (136.0° in 2′ and 132.7° in 3′) which should be 180° in an octahedron. The reason for this deviation most probably is that when the structures are allowed to relax, the hydrides slip out of the xy-plane to interact with the Ti $3d_{yz}$ orbital, as indicated by the higher $3d_{yz}$ population by 0.3 in the relaxed structure 3′ relative to the symmetry-adjusted structure of $TiF_2H_2(CH_2O)(C_2H_4)$ (3). It seems reasonable, however, to assume that when the hydride and fluoride ligands are replaced by the more relevant ligands alkyl and chloride, which have larger steric requirements, the complex will attain a geometry which is closer to an octahedron.

Table 3. Selected Geometry Parameters[a] for the Geometry-Optimized Structures $TiH_2F_2(CH_2O)_2$ (2′) and $TiH_2F_2(CH_2O)(C_2H_4)$ (3′)

structure	geometry parameter	value	structure	geometry parameter	value
2′	Ti–F	1.81	3′	Ti–F	1.79
	Ti–H	1.63		Ti–F′	1.81
	Ti–O	2.20		Ti–H	1.62
	C–O	1.22		Ti–O	2.18
	∠TiOC	133.0		Ti–BMP	2.97
	∠HTiH	136.0		C–C	1.34
	∠FTiO	81.5		C–O	1.23
	∠TiOCF	0		∠TiOC	132.3
				∠HTiH	132.7
				∠FTiO	171.7
				∠F′TiO	81.9
				∠TiOCF′	0
				H bend	2.0

[a] See Figure 3 for atom connectivity (the same for 2′ and 2, 3′ and 3). Bond lengths are given in angströms. Angles, torsions, and the H bend are given in degrees. H bend denotes the out of plane bending of the ethylene hydrogens, and BMP denotes the C–C bond midpoint.

The optimized Ti–BMP distance 2.97 Å in 3′ is longer than the distance found for the $[TiF_5(C_2H_4)]^{n-}$ complexes (Figure 2). The calculations, however, are not directly comparable since the 2.80-Å distance in $[TiF_5(C_2H_4)]^-$ was obtained with a frozen SP fragment and at the MCPF level, whereas the 2.97-Å distance in 3′ was obtained at the SCF level with a totally relaxed SP fragment. As has been discussed previously for TiF_5^{n-}, the potential surface of ethylene coordination is very flat, and the difference in the ethylene complexation energy for the two coordination distances is not expected to be large. Ethylene coordination to the SP $TiFH_2(CH_2O)_2$, which is a formal Ti(III) complex and was constructed in the same way[45] as the Ti(IV) structures 1–6, gives ethylene complexation energies of 11.2 and 9.8 kcal/mol with the Ti–BMP distances 2.80 and 2.97 Å, respectively, thus indicating a flatness of the potential surface also for ethylene coordination to the investigated titanium–formaldehyde complexes.

The energetics of the various steps are very informative (Figure 3). A carbonyl Lewis base such as formaldehyde will complex significantly stronger (approximately 15–20 kcal/mol) than ethylene to titanium, a point which has been suggested as evidence against the Cossee mechanism.[9] This is a large difference in binding energy, and if we translate it into equilibrium constants (approximating reaction energies with free energies), we get very small values. Even if the ester concentrations in the Ziegler–Natta processes are small relative to monomer concentrations, the esters should more or less inhibit polymerization as they normally are in excess relative to the catalyst. A possible exception is if carbonyl compounds and alkene were simultaneously coordinated as in 3. In fact, such effects may explain the observation that a high content of surface-bound titanium–ester complex in a catalyst can result in high catalytic activity.[31] Displacement of fluoride by ethylene in an octahedral titanium–formaldehyde complex requires a large amount of energy (approximately 60 kcal/mol; Figure 3, reaction II), so this is unlikely to occur. Also, for formaldehyde to replace fluoride, creating a more positively charged complex and thus a better acceptor for Lewis bases, requires a large amount of energy (approximately 50–150 kcal/mol; Figure

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[46] Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256.

3), regardless of whether this changes the complex from a negative to a neutral complex or from a neutral to a positive complex. However, the calculated energies for these heterolytic bond dissociations are probably too large because we are taking into account only an isolated part of the system (no counterions or effective field from the environment). Nevertheless, the stronger binding of the halide is experimentally well-known, and the generation of cationic species is very unlikely, unless fluoride (or chloride in real catalysts) acceptors, such as aluminum(III), are present.

The results presented in Figure 3 can be rationalized by considering the σ donating ability of the ligands. Because π back-donation from the metal is very small in these complexes, σ donation will regulate the binding energies. In accordance with chemical intuition and as is indicated by the Mulliken populations and charges of complexes 1–6 in Table 2, formaldehyde is a better σ donor than ethylene. Fluoride will of course bind far better than both. Thus, looking only at the reaction energies, it seems difficult to avoid poisoning the active sites if Lewis bases comparable to formaldehyde are present in the system.

Finally, a few words should be mentioned about the geometries as well as the methods used in the energy calculations. Adjusting[45] the gradient-optimized structures of 2′ and 3′ to give 2 and 3 reduces the calculated reaction energy of reaction III from 20.0 to 16.0 kcal/mol. It is reasonable to believe that this symmetry adjustment will have approximately the same influence on reaction V. Furthermore, in the first part of the present work we showed that it was sufficient to use approximate geometries for our purposes. The adoption of bond distances from 2′ and 3′ in the complexes 1–6 is thus not expected to introduce errors large enough to question the rather clear trends found in the energy evaluations. The augmentation of the basis sets to include polarization functions on all atoms (as described in the Appendix) may reduce the difference between ethylene and formaldehyde binding energies somewhat. While the basis set augmentation was seen to *increase* the ethylene binding energy in $[TiH_5(C_2H_4)]^-$ by 2.1 kcal/mol, a similar augmentation is found to *reduce* the binding energy of formaldehyde (reaction VII) by 3.0 kcal/mol. These corrections practically cancel if we add the 4 kcal/mol due to the adjustment of structures 2′ and 3′ as described above. Thus, the energies of reactions III (16.0 kcal/mol) and V (20.5 kcal/mol) should still be large enough to justify the conclusions made in the present work.

3. Conclusions

In the Cossee model for heterogeneous Ziegler–Natta catalysts, ethylene first coordinates to a neutral SP titanium complex, and then undergoes insertion. From the present calculations, it is clear that ethylene binds only weakly (<15 kcal/mol) to SP anionic and neutral complexes such as TiF_5^{n-}, $TiCl_5^{n-}$ (n = 1, 2), and $TiF_2H_2(CH_2O)$. This weak coordination seems to be valid irrespective of whether the catalytic centers are Ti(III) or Ti(IV) or whether the complexes are neutral or have an overall negative charge. There is thus no support for the much stronger back-donation in the Ti(III) case, which was suggested by the various calculations reported earlier.[27-29] Weak binding is not a problem in itself. Polymerization reactions using Ziegler–Natta catalysts are very fast, and it may be an advantage that the intermediate ethylene complex is not stable enough to represent a thermodynamic "pit". However, the problem is that the energy gained through relaxation of the SP structure to a TBP structure is larger than the binding energy of ethylene to titanium. This suggests that neutral or anionic complexes can only function as catalysts in a rigid environment, where relaxation is not possible. In contrast, cationic complexes such as $[TiCl_2(CH_3)(C_2H_4)]^+$, which have been used as models in calculations on homogeneous Ziegler–Natta catalysts,[17-19] coordinate very strongly to ethylene (>30 kcal/mol) and have a low calculated barrier to insertion (4 kcal/mol reported in ref 17). However, these complexes are extremely coordinatively unsaturated. The ethylene complex is only four-coordinate while a d^0 complex such as Ti(IV) could in theory be nine-coordinate according to the 18-electron rule. In addition, the calculated ethylene coordination energies above 30 kcal/mol are probably overestimated and may lead to an endothermic reaction from the π complex to the propyl product, or to a too large overall exothermicity.[22]

Another problem is the mechanism for the generation of cationic complexes from halide complexes. From our calculations on fluoride displacement from $[TiF_3H_2(CH_2O)]^-$ (1) and $TiF_2H_2(CH_2O)_2$ (2) (Figure 3, reactions I, II, IV, and VI), it is clear that dissociation of halide requires too much energy, even during the favorable simultaneous coordination of formaldehyde. Formaldehyde in turn binds stronger to Ti(IV) than ethylene (by 15–20 kcal/mol), as shown by our calculations. Spontaneous ionization therefore seems unlikely. Model complexes for homogeneous polymerizations, such as $[TiCp_2(CH_3)]^+$,[19] are more realistic since each of the cyclopentadienyl groups is capable of being three-coordinate, and thus, at least in theory, capable of filling many of the coordination sites on titanium. The binding energy of ethylene to the analogous $[Zr(SiH_2Cp_2)(CH_3)]^+$ has been calculated to be 33.5 kcal/mol, and the ethylene insertion barrier (relative to the ethylene complex), 6.0 kcal/mol.[21] The energy required to produce the cationic species $[Zr(SiH_2Cp_2)(CH_3)]^+$ from the corresponding halide is not known, but is probably far lower than for the complexes described above because of the influence of the cyclopentadienyl rings. In fact, several cationic complexes related to $[Zr(SiH_2Cp_2)(CH_3)]^+$ have been reported to be active centers in homogeneous polymerization of ethylene.[47-49] It is generally believed that the Lewis acid cocatalyst ionizes the active center, thus creating the active cationic species. The apparently far lower olefin coordination energy found in the present results for the more heterogeneous-like neutral or negative centers indicates that the support, or perhaps also the cocatalyst (neither of which are included in our calculations), should have an important influence on the charge (in the Mulliken sense) of the active metals in a real heterogeneous catalyst. Furthermore, inspired by the cocatalyst role during formation of the active cations in homogeneous catalysis, one could also imagine the cocatalyst inducing a partial ionization of the heterogeneous active center, as shown in Figure 4. This will also lead to less crowding of the active center. In fact, quantum chemical calculations[50] indicate

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7

8

Figure 4. Suggested scheme for partial ionization of the active center through action of the aluminum cocatalyst. In 8 the vacated position due to the partial ionization is occupied through coordination of an ethylene or a Lewis base (denoted by L). Further coordination to 8 is seen to be possible.

that one of the bridging chlorides in the realistic model 7[14,15] should almost entirely belong to aluminum, thus supporting, at least to some extent, the scheme in Figure 4. The vacated positions on titanium, resulting from the cleavage of the bridge, could then be filled by coordination of ethylene or Lewis base moderators (denoted by L in Figure 4). Coordination of more than one alkene to 8 is also seen to be possible (analogous with suggestions in ref 9), as is mixed coordination of alkene and carbonyl moderators.

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Appendix. Computational Details

A.1. Correlated Calculations. In all the reported correlated calculations extended atomic basis sets were used in a generalized contraction scheme,[51,52] and all valence electrons were correlated. Relativistic effects were accounted for by using first-order perturbation theory including the mass–velocity and Darwin terms.[53,54] For Ti, Wachters' primitive basis[55] was extended by adding one diffuse *d* function and two *p* functions, yielding a (14*s*, 11*p*, 6*d*) primitive basis. This primitive basis was contracted according to the generalized contraction scheme, giving a [5*s*, 4*p*, 3*d*] contracted basis. For chlorine, the Huzinaga[56] primitive basis (12*s*, 9*p*) was used, contracted to [4*s*, 3*p*] and augmented by adding one diffuse *p* function with exponent 0.044, yielding the contracted [4*s*, 4*p*] basis. Hydrogen as a ligand attached directly to Ti was described by the Huzinaga[57] primitive (5*s*) basis contracted to [3*s*]. This basis was augmented by one *p* function with exponent 0.8 to form the contracted [3*s*, 1*p*] basis. Oxygen, fluorine, and carbon were described by the Huzinaga[57] primitive (9*s*, 5*p*) basis contracted to [3*s*, 2*p*]. For fluorine, we augmented the basis with a diffuse *p* function with exponent 0.0795, giving the contracted [3*s*, 3*p*] basis. The ethylene and aldehyde hydrogens were described by the Huzinaga[57] primitive (4*s*) basis contracted to [2*s*] and with exponents scaled by a factor of 1.2.

In some of the calculations (where indicated) the basis sets were augmented with polarization functions on all atoms. In these calculations, three *f* primitives were added to the Ti basis, giving a (14*s*, 11*p*, 6*d*, 3*f*) primitive basis contracted to [5*s*, 4*p*, 3*d*, 1*f*]. Furthermore, for hydrogen, the contracted [3*s*, 1*p*] basis set described above was used on *all* the hydrogen atoms. The chlorine, fluorine, oxygen, and carbon basis sets were all augmented with one *d* function. The *d* exponents were 0.55, 1.0, 1.33, and 0.63, respectively.

The correlated calculations were all performed using the modified coupled pair functional (MCPF) method,[58] which is a size-consistent, single reference state method. The zeroth-order wave functions are defined at the SCF level. For the correlated calculations we used the STOCKHOLM set of programs.[59]

A.2. Gradient Optimizations. In all the reported SCF gradient geometry optimizations the effective core potentials (ECP) according to Hay and Wadt[60] were used in the description of titanium. The 3s and 3p orbitals were described by a single-ζ contraction. The valence basis set consisted of a double-ζ description of the 4s and 4p orbitals and a triple-ζ description of the 3d orbitals. Chlorine was described by the ECP according to Hay and Wadt.[61] The valence basis set was double-ζ in the 3s and 3p regions and single-ζ in the 3d region. For the first-row atoms the Dunning and Hay[62] primitive basis (9*s*, 5*p*) contracted to [4*s*, 2*p*] was used. Hydrogen was described by the Dunning and Hay[62] primitive basis (3*s*) contracted to [2*s*]. The gradient optimizations were performed using the GAMESS[63] and GRADSCF[64] programs.

A.3. Partial Optimizations. The reported SCF partial geometry optimizations (pointwise calculations) were performed using the same basis sets and programs as the correlated calculations.

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